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

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Abstract (max 500 words)

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 performing cellulose viscosimetric degree of polymerization (DP_v) and pH measurements on artificially aged systems. Scanning electron microscopy equipped with energy dispersed X-ray spectroscopy (SEM-EDX) was used for the evaluation of calcium distribution from the deacidification agent within samples cross section. Determinations of DP_v 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 homogeneously distributed over the treated surfaces.

Keywords (5-10 words, in bold, separated by slashes)

Alkaline nanoparticles/ deacidification/ paper / cellulose/ calcium hydroxide/ gelatin/ nanocomposite/ iron gall inks/ lamination / GeolNan

Research aims (max 200 words)

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

1. Introduction

Cellulose is a linear polymer consisting of several hundred to over ten thousand D-glucose units linked 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 15000 [1].

In the interconnected supramolecular structure of cellulose, which is created by both intermolecular and intramolecular hydrogen bonds, two zones can be identified: (i) the crystallites, highly crystalline sites, having a compact structure that makes them resistant to degradation; (ii) 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 (DP_v) 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 dispersed X-ray spectroscopy (SEM-EDX). The proposed method was also test 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/m²) 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.

2. Materials and methods

2.1 Chemicals

Arabic Gum, and Gall Nuts were provided by Zecchi, ArtShop 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 M Ω cm) produced by a Millipore Milli-Q UV system was used during the experiments.

2.2 Ink preparation and application on samples

Pure iron gall ink was obtained following a recipe by Petrus Caneparius reported in a work called *De Atramentis cujuscunque generis* from 1619 [13,14]. The composition of the prepared writing fluid is reported in Table 1.

For the preparation of the ink, gall nuts were ground in a mortar. The powdered gall nuts were immersed in a mixture of ethyl alcohol, acetic acid, and water, which was subsequently heated to favor the extraction of tannic acid.. After a certain amount of time, the mixture, reduced to about 35% by volume, was cooled. In order to complete the extraction of tannic acid, the suspension was left to rest for four days,. The powder was then separated from the yellowish solution by filtration and iron sulfate was slowly added to the boiling filtrate solution. The solution suddenly turned black because of the formation of the pyrogallate-iron

complex. Gum Arabic, subsequently added to the solution, acts as a binder and as a dispersing agent for the insoluble iron(III) gallate complex.

Whatman paper no.1 (Schleicher & Schuell, 99% made with cotton fibers; paper density = 88.0 g/m²; DPv = 1200) was selected for the experiments. The ink was applied on paper by means of a brush. After a week from the preparation (RH = 50%, T = 25°C), samples were weighed to evaluate the amount of ink on paper. The average value was 50 mg ±2 mg at normal laboratory conditions with water content in the paper of about 5%. Figure 1 shows a typical inked sample: the ink is on one side of the reference paper (*recto*), whereas on the *verso* side only some spots due to ink penetration are visible.

2.3 Combined treatment preparation

The hydroalcoholic solution of gelatin, commonly used by one of the authors (C.S.) for the strengthening of manuscripts containing iron gall ink, was prepared following a standard procedure: an aqueous solution of gelatin at 5% (w/w) was prepared by adding 5 g of granular powder to cold water. The dispersion was then kept under stirring for about 20 minutes at 45°C, in order to completely dissolve gelatin. A final concentration of 3% was achieved by adding alcohols (ethanol or n-propanol) to the solution. The ratio between water and alcohol was fixed at 60:40 (v/v). Hydroalcoholic solutions of gelatin, both in ethanol and or n-propanol, are stable for at least two months. Once cooled, the solution of gelatin in water and ethanol turns into a gel, but it easily turns back to the liquid state once warmed. Several cycles of warming-cooling were performed in order to test the durability of this system. A vial containing the gelatin solution in water and ethanol was immersed in warm water (45°C) until the mixture melted. The vial was then removed from the heating bath and rapidly cooled to room temperature using cold water. No significant differences were observed during these warming-cooling cycles.

The combined treatment was obtained by adding nanoparticles dispersed in alcohol to the starting gelatin aqueous solution at 5%. Calcium hydroxide nanoparticles were synthesized in an autoclave system working at high temperature and pressure, via a solvothermal process

described elsewhere [26]. For the present work, calcium hydroxide nanoparticles dispersed in ethanol (E system) and in n-propanol (1P system) at a concentration of 30 g/L were used. For the application on mockups and real samples, different concentration of nanoparticles were tested, while gelatin concentration was kept at 3% and the ratio between water and alcohol at 60:40 (v/v).

2.4 Mockups treatment

500 μ L of the two hydroalcoholic solutions of gelatin was applied by brush on each side of inked samples. Samples treated with gelatin in ethanol are labeled as “Gelatin E”, whereas samples treated with gelatin in n-propanol are labeled as “Gelatin 1P”.

Other inked samples were treated with 1ml of the two combined treatments (nanoparticles in hydroalcoholic gelatin solution, 8 g/L), brushing 500 μ L on each side of the paper. Samples treated with the combined treatment in ethanol are labeled as “GeolNan E”, whereas samples treated with the combined treatment in n-propanol are labeled as “GeolNan 1P”. All the treated samples were then left to dry at RH = 50% and T = 25°C for 10 days before the artificial aging.

2.5 Mockups aging protocol

In order to accelerate the degradation of cellulose, untreated, Gelatin, and GeolNan samples were artificially aged in strong hydrothermal conditions. The samples (about 6 g) were placed in a sealed vessel (5 L), which was put in an oven set at 80°C. Inside the sealed vessel, humidity was kept at 75% using sodium chloride saturated aqueous solution. Samples pH and DP_v were monitored during the aging.

2.6 Mockups characterization

For pH measurements of paper, 125 mg of sample, preconditioned at 25°C and 50% RH for two days, was weighted, cut in small pieces (about 9 mm²) and placed inside screw top vials. 9 mL of ultrapure water was added inside each vial, subsequently sealed in order to avoid the

solubilization of CO₂ from air into the extracting water. Vials were kept under stirring for one hour, before measuring the pH of the extraction by using a digital pH-meter (CrisonBasic 20, equipped with a combined electrode, model 52-21). Three measurements were performed on each sample. The error associated to pH measurements on these samples is ±0.2.

To evaluate treatments efficacy, viscosimetric determinations of the degree of polymerization (DP_v) were performed [27]. The data are presented in terms of scissions per initial cellulose chain (S*), calculated using the following equation [28,29]:

$$S^* = DP_{v_0} / DP_{v_t} - 1$$

where DP_{v₀} is the degree of polymerization at time zero, and DP_{v_t} is the degree of polymerization at time t. It is worth noting that an accurate calculation of the number of scission cannot be extracted from DP_v, due to the fact that polydispersity cannot be assessed by viscosimetric determinations [30]. Nevertheless, in the present work, the comparison of S* values calculated from DP_v can be considered fully acceptable, because the experimental data refer to homologous series of samples. Three measurements were performed on each sample. Error bars reported in the graphs are calculated from the experimental error of DP_v measurements (±50).

The penetration of the combined treatment within the cross section of samples was assessed with SEM-EDX maps acquired on GeolNan samples. The mapping was also performed on untreated inked paper and on Gelatin samples, which can be considered as blank systems.

For the preparation of samples, small portions of paper (1x1 cm²) were used. Half of each portion was glued to an aluminum stab while the other half was folded in order to have a piece of paper perpendicular to the surface of the stab. Therefore, SEM-EDX maps were acquired within samples cross section in an area of about 25*10³ μm². A field emission scanning microscope SIGMA (Carl Zeiss Microscopy GmbH, Germany), equipped with a OXFORD X-ACT system, was used.

2.7 Application on 16th and 18th century manuscripts

For the application on real samples, original manuscripts dating from 18th century were used. Selected manuscripts are common administrative documents written with metal gall ink on rag handmade paper. Sample named M13.20a was left untreated, while sample M13.21b was deacidified using the combined treatment of gelatin and nanoparticles in ethanol. Sample M13.24b was laminated on both sides with the combined treatment and Japanese tissue (paper density = 3 g/m²), following a standard conservation procedure. The pH of 18th manuscripts was measured using a Crison micro-pHmeter (model number 2000) equipped with a combined glass electrode; pH measurements on cold extracts were performed following an adapted procedure (ISO 6588-1). For each sample, about 10cm² were obtained and cut in small pieces (about 1 mm²). Prior to pH measurements, samples were stirred for 30 minutes in a mixture consisting of 100 mL of Millipore water and 1 mL of KCl.

Several 16th century manuscripts (1551-1591) were selected from volumes from the Archive of the Crown of Aragon. The combined treatment was used for the lamination of paper sheets showing extreme corrosion. The reinforcement was achieved using Japanese tissue and the combined treatment in ethanol. After the application, as in a traditional restoration procedure, paper sheets were dried on blotting paper covered with Reemay, which partially absorbs the treatment. Therefore, some of the applied nanoparticles do not participate to the neutralization of the acidity. The application on 16th century manuscripts was carried out considering this phenomenon. After 2 days, 10 days, 1 month, and 3 months from the treatment, the surface pH was measured using a Crison Digilab 517 pHmeter equipped with a surface electrode following a standard procedure (T-529 om-99). SEM pictures and EDX maps of historical samples were acquired using a JEOL-SEM 7100F equipped with an Oxford EDS INCA Energy 200 (20 kV accelerating voltage).

3. Results and discussion

Calcium and magnesium hydroxide nanoparticles dispersed in short-chain alcohols were proposed as deacidifying agents for paper about 15 years ago [10–12] and their efficiency

was assessed in several studies [13,14,26,31–34]. Stable and highly concentrated nanoparticles dispersions in ethanol and n-propanol have been recently obtained by a solvothermal reaction [26]. These dispersions were used for developing the GeolNan method, a restoration procedure for the concomitant deacidification and reinforcement of highly corroded manuscripts containing iron gall inks.

The role of gelatin in hampering cellulose degradation due to iron gall ink is still debated. Gelatin is believed to slow down iron gall ink corrosion as it reduces ion mobility or it complexes metal ions [35–37]. Others authors have shown that, on strongly unbalanced inks, its action is incidental [38].

For what concerns the prepared mockups, the presence of gelatin does not affected the pH, as can be seen from data reported in Figure 2; the starting pH of inked system is highly acidic and it remains quite stable upon the artificial aging. Under this condition, the degradation of cellulose due to acid-catalyzed hydrolysis of the glycosidic bonds is favored and occurs at a high rate [13,14,38]. Despite the fact that pH values of untreated and Gelatin E and 1P mockups are similar, the application of the strengthening treatment partially reduces the degradation of paper due to the artificial aging as indicated by the S^* of samples during the aging, reported in Figure 3. Considering that the pH is not increased by the presence of gelatin, its beneficial action could be due to the hampering of the metal-catalyzed oxidation of cellulose, by reducing ion mobility or complexing metal ions [35–37].

After 12 hours of artificial aging, the scission number of untreated sample is two times higher than the corresponding S^* values of Gelatin E and Gelatin 1P samples. This difference become more significant at the end of the aging (48 hours), when the S^* of the untreated sample is about 4.5, whereas the S^* of Gelatin E and Gelatin 1P are 1.6 and 1.3, respectively. The difference in S^* between Gelatin samples is very close to the experimental error and is not significant.

In the untreated sample, the mechanical resistance of paper changes as a function of the aging time. As can be seen in Figure 4-A, the 24-hours-aged sample is very fragile, and cannot be easily handled without cracking the paper. At the end of the aging, the untreated sample

shows the complete loss of the original mechanical resistance (see Figure 4-C). On the other hand, Gelatin E and Gelatin 1P samples show a better resistance to the aging (see Figure 4-B), even though they are quite fragile after 48 hours and should be handled with care.

The combined treatment was tested on inked samples; after the treatment, deacidified samples pH is around 9, indicating that both the combined treatments are efficient in neutralizing the acidity due to the presence of the iron gall ink. As shown by Strlič et al., around pH 9 the catalytic activity of iron ions is low; under this condition, cellulose oxidation catalyzed by metal ions is not favored [24]. For what concerns the application on real samples, which can potentially contain traces of copper ions, the stabilization of pH around neutrality is preferable. The application by brushing of 500 μL on each side of the paper (about 20 cm^2) leads to an increase of 6 pH units in both GeolNan E and 1P samples; the obtained values remain stable during the 48 hours of artificial aging, as reported in Figure 5.

The S^* of untreated sample and GeolNan systems are reported in Figure 6: after 6 hours of aging, both treated samples (GeolNan E and GeolNan 1P) do not display significant changes in S^* with respect to the corresponding unaged samples. On the other hand, the S^* of the untreated mockup is significantly increased. The beneficial action of the combined treatment is manifest after 24 hours of artificial aging, when the S^* of untreated sample is more than 20 times higher than the corresponding values of GeolNan systems. At the end of the aging, the S^* of deacidified samples are typical of well-preserved samples.

The visual aspect of samples is consistent with the S^* of inked mockups: as can be seen in Figure 4-D, GeolNan 1P retains the original mechanical properties after 48 hours of aging. Paper is elastic and can be manipulated without altering the surface of the samples. The same behavior has been observed on GeolNan E sample. As a comparison, in Figure 4-C, the untreated sample at the end of the aging is reported: as a result of the depolymerization of cellulose, paper is easily broken, making the manipulation of sample very difficult.

From the experimental data here presented, it is evident that the GeolNan combined treatment significantly increase cellulose resistance to the concomitant action of hydrolysis and oxidation, induced by the accelerated aging; the benefits arising from the combined

treatment could be mainly ascribed to the presence of nanoparticles, even if gelatin itself partially hampers the depolymerization of cellulose, probably slowing down the oxidation reaction, by reducing ion mobility or complexing metal ions [35–37].

The distribution of GeolNan treatment within paper samples was assessed by SEM-EDX maps. In Figure 7, the SEM-EDX maps of iron and calcium ions for GeolNan E sample are reported. Iron is unevenly distributed on inked samples, being the writing fluid only on the recto side, as can be clearly seen in Figure 1. On the other hand, calcium ions are homogeneously distributed within the cross section of the deacidified sample (sample thickness = 180 μm). It is worth noting that calcium was not detected on untreated and Gelatin mockups; therefore, it can be concluded that the presence of calcium in deacidified samples is only due to the application of the GeolNan treatment.

For the application on real samples, original manuscripts dating from 18th century were used. The selected manuscripts are common administrative documents consisting of metal gall ink and rag handmade paper. A pH of 4.4 was measured on the inked areas of original manuscripts. The application of the combined treatment was tuned in order to reach neutrality (measured pH = 6–6.5). In a neutral environment the catalytic activity of both copper and iron ions is very low; therefore, a pH around 6.5 is preferable if ink composition is unknown. As expected, the presence of Japanese tissue in the laminated sample (M13.24b) does not induce any significant changes in the pH of sample, whose acidity is efficiently neutralized by calcium hydroxide nanoparticles.

SEM images, reported in Figure 8, clearly show that the combined treatment is homogeneously distributed over the samples surface; the adhesion of nanoparticles to cellulose fibers is shown in Figure 8-D, in which small clusters of calcium hydroxide platelets can be seen.

The distribution of nanoparticles on manuscript surface was assessed with SEM-EDX calcium maps (Figure 9): white spots in Figure 9-D are due to presence of calcium, which is homogeneously distributed over the surface. The comparison between maps acquired on treated and untreated samples (Figure 9-B) clearly shows that the presence of calcium presence is mainly ascribed to the applied treatment. It is worth noting that, in the case of

the laminated manuscript, the presence of Japanese tissue does not limit the spreading of particles over the surface.

The application of the GeolNan combined treatment to extremely corroded 16th century manuscripts from the Archive of the Crown of Aragón leads to a significant improvement in the manipulation of paper sheets. It is worth noting that the proposed method can be directly applied manuscripts bound in volumes (see Figure 10). As a result of the application of the GeolNan combined treatment, the pH of manuscripts increases. In particular, surface pH measurements conducted on treated 16th century manuscript show that the amount of nanoparticles to be applied for the neutralization of acidity depends on the initial pH of paper. In particular, for pH around 3, the appropriate nanoparticles concentration of the combined treatment is 8 g/L; lower concentration are preferable if the inked areas of the manuscripts have a starting pH higher than 3.5. As expected, the uninked portions of the manuscripts (pH = 5), require lower amount of neutralizing agent.

Conclusions

A new method, combining a deacidification treatment based on calcium hydroxide nanoparticles and a reinforcement process with gelatin and Japanese tissue, has been proposed for the conservation of paper containing iron gall inks. The treatment, which can be prepared in water and ethanol or water and n-propanol, was applied by brushing on inked mockups, which were artificially aged at high temperature and relative humidity.

Significant differences in cellulose viscosimetric degree of polymerization between treated and untreated mockups were observed upon artificial aging, beginning after 6 hours and increasing thereafter. This confirms that the treatment could limit the depolymerization of cellulose during long-term aging of manuscripts and books in archival, museums, and private collections. Both formulations, in ethanol and n-propanol, were effective in hampering cellulose depolymerization, as shown by cellulose degree of polymerization. Treated mockups retained a pH of 9 even after 48 hours of accelerated aging, suggesting that the treatment could be effective in stabilizing the pH of paper during long-term natural aging. In

treated mockups, the presence of calcium within samples cross section was assessed using scanning electron microscopy equipped with energy dispersing x-ray spectroscopy. On historical manuscripts, the combined treatment was used to reach a pH around 6.5, which is preferable if the ink composition is unknown. Calcium map acquired using SEM-EDX showed that the deacidifying agent is homogeneously distributed over the treated surfaces and that the presence of the Japanese tissue, used for the lamination of paper, does not hamper the spreading of particles.

In conclusion, the here proposed combined treatment may represent an efficient method for stabilizing historical manuscripts, whose preservation is of fundamental importance. The experimental data show that the method could overcome the limit of a traditional methodology, potentially improving the useful life of historical manuscripts and granting, at the same time, their manipulation.

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Table 1. Composition of the reaction mixture for the preparation of the iron gall ink.

Ingredient	Amount
Gall Nuts	4.8 g
Water	132 mL
Ethanol	18 mL
Acetic Acid	17.4 mL
Iron sulfate	4.8 g
Arabic Gum	14.4 g

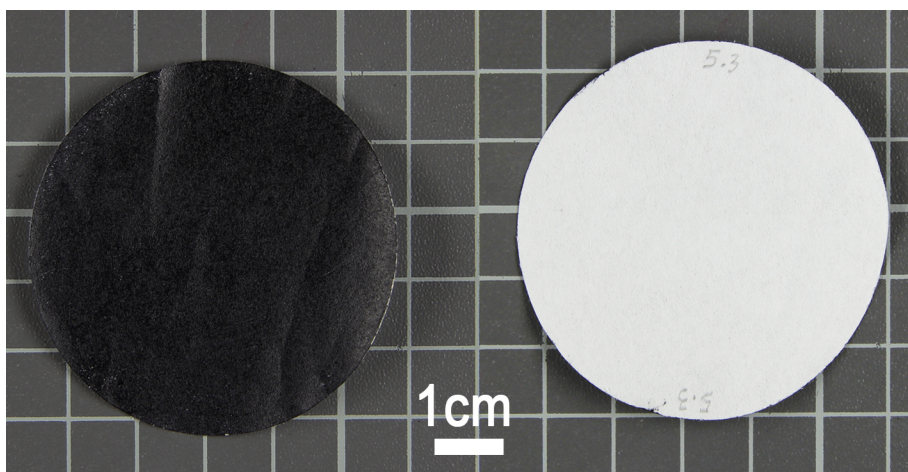


Figure 1. *Recto* and *verso* sides of iron gall inked Whatman filter paper. Each square on the background measures 1 cm².

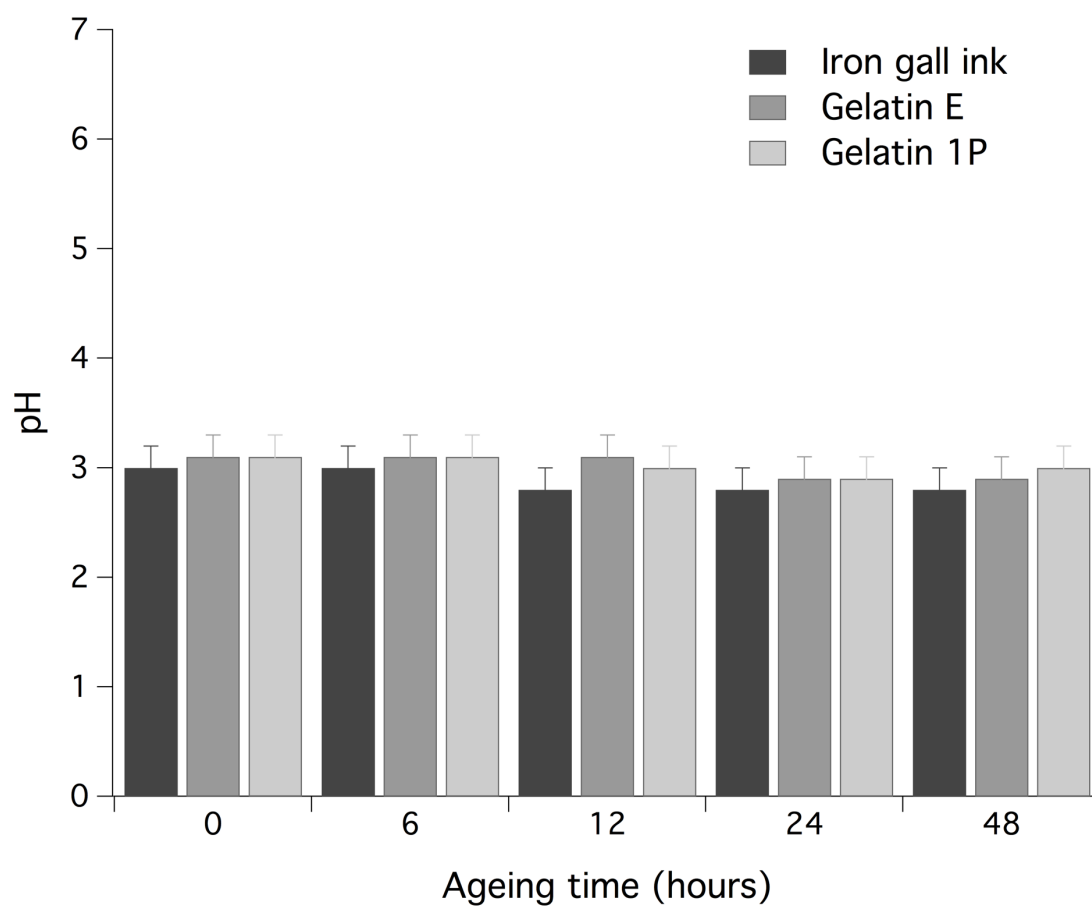


Figure 2. Comparison between pH values of untreated inked samples and samples treated with the two hydroalcoholic gelatin solutions, in ethanol (Gelatin E) and in n-propanol (Gelatin 1P). The application of the strengthening treatment alone does not affect the pH of the systems.

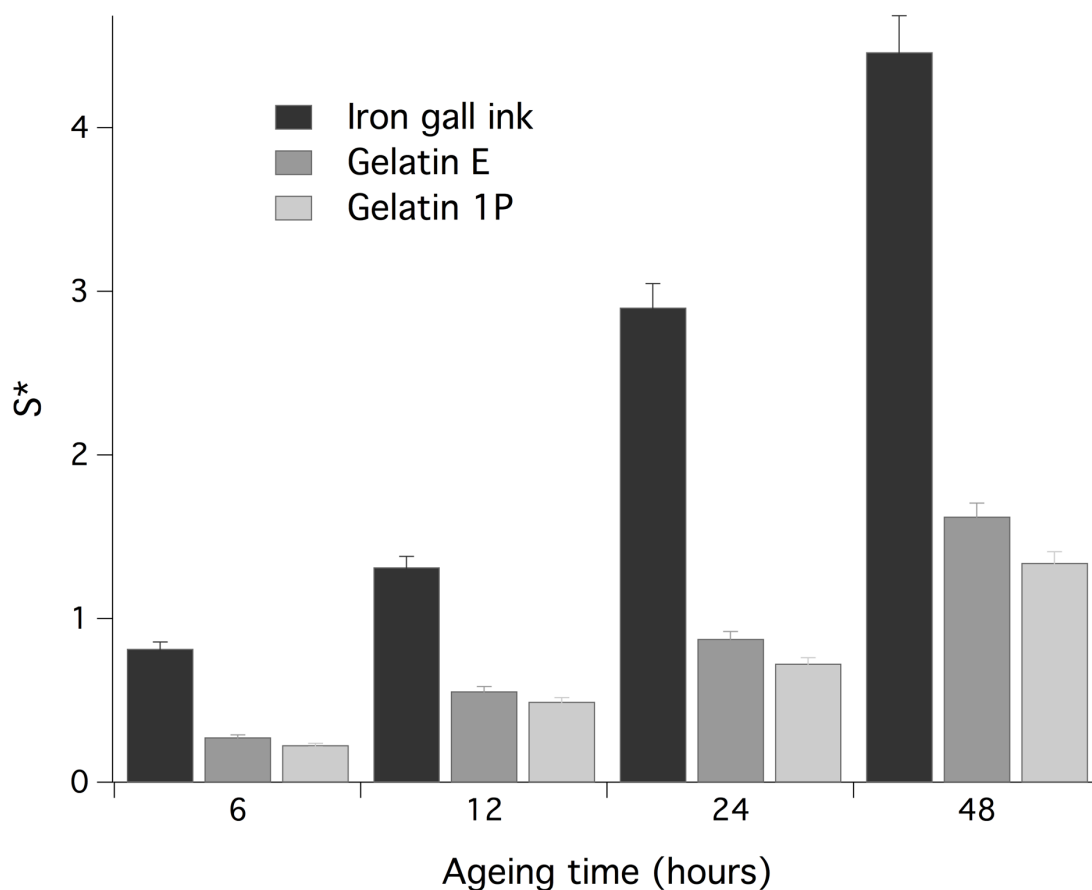


Figure 3. Comparison between scission numbers (S^*) of untreated inked samples and samples treated with the two hydroalcoholic gelatin solutions, in ethanol (Gelatin E) and in n-propanol (Gelatin 1P). The application of the strengthening treatment partially reduces the degradation of paper due to the artificial aging.

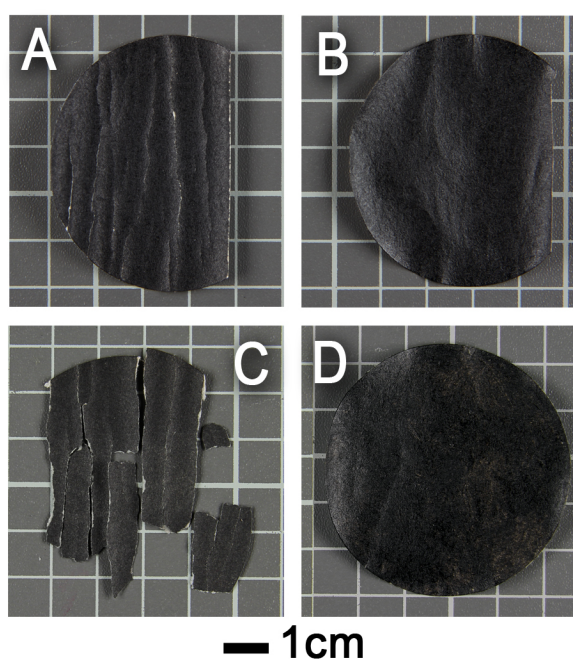


Figure 4. *Recto* side of iron gall inked sample (A) and of Gelatin 1P sample (B) after 24 hours of aging. A complete loss of mechanical resistance is evident on the untreated sample, whereas Gelatin 1P shows a good resistance to the aging. *Recto* side of iron gall inked sample (C) and of GeolNan 1P sample (D) after 48 hours of artificial aging. The different resistance to artificial aging is manifest. GeolNan sample retains its original mechanical properties.

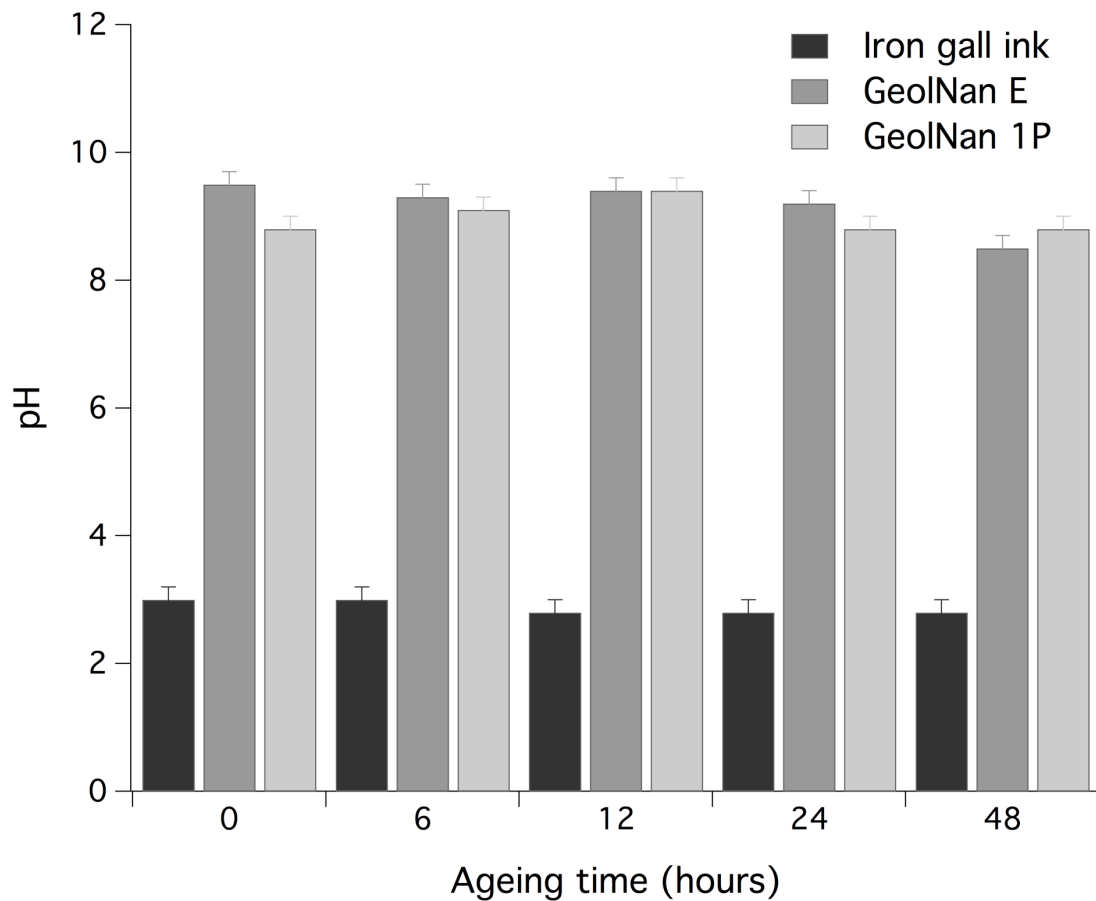


Figure 5. Comparison between pH values of untreated inked samples and samples treated with the two combined treatments, in ethanol (GeolNan E) and in n-propanol (GeolNan 1P). Samples pH is stabilized around 9, which can be considered a safe value in the case of pure iron gall ink.

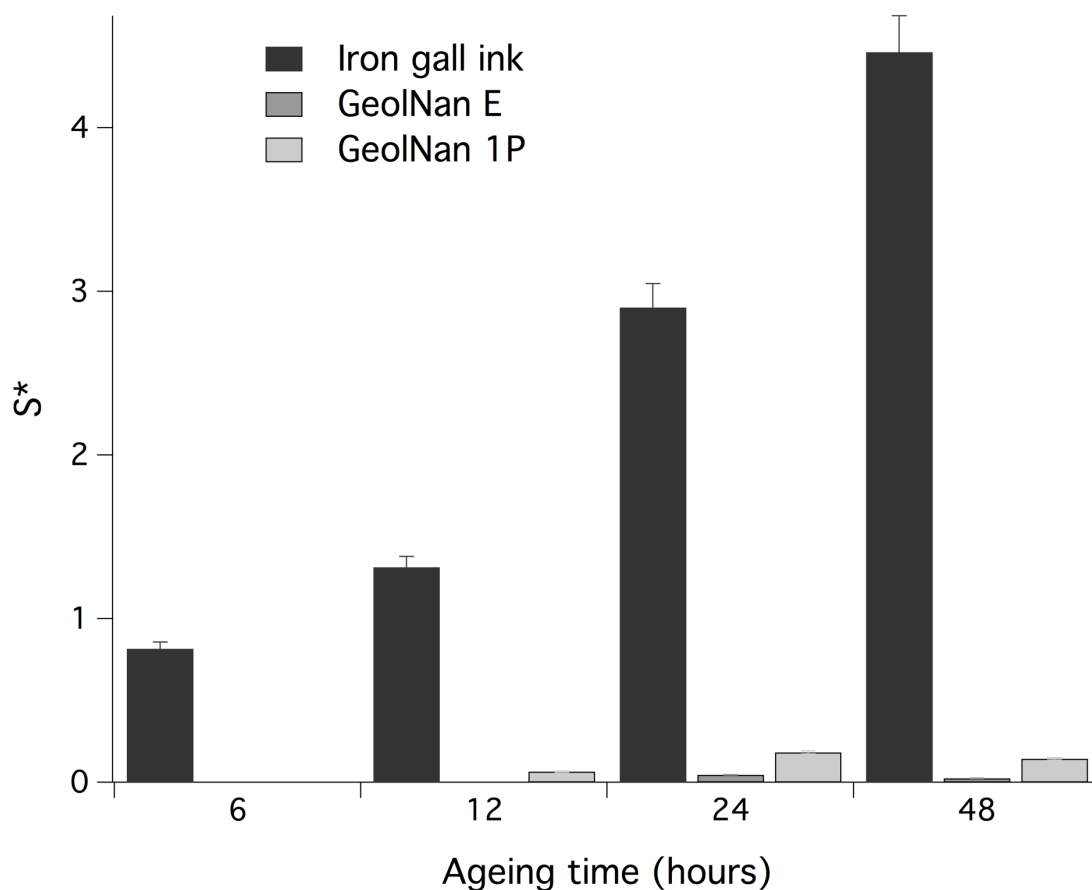


Figure 6. Comparison between scission numbers (S^*) of untreated inked samples and samples treated with the two combined treatments, in ethanol (GeolNan E) and in n-propanol (GeolNan 1P). The application of both combined treatments significantly hampers the detrimental action of iron gall ink on cellulose-based samples.

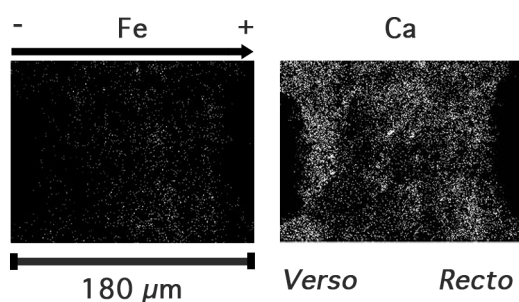


Figure 7. SEM-EDX mapping of Fe (left) and Ca (right) on GeolNan E system before the aging as a function of sample thickness. It is evident that calcium hydroxide nanoparticles are homogeneously distributed in treated samples, whereas ink can be found mainly on the *recto* side.

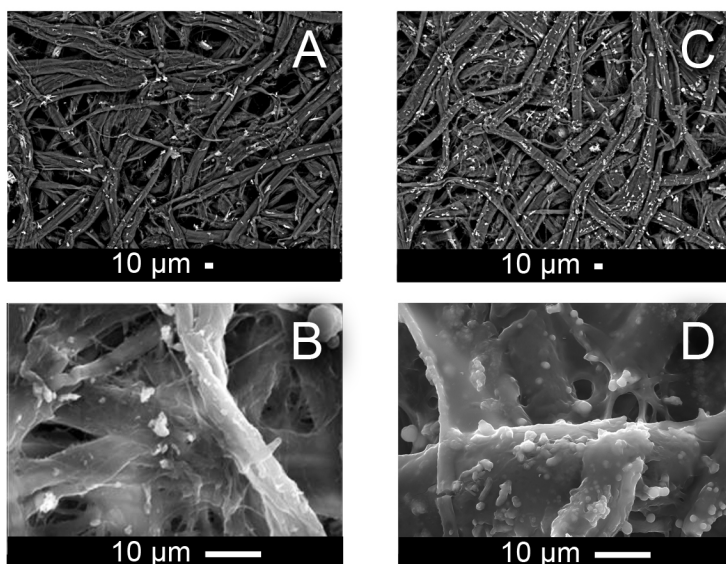


Figure 8. SEM images of original 18th manuscripts: (A-B) untreated sample, respectively 300 and 2k nominal magnification; (C-D) sample treated with the combined treatment in ethanol, respectively 300 and 2k nominal magnification. The presence of small clusters of nanoparticles adhering to cellulose fibers is evident in panel C and D.

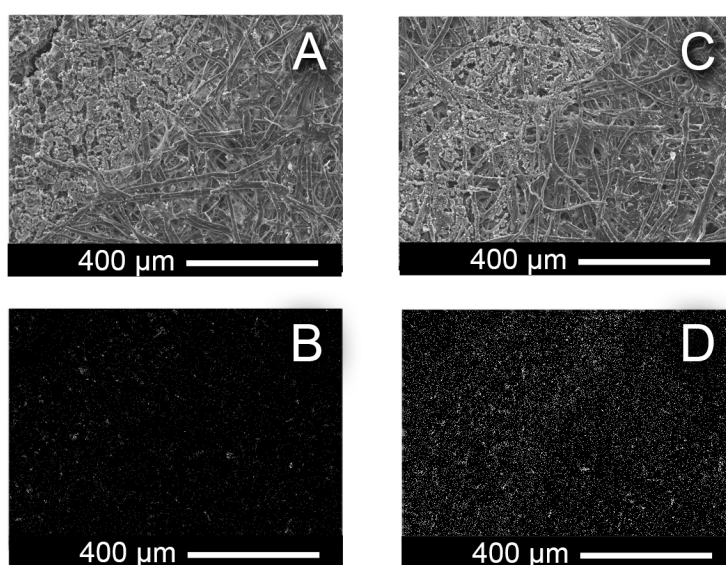


Figure 9. SEM-EDX mapping of Calcium on original 18th manuscripts: (A-B) untreated sample, 200 nominal magnification; (C-D) sample treated with the combined treatment in ethanol, 200 nominal magnification. The surface distribution of calcium shows a homogenous distribution of nanoparticles over the manuscript surface.

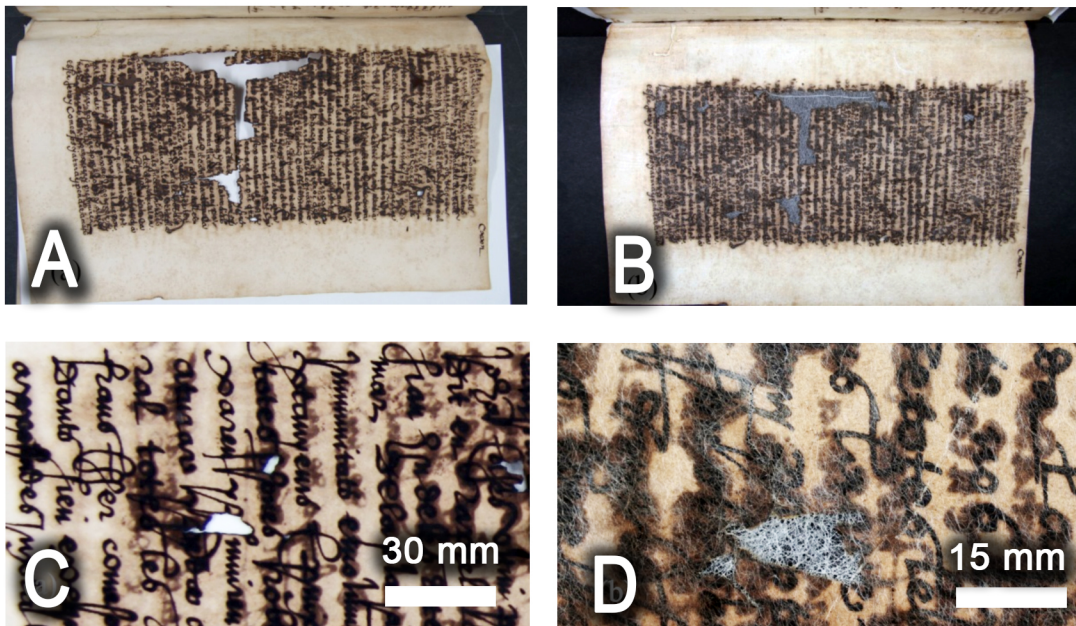


Figure 10. (A) Extreme corrosion of paper sheets in a 16th century volume. (B) The same sheet after the lamination using GeolNan E applied on both sides. The reinforcement with Japanese tissue allows for manuscript manipulation. (C) Detailed view of an extremely corroded paper sheet in a historical book (1580). (D) The same page after GeolNan E lamination (6.4 g/l nanoparticles concentration).