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Nano calcium carbonate versus nano calcium hydroxide in alcohols as a deacidification medium for lignocellulosic paper

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Abstract

Deacidification is an established conservation treatment for the prolongation of the acidic paper stability. Several different deacidification systems are in use today, such as the dispersions of alkaline nanoparticles in organic solvents. The aim of the study was to compare the effects of different calcium nanoparticle dispersions in alcohols on lignocellulosic paper. Commercially available nano calcium hydroxide dispersions for paper deacidification, and laboratory prepared nano calcium carbonate dispersions in ethanol and 2-propanol were investigated and compared as to their effectiveness in increasing the stability of paper. The FE-SEM analyses were used to determine the size of $Ca(OH)_2$ and $CaCO_3$ particles in the dispersions. The SEM–EDS analyses were performed both on the paper surface and its cross-section in order to ascertain the distribution of calcium ions following the deacidification treatment. An evaluation of the changes of color, molecular weight, pH and alkaline reserve on different lignocellulosic papers was performed. In comparison to untreated samples, our results indicate all the investigated deacidification treatments decrease the degradation rate constant of cellulose, as determined by accelerated degradation. However, the treatments involving nano calcium hydroxides in both alcohols noticeably affect the color of the treated lignocellulosic papers. According to the obtained results, nano calcium carbonate is therefore the more suitable deacidification agent for the lignin containing papers.

Keywords: Paper, Deacidification, Lignocellulosic, Nano particles, Nano calcium hydroxide, Nano calcium carbonate

Introduction

The acidity of paper presents a serious problem for many archive and library collections, thus motivating the development of many different deacidification treatments. The deacidification was recognized as a more sustainable and energetically less demanding alternative to the established cooling of the endangered collections [1–3]. Consequently, the development in this field is still subject of interest for several researchers and conservators.

Acids in papers can be neutralized by their immersion into variety of aqueous and non-aqueous solutions [4–6]. Beside neutralization, most of the paper deacidification procedures also provide an alkaline reserve to neutralize acids that may be introduced later; either generated within the paper itself, or absorbed from its storage environment [5]. For deacidification purposes, most often weak bases, such as alkaline-earth carbonates, hydroxides, and oxides are used. The pH value of paper after the deacidification is crucial, as an increased alkalinity might induce color changes of the inks, pigments, and dyes [7]. Color changes of watercolor pigments during the deacidification were observed, and it was concluded that calcium and barium hydroxides cause more pronounced color changes compared to the magnesium or calcium hydrogen carbonates [8]. Although various metal hydroxides provide a very effective reduction of acidity, they

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tend to yield significantly higher than neutral pH values [5]. The alkalinity of the paper in the presence of $CaCO_3$ is lower compared to that in the presence of hydroxides, and is therefore regarded as favorable among the conservation scientists.

It is known, that the degradation reactions after the deacidification are influenced both by the alkaline-earth metals and the pH achieved [9–11]. With increasing pH, the relative importance of acid hydrolysis decreases, and within around the neutral region the degradation slows down. Two other phenomena are thought to play a major role in the degradation of cellulose under moderately alkaline conditions: oxidation and ß-alkoxy elimination [5, 11].

For the cases of water-sensitive inks, bound paper volumes, etc., where water-based procedures cannot possibly be applied, non-aqueous deacidification procedures have been developed. The active alkaline Ca and Mg components, present in the organic solvents, supposedly turn into their respective carbonates after evaporation of the solvent, followed by the reaction with atmospheric CO_2. There are several problems associated with these procedures: by-products of acid-catalyzed degradation are not washed out of the treated object, and many alkaline active constituents are either too reactive (e.g. alkoxides) or turn into their respective carbonates too slowly [12]. Additionally, alkoxides can react with some components of the paper, predominantly with lignin [13].

During the past 20 years, nanotechnologies have been increasingly implemented in the deacidification of paper artefacts. Nano and micron sized calcium hydroxide particles in alcohol media were introduced by Giorgi et al. already in 2002 [14], followed by the study of application of the $Mg(OH)_2$ nanoparticles in 2005 [15], and several other studies [16–26]. There are several advantages to the use nanoparticles for the deacidification of paper, such as high specific surface area, which influences system's many physico-chemical properties. Particles' small size facilitates a better penetration and adhesion within the paper substrate, minimizing the white deposit formation on the paper's surface. An excellent kinetic stability of the nano calcium hydroxide dispersions were obtained using short chain alcohols [14]. Although the dispersions were claimed to be effective deacidification agents by some authors, others reported on the evidence of cellulose breakdown in the lignocellulosic and cellulosic papers, which was attributed to high pH values of the paper after the treatment, concluding the procedure was not advisable as a conservation intervention [18]. Another study demonstrated that an increased concentration of alkali resulted in no negative effect on Whatman filter paper, on the contrary, with an increased nano $Mg(OH)_2$ content and with higher paper alkalinity, resistance of the samples against degradation also increased [26].

Recently, the dispersions of nano calcium carbonate and nano calcium propionate have been developed for the deacidification of library and archival materials since the official methods, permitted in Italy on cultural heritage objects forbid the use of hydroxides, due to the too high localized pH of hydroxides that can induce ß-alkoxy elimination with subsequent depolymerization of cellulose [27].

The items that would benefit the most from the single item non-aqueous deacidification in paper conservation workshops are the manuscripts or the works of art on modern paper; i.e. those with low pH values, produced on lignocellulosic paper. Whereas bleached chemical pulp fibers are mostly composed of cellulose, with a smaller proportion of hemicelluloses, mechanical pulps fibers retain almost all of the lignin originally present in the wood [28]. Lignin containing papers may react differently to the alkaline treatment, in contrast to rag or purified wood pulp papers [29]. It is well known that ground wood darkens in the alkaline water solutions [30, 31]. For some wood pulp papers, the use of deacidification sprays is not recommended as it might cause problems, such as darkening, staining, and changing the hue of the colored media and supports [32].

Therefore, the aim of the work was to evaluate the effects of different commercially available deacidification dispersions containing nano calcium hydroxide on different lignocellulosic papers. The dispersion based on calcium carbonate nanoparticles was prepared and applied to lignocellulosic papers as well, in order to study the effect of milder alkaline condition on the properties of deacidified papers.

Experimental

Paper samples

Investigated paper samples were:

- P1 paper produced and investigated in the project PaperTreat: evaluation of mass decidification processes SSPI-006584 (made from 90% ground wood, 10% softwood bleached pulp with approx. 20% kaolin and aluminium sulfate). Initial pH value of the paper was 4.8 ± 0.2.
- P2 acid writing paper used previously for the Step CT-90-0100 project (made from 75% ground wood, 25% softwood fibers with approx. 20% kaolin and aluminium sulfate). Initial pH value of the paper was 6.0 ± 0.1.
- Book 1, Book 2 and Book 3, paper sheets, which were taken from the books dated from the years 1890, 1937 and 1956, respectively. Initial pH values of the paper from books were 5.0 ± 0.2 (Books 1), 5.4 ± 0.1 (Book 2), and 5.8 ± 0.1 (Book 3).

Table 1 Designations for various deacidification agents

Designation	Deacidification agent (product name)	Nanoparticle dispersion
NR E	Nanorestore Paper Ethanol 3	$Ca(OH)_2$ in ethanol 3 g L^{-1} (0.04 mol L^{-1})
NR iP	Nanorestore Paper Propanol 3	$Ca(OH)_2$ in 2-propanol 3 g L^{-1} (0.04 mol L^{-1})
CS E	CaLoSil E5	$Ca(OH)_2$ in ethanol 5 g L^{-1} (0.07 mol L^{-1})
CS iP	CaLoSil IP5	$Ca(OH)_2$ in 2-propanol 5 g L^{-1} (0.07 mol L^{-1})
C E		$CaCO_3$ in ethanol 20 g L^{-1} (0.2 mol L^{-1})
C iP		$CaCO_3$ in 2-propanol 20 g L^{-1} (0.2 mol L^{-1})

Deacidification agents

Investigated deacidification agents are presented in Table 1. Four commercially available deacidification agents were used: Nanorestore Paper Ethanol 3 or Nanorestore Paper Propanol 3 (C.S.G.I. Consorzio per lo sviluppo dei sistemi a grande interfase, Sesto Fiorentino, Italy) and CaLoSil E5 or CaLoSil IP5 (IBZ-Salzchemie GmbH & Co.KG, Halsbrücke, Germany).

The dispersion of nano calcium carbonate was prepared from calcium carbonate nanoparticles powder (99.9%, 20 nm, CNM, Saint-Cannat, France), added to ethanol (Sigma-Aldrich, Steinheim, Germany, puriss, 96 vol%) or 2-propanol (Sigma-Aldrich, Steinheim, Germany, puriss, p.a. $\geq$ 99.8%) and sonicated using HIELSCHER Ultrasonics GmbH, model UP400S three times for 3 min. The dispersions were used for deacidification within 1 day from preparation.

Higher concentration of $CaCO_3$ was selected as its solubility in water (and consequently in water-containing cellulosic fibres) is much lower in comparison to $Ca(OH)_2$.

Deacidification treatment

Paper samples were immersed in the dispersions and treated there for 5 min with constant agitation. Then they were taken out of the dispersion and air dried on a polyethylene terephthalate (Mylar) foil.

Accelerated degradation

Part of the paper sheets from books (Book 1, 2, 3) were humidified prior to accelerated degradation for 4 days at 25 °C and 75% RH (relative humidity).

Both the treated and untreated samples were subjected to accelerated degradation conditions in a Vötsch VC 0020 climatic chamber under the following conditions: 80 °C and 65% RH for up to 14 days.

Analytical methods

pH measurements The pH of water extracts was measured according to the standard [33], modified to smaller samples: 7 mL of deionised water was added to 100 mg of paper sample. pH was determined in the water extract after one hour using a flat membrane electrode (Metrohm 6.0256.100) connected to a Mettler Toledo MP 220 pH meter.

Alkali reserve Alkali reserve was determined according to the standard [34] modified for smaller samples (250 mg).

Fiber furnish analyses Fiber furnish analyses were performed according to standard [35] using Nicon Eclipse 80 I digital microscope.

Color measurements The color of paper was determined using a Minolta CM-3610d diffuse reflectance UV–VIS spectrophotometer, with specular component excluded and a D65 light source. The instrument has a d/8° geometry, and reflectance was measured in percent relative to a polymeric Minolta standard. The values for the color are expressed in the CIE 2000 LAB system.

The co-ordinate values L*, a*, b* correspond to the blackness (L* = 0), whiteness (L* = 100), redness (+a*), greenness (−a*), yellowness (+b*) and blueness (−b*). The differences between the co-ordinate values (ΔL*, Δa*, Δb*) and the total color difference between two samples (ΔE*) was calculated according to reference without deacidification treatment and without accelerated degradation.

Determination of degree of polymerization (DP) The determination of the weight-average molar mass was performed using size exclusion chromatography (SEC) of cellulose carbanilates [36, 37]. Typical RSD of duplicate determinations was 5%.

The size-exclusion chromatography (SEC) measurements were performed on an Agilent HPLC system 1100 (Palo Alto, USA) equipped with a degasser, a binary pump, an auto-sampler and a UV–VIS detector set at 235 nm for determination of cellulose carbanilates and 210 nm for the determination of polystyrene standards. The separation was achieved on two Jordi Gel DVB mixed bed 250 × 10 mm columns, preceded by a 50 × 10 mm precolumn (Bellingham, USA) at 35 °C using tetrahydrofuran (THF) as a mobile phase at a flow rate of 1 mL min^{-1}. The injection volume was 50 µL. The chromatographic data were processed with Cirrus software. The polystyrene standards (PS, Polymer Standards Service) were prepared as mixed standards in three separate solutions containing in total 0.1 g L^{-1} of standards in THF. The first standard solution contained PS of the following peak molecular weights

(Mp): 1,090,000 g mol^{-1}, 130,000 g mol^{-1}, 17,800 g mol^{-1} and 1620 g mol^{-1}, the second standard solution contained 2,570,000 g mol^{-1}, 246,000 g mol^{-1}, 34,800 g mol^{-1} and the third 579,000 g mol^{-1}, 67,000 g mol^{-1} and 8400 g mol^{-1}.

To calculate weight-average degree of polymerization (DP_w) [36], weight-average molar masses determined by SEC were divided by molar mass of carbanilated glucosidic monomer unit. DP_w was then used to calculate the degradation rate constant of cellulose according to Ekenstam equation [38]:

$$1/\mathrm{DP} = \left(1/\mathrm{DP}_0\right) + k \cdot \mathrm{t}$$

where DP = degree of polymerization after accelerated degradation, DP_0 = degree of polymerization before accelerated degradation, k = degradation rate constant [h^{-1}] and t = time of accelerated degradation [h]. Higher values of k represent a higher sample degradation rate.

Standard deviation (SD) of the degradation rate constant (k) determination was calculated by fitting Ekenstam equation to data using linear regression, where k was the regression slope and SD was the error of the regression slope.

FE-SEM microscopy and EDS analyses A field emission scanning electron microscope (FE-SEM, Zeiss ULTRA plus, Carl Zeiss, Germany) was used to determine the size of $Ca(OH)_2$ and $CaCO_3$ particles in various dispersions. The dispersions were applied to a conductive double-sided adhesive carbon tape and dried at 80 °C. In order to ensure the samples' conductivity, the dry samples were further coated with a conductive layer of Au/Pd metal at a thickness of 10 nm. The analyses were performed at an accelerating voltage of 2 kV to 5 kV and 30 µm aperture size. Working distance between samples and electron source was 5.5 mm. The micrographs were captured by a secondary electrons (SE) detector.

EDS (Energy-Dispersive X-Ray Spectroscopy) analyses were performed to determine the element distribution both on the paper surface and its cross-section. Samples were fixed in the aluminium stub using carbon tape. The cross-sectional patterns of the papers were sputtered with an Au/Pd layer to a 10 nm thickness. EDS analyses were performed using EDS Oxford detector using accelerating voltage 15 kV, aperture size 60 µm and working distance of 5.5 mm.

Results and discussion

Characterization of nano calcium dispersions

Nano calcium carbonate dispersions were prepared from calcium carbonate nanoparticles powder and ethanol or 2-propanol using ultrasonic homogenizer. In order to determine the size of the particles, the dispersion was applied to a slide. As evident from Fig. 1a, the size of the smaller $CaCO_3$ particles was under 100 nm. At lower magnification (Fig. 1a) we can see agglomerates of various sizes, from nano to micrometric dimensions.

The sizes of the particles in commercially available dispersions of nano calcium hydroxide (NR presented in Fig. 1b and CS presented in Fig. 1c) were determined as well. As evident from SEM micrographs, the shapes and the sizes of the nano calcium hydroxide particles were different from those of the nano calcium carbonate particles. Nano calcium hydroxide particles were slightly larger and form larger agglomerates.

The dispersion solvent (ethanol or 2-propanol) exerted no influence on the particle size and shape.

SEM analyses of paper samples after deacidification

Element distribution of the untreated paper P1 is presented in Fig. 2. Lightly-colored points represent higher amount of element listed. The analysis using SEM–EDS was performed on the untreated paper surface, which indicated the presence of Al, Si and S, due to the use of kaolin fillers and aluminium sulfate as sizing agent. The amount of sulfur was lower in comparison to Al or Si, which were added to the paper in higher amount as filler. Sulfur was near-uniformly distributed over all sample surface, with the exception of the pore sites where the signal path from the sample to detector was interrupted.

From the SEM–EDS analyses of the surfaces of the deacidified paper samples (Fig. 3) it was clear that calcium was present in all examined paper samples (except in the reference material, which was untreated paper). The distribution of calcium on the surface of the paper was not very homogeneous, which could be due to roughness of the sample paper's surface, as evident from the SEM micrograph in Fig. 3. There were no noticeable differences of calcium distribution on the surface between the samples (C, NR, CS in both solvents, all results are not shown).

The distribution of calcium ions was measured also on the cross-sections of the paper samples in order to verify the depth of penetration of alkali in different dispersions.

As is evident from Fig. 4, in all cases, the amount of calcium was higher on the paper surface, but calcium was also detected on the different locations of the cross-section thus proving penetration of nano particles into the bulk of the paper. In the cases where ethanol was used as a dispersing medium, a higher amount of calcium was present deeper in the paper compared to the 2-propanol nano dispersion media. This could be explained considering a relatively higher polarity of the ethanol molecules that can swell cellulose fibers more efficiently compared to those of 2-propanol. It should also be noted

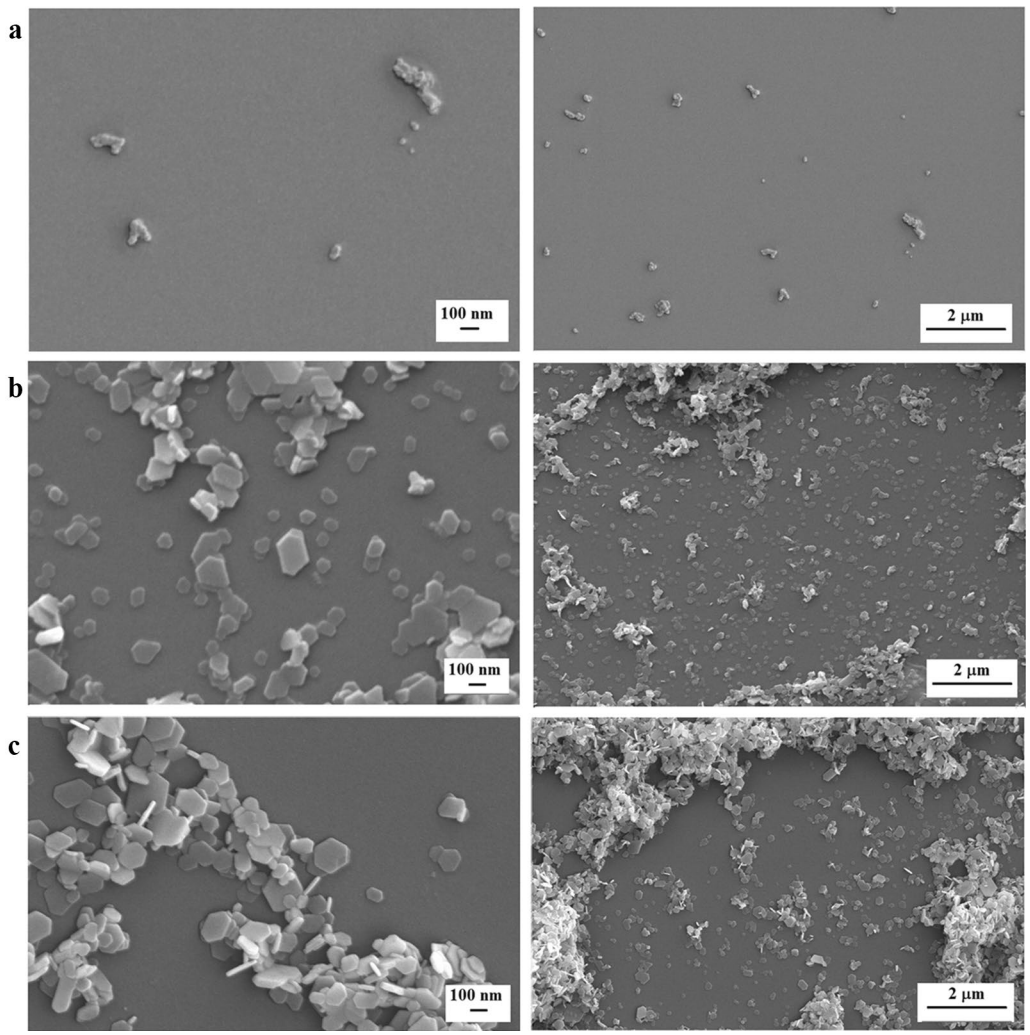

Fig. 1 SEM micrograph of the $CaCO_3$ in C dispersion (**a**), $Ca(OH)_2$ in NR dispersion (**b**) and CS dispersion (**c**) at different magnifications (left ×120,000 and right ×30,000)

that during the elemental analyses, the samples were tilted (the recordings of the element maps took place at an angle), so that one edge appears thicker, and the other thinner than it was.

pH values and alkaline reserves after deacidification treatment

In order to evaluate the effects of various deacidification dispersions, two papers P1 and P2 made from wood pulp were used (Fig. 5) with initial pH values of water extracts 4.8 ± 0.2 (P1) and 6.0 ± 0.1 (P2) treated according to description in experimental part.

After the nano calcium hydroxide particle dispersion treatment, the pH values of water extracts, determined 3 h after the application of dispersions, indicate pH values above 9. After the application of nano calcium carbonate dispersions, pH values of water extracts were below 9, which is recommended for treatment of cultural heritage objects.

The results for pH of treated samples with nano calcium hydroxide were consistent with literature data [17]. The use of nano calcium hydroxide dispersion in 2-propanol on early twentieth century paper samples with initial pH value of 5.3 ± 0.9 resulted in pH of 10 after deacidification with 0.5 g L^{-1} dispersion with only slight increase of pH value, when the concentration of dispersion was increased to 4 g L^{-1} [17].

In the study by Giorgi et al. [14], the pH values of paper samples were measured 1 month after the treatment, claiming increase of pH values of nineteenth and twentieth century acidic paper samples for 3–4 pH units up to a proper pH of around 9. The carbonate formation from calcium hydroxide was proved using FT-IR during

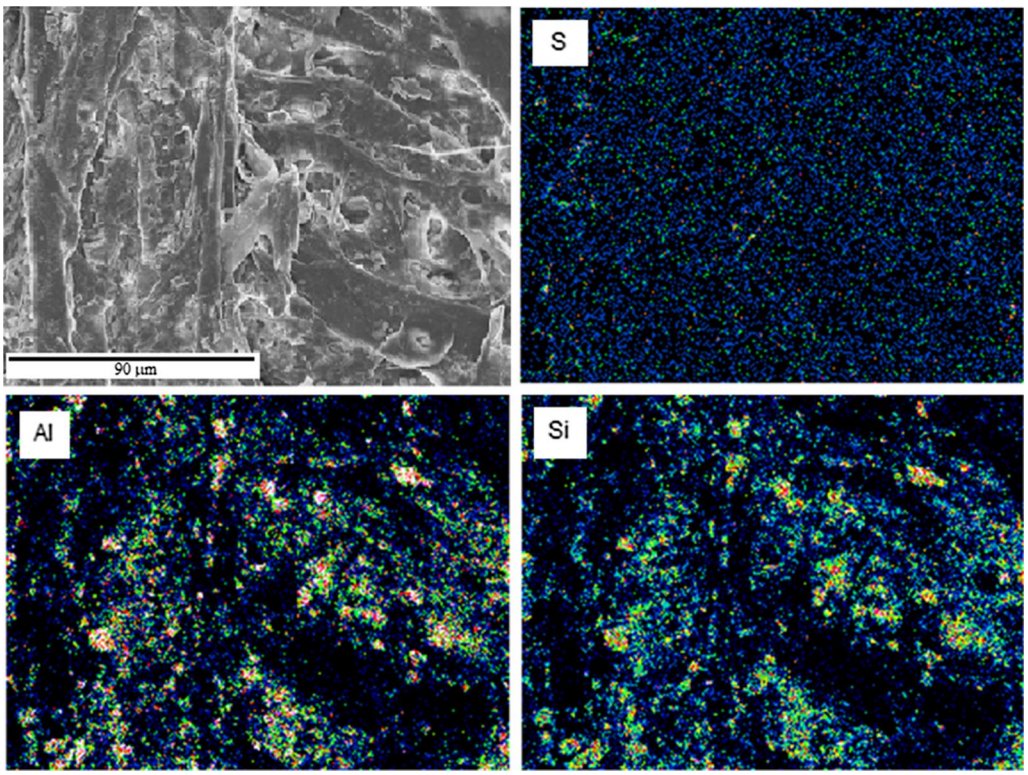

Fig. 2 SEM micrograph and element surface distribution of sulfur, aluminium and silicon for untreated paper P1

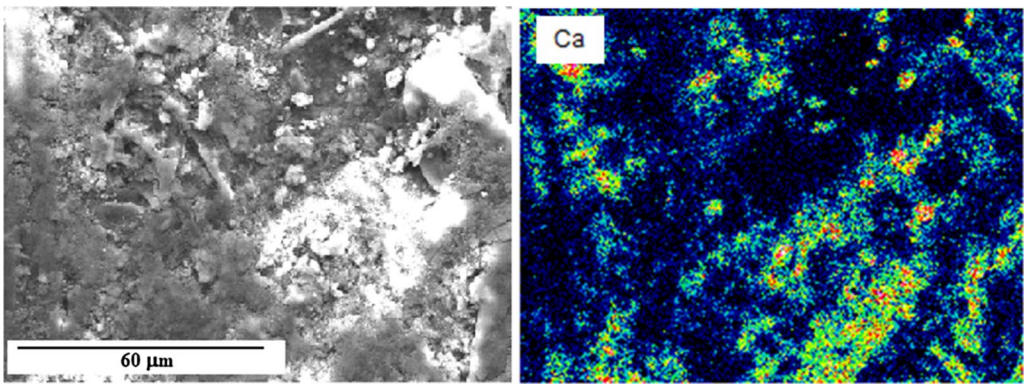

Fig. 3 SEM micrograph and calcium surface distribution after the deacidification treatment with $CaCO_3$ in 2-propanol

2 weeks after application of dispersion. Therefore, in order to investigate the changes of pH values during time for paper samples containing calcium hydroxides, the measurements were performed on paper P1 after deacidification, and after storage at ambient conditions for 20 and 80 days.

As evident from the Fig. 6, the highest decrease of pH value was observed with Nanorestore treatment dispersion, resulting in pH values around neutral after 80 days, which can be attributed to the formation of calcium carbonate in the paper.

The pH value of saturated solution of $CaCO_3$ in equilibrium with atmospheric CO_2 is 8.35, while the pH of saturated solution in water at 20 °C of $Ca(OH)_2$ is 12.6 [11, 39]. The important difference between calcium hydroxide and carbonate is also their solubility in water. Calcium carbonate is practically insoluble in water (0.013 g L^{-1} at 25 °C), while calcium hydroxide is more soluble (1.59 g L^{-1} of

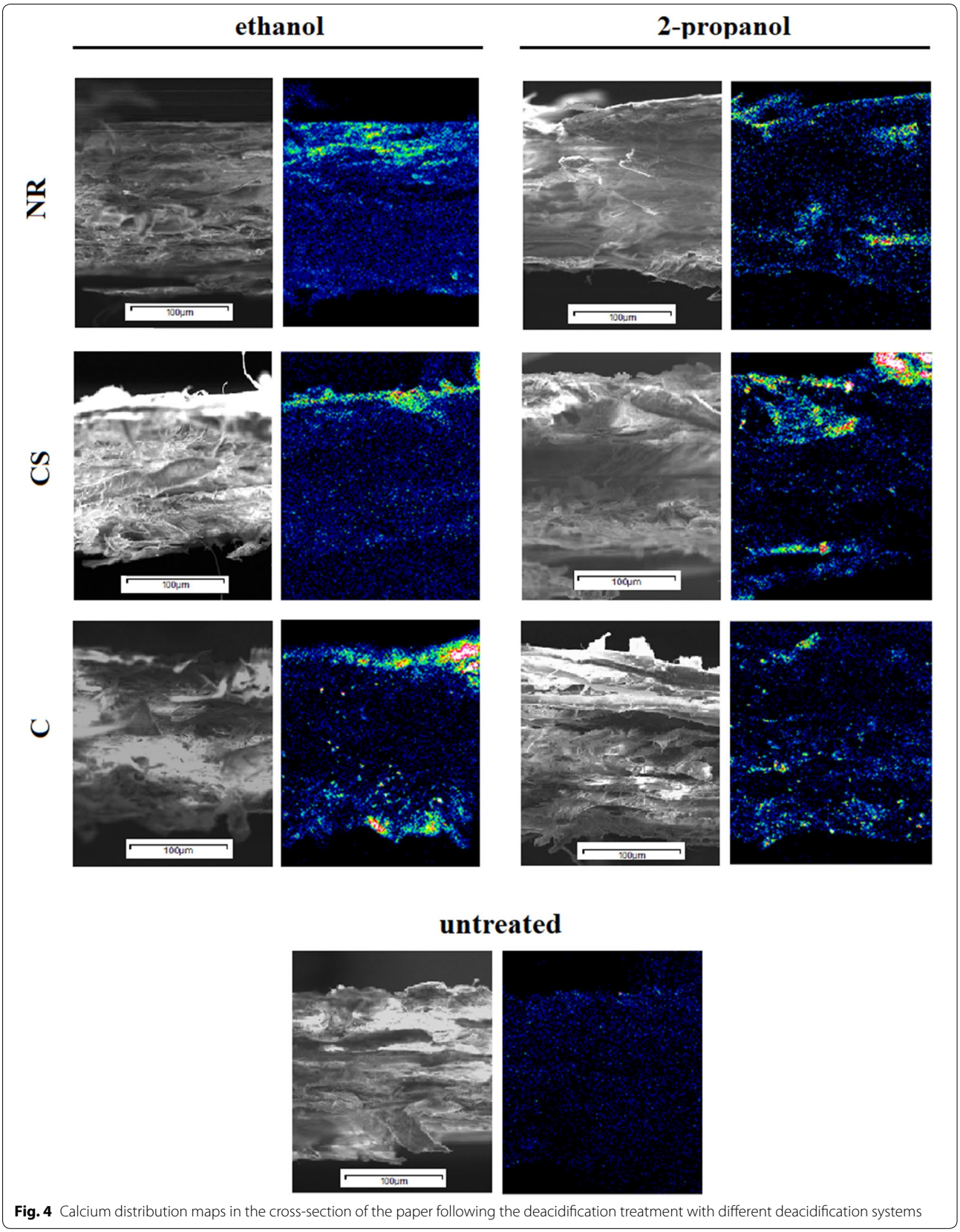

Fig. 4 Calcium distribution maps in the cross-section of the paper following the deacidification treatment with different deacidification systems

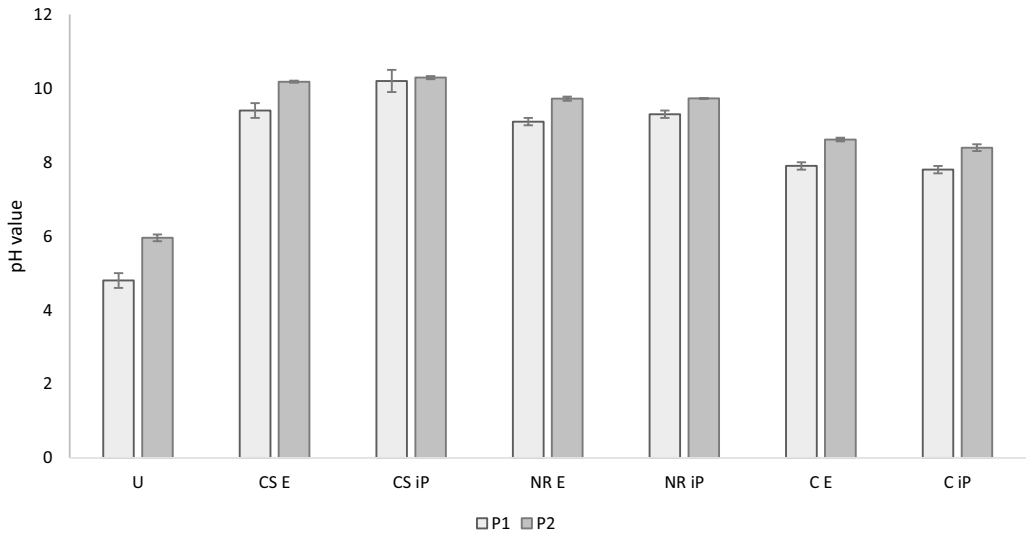

Fig. 5 pH values of paper samples (P1 and P2) before (U) and after the treatment with different deacidification agents (designations in Table 1)

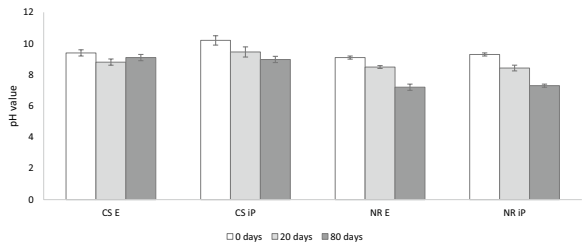

Fig. 6 pH values of paper P1 after deacidification and after storage at ambient condition for 20 and 80 days

Table 2 Alkaline reserves of deacidified paper samples

Sample	Alkaline reserve (% $CaCO_3$)[a]	
	P1	P2
CS E5	1.1	1.2
CS iP5	1.8	1.9
NR E	0.8	0.7
NR iP	1.1	1.0
C E	1.4	1.0
C iP	2.1	1.4

[a] Average standard deviation (SD) of duplicate measurements was 0.1

saturated solution at 25 °C) [39, 40]. Transformation of $Ca(OH)_2$ to $CaCO_3$ after reaction with atmospheric CO_2 is a well-known process:

$$Ca(OH)_2 + CO_2 = CaCO_3 + 2H_2O.$$

The kinetics of the reaction depends on the particle size and the hydrothermal conditions [41].

It was shown recently [42] that $Ca(OH)_2$ in alcohol (e.g., ethanol or 2-propanol), can partially form Ca-alkoxides via the reaction:

$$Ca(OH)_2 + 2ROH \leftrightarrows Ca(OR)_2 + 2H_2O.$$

It was shown that, although the rate of carbonation is slower, Ca-alkoxides eventually hydrolyze and are converted into $Ca(OH)_2$, which then undergoes full carbonation [43].

Some researchers proposed [17, 23] that a lower pH after treatment can be achieved by adjusting the concentration of nano calcium or magnesium hydroxide particles, however this procedure is not fully applicable during the work in paper conservation workshops.

During the 14 day accelerated degradation, pH of deacidified samples decreased, but except for Nanorestore treated samples, remained alkaline. Nanorestore samples were neutral or slightly acidic after accelerated degradation. The pH value of untreated paper P2 did not change after accelerated degradation. The pH values of deacidified samples CS or NR decreased, but to a smaller extent in comparison to paper P1.

The alkaline reserve, expressed as % $CaCO_3$ was determined for all of the treated samples. As evident from Table 2, all the determined alkaline reserves are above 0.6% of $CaCO_3$%, which is the minimum requirement recommended in the ISO standard [44]. Interestingly, the dispersions prepared in 2-propanol yielded in higher alkaline reserve of the paper samples in comparison to dispersions in ethanol. As it is evident from Fig. 4 higher amount of alkali penetrated deeper into the paper with dispersions in ethanol, while with 2-propanol more alkali was at the surface and this could

Table 3 pH values of paper samples before and after accelerated degradation

Sample designation	P1				P2			
	After deacidification treatment		After accelerated degradation		After deacidification treatment		After accelerated degradation	
	pH	SD	pH	SD	pH	SD	pH	SD
U	4.8	0.2	4.7	0.1	6.0	0.1	6.0	0.1
CS E	9.4	0.2	7.7	0.1	10.2	0.1	8.3	0.1
CS iP	10.2	0.3	8.0	0.1	10.3	0.1	8.3	0.1
NR E	9.1	0.1	6.9	0.1	9.7	0.1	7.9	0.1
NR iP	9.3	0.1	6.8	0.1	9.7	0.1	7.9	0.1
C E	7.9	0.1	7.6	0.1	8.6	0.1	7.8	0.1
C iP	7.8	0.1	7.6	0.1	8.4	0.1	7.7	0.1

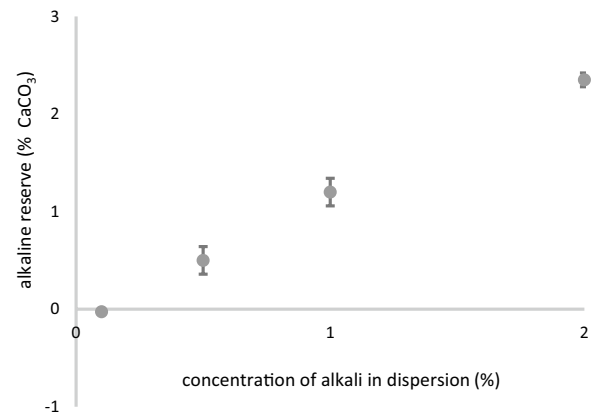

Fig. 7 Alkaline reserve (% $CaCO_3$) in paper P1 after application of 2-propanol dispersions of nano $CaCO_3$ in concentrations up to 2%

affect the determination of alkaline reserve. Nanorestore dispersions resulted in a lower amount of alkali in paper in comparison to CaLoSil treatment dispersion, which could be attributed to a lower concentration of alkali in the dispersions. Lower amount of alkali with NR samples are also reflected in lower pH values of samples after deacidification and even more significantly after accelerated degradation (Table 3).

At higher concentrations of calcium carbonate in dispersions a white deposit on the paper samples appeared which could be visually disturbing. The amount of white deposit on the paper could be reduced by treating the papers with lower concentrations of nano calcium carbonate dispersions. As evident from Fig. 7, the concertation could be safely lowered to 0.5–1%, still yielding alkaline reserves as recommended in the standard [44].

Effect on the paper color

One of the most important parameters for conservators are the color changes of the paper after conservation procedures. Color changes are undesirable if the change is of a degree large enough to be perceptible. Most frequent causes of perceptible color changes are pH-induced changes, the introduction of colored substances or compounds that form colored products after application or during accelerated degradation, or the formation of deposits on the paper [45]. The color of the samples after deacidification treatment and after thermal accelerated degradation was determined with a diffuse reflectance spectrophotometer. Different studies proposed different ΔE^* values (total color difference between two samples) that have a just noticeable color difference, which is the difference perceived by the human eye. Usually, the color difference (ΔE^*) of 1–1.5 is suggested [45].

Effects of different alcohols and nanoparticles dispersions on color of the treated papers were investigated. The color changes after application of different alcohols or calcium carbonate containing dispersions (below $\Delta E^* < 1.5$) are not significant (Fig. 8). Increase of Δb^* values, slight decrease in ΔL^* value and consequently increase of ΔE^* values were observed after treatment due to yellowing of all samples, treated with nano calcium hydroxide containing dispersions (CS and NR). The results for paper P1 are similar to paper P2 (data not shown). Interestingly, on both samples, yellowing was much intensive after application of nano calcium hydroxide dispersion in ethanol in comparison to dispersions in 2-propanol. Higher increase of yellowing was observed for paper P2 after application of CS dispersion in ethanol in comparison to NR dispersion. The results are in accordance with the EDS analyses of the paper, proving better alkali penetration with the dispersions in ethanol and also higher amount of calcium hydroxide in the case of CS treated papers, resulting in higher pH of the papers. Also, better penetration of the reagents enables (unwanted) reactions to take place within the paper.

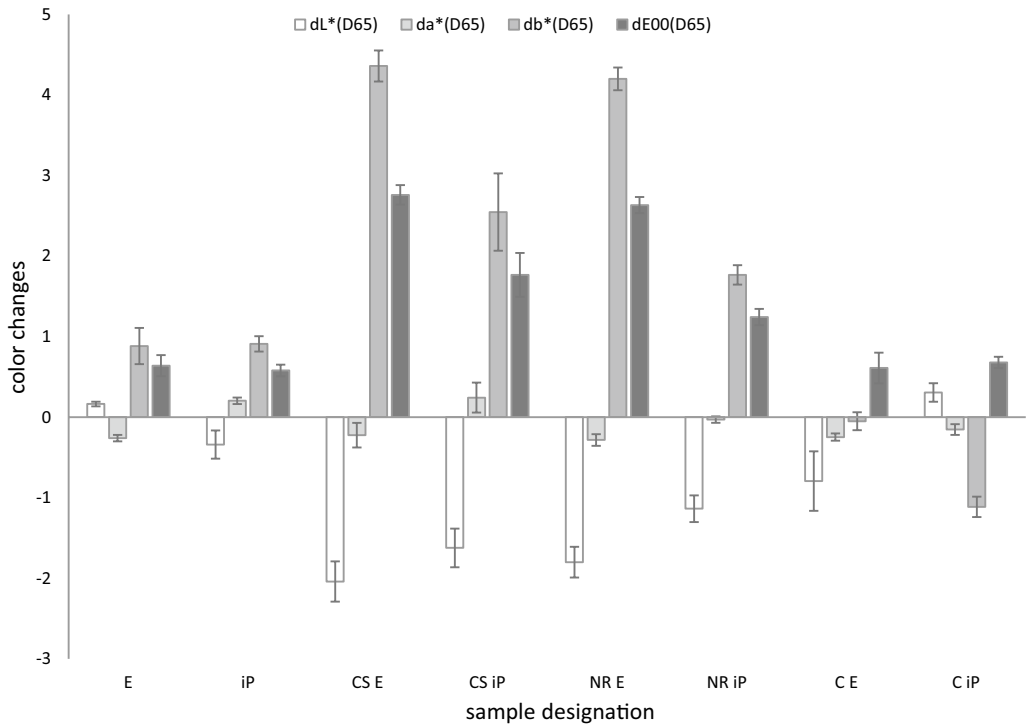

Fig. 8 Color changes (dL*, da* and db* representing ΔL*, Δa*, Δb* and ΔE*) of the samples after treatment of paper P1 in respect to the untreated (U) and unaged sample. Error bars represent standard deviation of triplicate measurements

After applying the calcium carbonate dispersions, a white deposit was observed on the paper surface, which could be decreased by using lower concentrations of calcium carbonate in the dispersions.

After the accelerated degradation, color of all samples changes to a perceptible degree (Fig. 9). The samples treated with nano calcium hydroxide containing dispersions appear more yellow (increase of Δb* value), and after the application of nano calcium carbonate less yellow, in comparison to untreated degraded sample (U). The results obtained for the paper P2 after accelerated degradation were similar, with the higher changes of color obtained after application of CS dispersions (data not shown).

Yellowing is usually attributed to the magnesium containing deacidification agents [4]. The lowest changes of brightness were observed with calcium hydroxide treated paper [46], but other researchers reported that calcium hydroxide aqueous application (in approximately 0.01 mol L^{-1} solution), high pH (10–12.3) could adversely affect some colorants and cause slight yellowing of the paper [5]. Despite conflicting results of different researchers, this might be proper for papers with low lignin content. According to Hey, the high pH value of aqueous deacidification bath with calcium hydroxide was considered as the most serious drawback of the method, as it might cause yellowing of the lignin containing papers [47].

Sequeira et al. demonstrated that higher yellowing and darkening of the samples after accelerated degradation was observed after non-aqueous treatment in comparison to the aqueous, using calcium hydroxide nanoparticles [17].

Yellowing of lignocellulosic paper could therefore be attributed to the high pH obtained in the paper after application of nano calcium hydroxide containing dispersions. It was proved previously that alkaline medium facilitates lignin degradation and that some deacidification treatments induced yellowing of ground wood paper [48]. Alkaline darkening of some high-yield pulps was caused by the formation of *o*-quinones and coniferaldehydes [49]. Unreported additives might also be present in the commercial deacidification dispersions which could additionally induce color changes.

Degradation of the samples

Size exclusion chromatography of cellulose carbanilates was utilized to determine degradation of cellulose according to the procedure described in the experimental part.

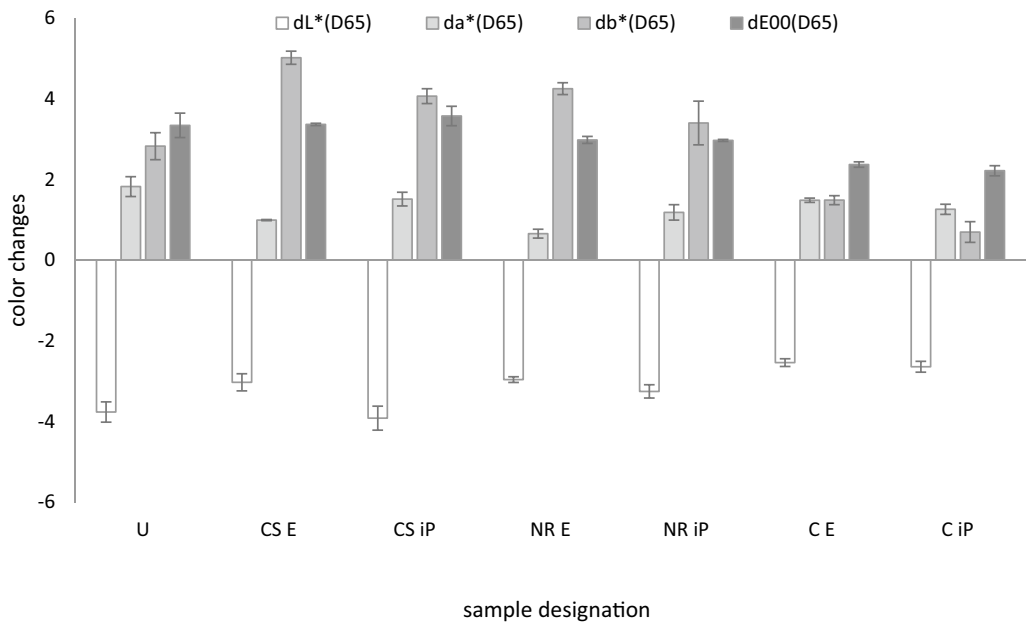

Fig. 9 Color changes (dL*, da* and db* representing ΔL*, Δa*, Δb* and ΔE*) of the samples after 14 day accelerated degradation of sample P1 in respect to the untreated (U) and unaged sample. Error bars represent standard deviation of triplicate measurements

Results indicate (Fig. 10) that all paper samples degrade slower after deacidification treatment compared to the untreated control samples. Stabilization with nano calcium hydroxides was slightly better in comparison to nano calcium carbonate treated samples for paper P2. In the case of paper P1, the differences are not significant, except for CE treated sample. Paper P2 degraded much slower than paper P1, which might be attributed to a lower initial pH of the paper P1 (Table 3).

The results were in agreement with literature data [18], where lignocellulosic print paper was deacidified either with micro particles or with nanoparticles of calcium or magnesium hydroxide. The changes of DP and tensile strength were smaller in the case of nanoparticles deacidification in comparison to treatment with micro particles. Also, in the study by Wojciak [26], it was proven that increased amount of nano $Mg(OH)_2$ and higher paper alkalinity improved the samples' resistance against degradation.

Slightly better stabilization of paper samples with nano calcium hydroxide containing dispersions in comparison to nano carbonate could be attributed to the higher reaction rate of sulfuric acid neutralization with calcium hydroxide in comparison to calcium carbonate [50].

The degradation of the paper after the deacidification with nano calcium carbonate was tested on acidic real paper sheets, taken from the books (Book 1, Book 2 and Book 3 dated from the 1890, 1937 and 1956 with initial pH values 5.0 ± 0.2, 5.4 ± 0.1 and 5.8 ± 0.1, respectively). The papers were composed of ground wood and cellulose fibers (Book 1: 71% ground wood, 29% cellulose fibers; Book 2: 70% ground wood, 30% cellulose fibers, Book 3: 66% ground wood, 34% cellulose fibers). In order to enhance the permeation of carbonate into the paper, deacidified papers were subjected to an increased relative humidity (75%) for 4 days. As evident from Fig. 11, the stabilizing effect of deacidification was observed. The efficiency was not the same for all investigated real lignocellulosic papers, since it depended not only on the initial pH of the paper, but most probably also on the extent of sizing. Increased humidity did not significantly affect the degradation rate constant.

Conclusions

The effects of nano calcium dispersions in alcohols on lignocellulosic papers were investigated. The outcomes of paper stabilization procedures with commercially available dispersions of nano $Ca(OH)_2$ in ethanol or 2-propanol were compared to those of the laboratory prepared nano dispersions of $CaCO_3$ in both alcohols.

All tested deacidification treatments on mock up papers resulted in alkaline pH values. The pH values with nano $Ca(OH)_2$ dispersion treatment in ethanol and 2-propanol were above 9, which is not recommended, as some undesirable chemical reaction could appear, especially for the lignocellulosic papers. It was demonstrated it takes several weeks under ambient conditions the pH to reach the desired value below 9.

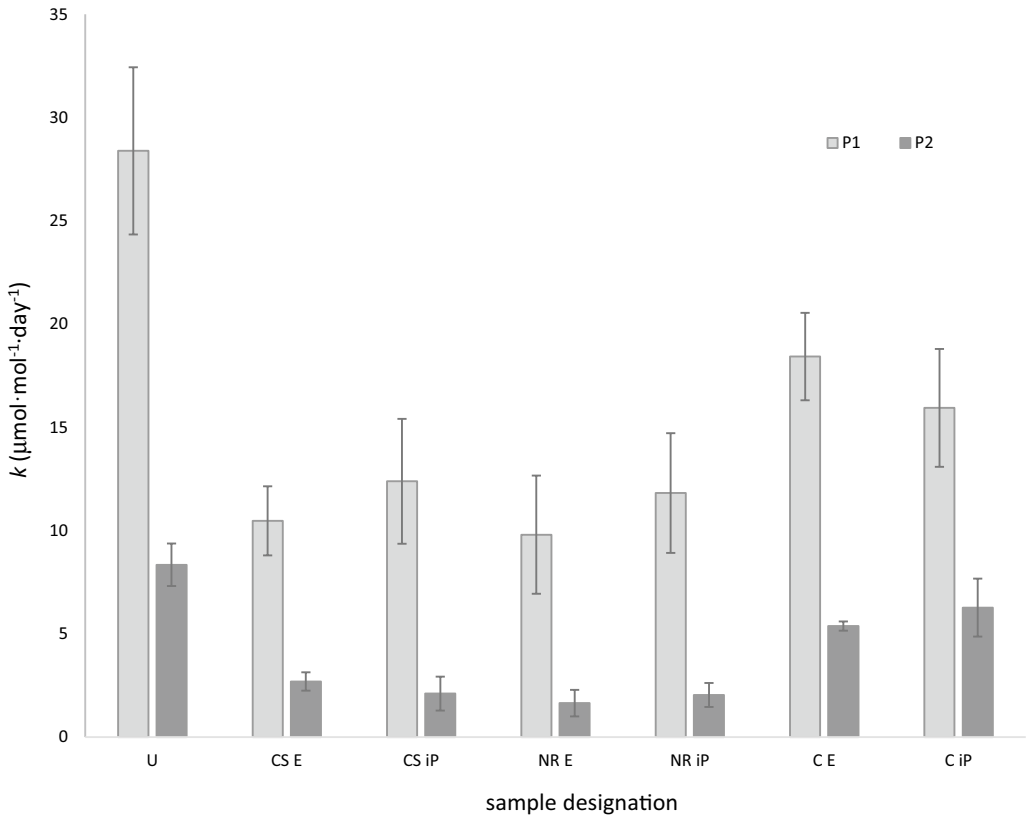

Fig. 10 Degradation rate constants of paper samples (P1 and P2) before (U) and after various deacidification treatments and accelerated degradation for up to 14 days. Error bars represent standard deviation (SD)

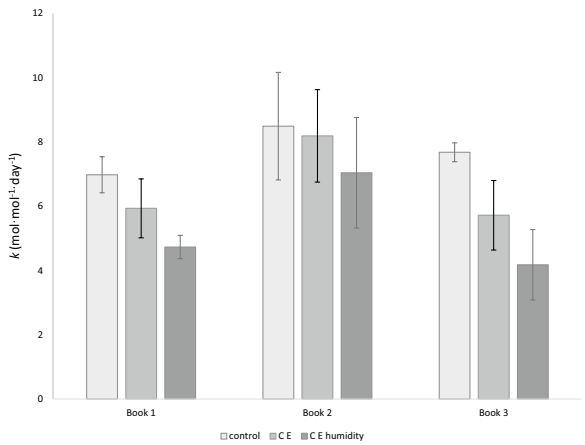

Fig. 11 Degradation rate constants for untreated (control) and deacidified papers using CE treatment and after humidifying (CE humidity) from the books (Book 1, Book 2 and Book 3). Error bars represent standard deviation (SD)

For all investigated deacidification treatments, a sufficient alkaline reserve according to ISO standard was obtained.

No differences in surface distributions of calcium particles using different treatments was observed using SEM–EDS analyses. Cross-section analyses revealed a higher amount of calcium ions inside the paper using dispersions in ethanol in comparison to those in 2-propanol.

The results indicate that all investigated deacidification systems decrease the degradation rate constant of lignocellulosic papers. In the case of calcium hydroxide dispersions the yellowing of lignocellulose paper was observed. In the case of $CaCO_3$, a slightly lower stabilizing effect in comparison to $Ca(OH)_2$ dispersion was observed, however, the treatment induced less color changes. The reason could be a lower pH obtained after the deacidification treatment.

Noticeable color changes are particularly important when the works of art or manuscripts are treated, since the contrast between the support and the image or manuscript might be diminished. On the basis of presented results, deacidification treatments containing nano calcium hydroxide could not be advised, and a less invasive treatments, such as that with nano calcium carbonate, would be preferable. In conclusion, the

application of the investigated nano calcium carbonate dispersions as a stabilizing treatment for lignocellulosic papers needs to be furtherly studied on a variety of paper samples to assess their thermal and photo stability, before it could be safely used by conservators.

Abbreviations

DP: degree of polymerization; DP_w: weight-average degree of polymerization; EDS: energy dispersive X-ray spectroscopy; FE-SEM: field emission scanning electron microscopy; *k*: degradation rate constant; PS: polystyrene standards; RH: relative humidity; SD: standard deviation; SEC: size exclusion chromatography; THF: tetrahydrofuran.

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Authors' contributions

JM managed the investigation, performed part of the analytical work and wrote the article, MKa performed most of the analytical work, TS performed FE-SEM microscopy and EDS analyses, MKu provided suspensions of calcium carbonate and their basic characterization, IKC was responsible for design of experiments and SEC analyses. All authors contributed to the interpretation of results. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

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