Original article

A stabilizer-free non-polar dispersion for the deacidification of contemporary art on paper

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ABSTRACT

The preservation of cellulose-based works of art is threatened by the presence of acidity within the substrates, native, i.e., due to the papermaking process, or developed upon aging. The depolymerization of cellulose catalyzed by acidic compounds leads to a decrease in the mechanical properties of the artworks. Many strategies for hampering the acid-catalyzed degradation of cellulosic substrates have been developed in the past; unfortunately, few of them can be safely used on contemporary artworks, drawings or archival materials. In this paper, a new method for the pH control of paper, potentially compatible with most of ballpoint pen drawings and manuscripts, and also safely usable on folded or creased paper, is proposed. A deacidifying dispersion of calcium hydroxide in cyclohexane has been prepared starting from alkaline nanoparticles obtained via a solvothermal reaction. The most interesting feature of this formulation is that a stabilizer is not required for the preparation of a stable dispersion, differently from other commercial non-polar products. Cyclohexane is a colorless, non-polar, and volatile liquid that allows fast and simple applications by spraying. In order to evaluate the efficacy of this $Ca(OH)_2$ nanoparticles dispersion in cyclohexane, mockups were prepared on acidic paper using a ballpoint pen. The protective action arising from the applied treatment was evaluated upon artificial aging, measuring cellulose viscosimetric polymerization degree (DPv), cellulose pyrolysis temperature, samples pH, and colorimetric coordinates. The interesting results obtained on mockups led to the application of this new formulation on a series of creased, perforated and burnt drawings from a private collection.

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1. Research aims

Paper is one of the most common substrates used for works of art, and acid-catalyzed hydrolysis has a primary role in its degradation. A deacidification treatment is usually advisable on acidic substrates. Traditional deacidification methods include aqueous solutions of calcium bicarbonate and calcium hydroxide. About fifteen years ago, dispersions of alkaline nanoparticles in short-chain alcohols were proposed for deacidification and pH control of cellulose-based artworks. It is worth noting that the use of paper changed in the middle of 20th century, moving from a simple support for studies or sketches to being the heart of autonomous works, at time torn, burnt, folded, or creased. At the same time, new media, such as acrylic and vinyl resins, pressure sensitive adhesives, ballpoint and felt-tip pens and markers have become popular among artists. These media are rarely compatible with traditional restorative procedures. In particular, few are the available deacidification treatments that can be safely used on contemporary drawings or contemporary art on paper, as well as on contemporary documents and manuscripts. The aim of this paper is the development of a method for the pH control of paper, which can be safely used on some ballpoint pens artworks, even if folded or creased.

2. Introduction

Cellulose is a linear natural polymer, which consists of several hundred to over ten thousand D-glucose units linked each other

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by a β-(1,4)-glycosidic bond. The degree of polymerization (DP) of native cellulose ranges from 7000 to 15,000 [1].

Intermolecular and intramolecular hydrogen bonds are responsible for the supramolecular structure of cellulose, in which highly crystalline sites (crystallites) and amorphous zones can be identified. The latter are less oriented and more prone to be degraded by chemical reagents, while crystallites, due to their compact structure, are more resilient to degradation.

Depolymerization of cellulose is due to the hydrolysis of β-(1,4)-glycosidic bonds, mainly catalyzed by acidity. A three steps mechanism has been proposed for this reaction [2,3], which occurs at room temperature, resulting in a self-accelerating mechanism [4,5]. PH, temperature, moisture content and degree of crystallinity, affect the hydrolysis reaction. The depolymerization of cellulose results in a decrease of mechanical properties of cellulose-based materials [6].

The so-called "spiraling effect" [7,8] describes the connection between acidity and oxidation in promoting cellulose degradation. For instance, as a result of oxidation reactions in acid environment, several organic acids, such as uronic, glucuronic, aldaric, glucaric, are produced, promoting the hydrolysis of cellulose.

Paper is one of the most common substrates used for works of art, and acid-catalyzed hydrolysis has a primary role in the degradation of cellulose-based artefacts. Paper sheets produced in the past four centuries may be carriers of acidic compounds that could catalyzed the degradation of cellulose, as above described. For instance, the corrosive action of iron and metal gall ink is mainly ascribed to the presence of sulfuric acid released during the ink preparation [9,10]. In addition to that, compounds from the paper manufacturing process, i.e. alum and rosin sizing, could be sources of acidity [11]. Therefore, as recently revealed [12], it is not surprising that an average of 30% objects in European libraries are in poor condition, and that another 30% will be by the end of this century, or earlier.

There is a long tradition in deacidification and pH bcontrol of cellulose-based works of art. Traditional procedures include aqueous solutions of calcium (or magnesium) bicarbonate and calcium hydroxide. About fifteen years ago, the use of dispersions of alkaline nanoparticles, mainly calcium and magnesium hydroxide in short-chain alcohols, was proposed as an efficient way for the deacidification and pH control of several cellulose-based works of art [13–15]. Since then, several systems have been formulated and applied to paper [16,17], iron gall inked manuscripts [18–20] and archeological wood [21–23]. Nanoparticles high reactivity grants a fast neutralization of acidity, providing a neutral environment due to the conversion of hydroxides into carbonates, which are milder alkaline species. The stabilization of pH around neutrality hampers the alkali-catalyzed degradation of strongly oxidized paper, which could occur during the application of traditional methods, such as aqueous deacidification treatments [24–26].

The use of paper started to change in the middle of 20th century, moving from a simple support for studies or sketches to being the heart of autonomous works, at time torn, burnt, folded, perforated, twisted or creased. This is the case of Simon Schubert, Kiki Smith or Stefano Arienti artworks. At the same time, the world of art has seen the arrival of a large number of new media, such as acrylic and vinyl resins, pressure sensitive adhesives, ballpoint and felt-tip pens and markers. The same pens and markers used by contemporary artists can be found in manuscripts and archival documents. Most of these media and techniques are poorly compatible with traditional restorative procedures. This makes the conservation and restoration of the wide field of contemporary drawings and archival documents unexplored. In particular, few are the available deacidification treatments that can be safely used on contemporary drawings or contemporary art on paper, as well as on contemporary documents and manuscripts.

In this paper, a deacidification method based on calcium hydroxide nanoparticles stably dispersed in cyclohexane is proposed. The efficacy of this method was tested on acidic paper mockups featuring ballpoint pen ink (Bic Cristal Blue). The protective action arising from the deacidifying treatment was evaluated upon artificial aging, measuring cellulose viscosimetric polymerization degree (DP_v), cellulose pyrolysis temperature, samples pH, and colorimetric coordinates. The method was also tested on contemporary drawings from a private collection. Reflectance transformation imaging (RTI), a computational photographic method that captures the surface shape of artifacts in a non-invasive way, was used to evaluate the compatibility of the newly developed cyclohexane dispersion with burnt, perforated and creased paper.

3. Materials and methods

3.1. Chemicals

n-Propanol (99.5%, Sigma-Aldrich), metal granular calcium (99%, Aldrich), and cyclohexane (99.5%, Panreac) were used for the preparation of nanoparticles dispersion. Highly pure water (having a resistivity of 16 MΩ·cm) produced by a Millipore Milli-Q UV system was used during the experiments. For DP determination via viscosimetric measurements, bis(ethylenediamine) copper(II) hydroxide solution (Sigma-Aldrich) was used.

3.2. Particles preparation and characterization

Calcium hydroxide nanoparticles were synthesized in an autoclave system (Parr Instrument) working at high temperature and pressure via a solvothermal reaction. Calcium metal and *n*-propanol were used to prepare *n*-propoxide, which turned to hydroxide after hydrolysis, in a one-pot process described elsewhere [17,23]. Nanoparticles were then dried under vacuum and dispersed in cyclohexane using an ultrasonic bath at a concentration of 1 g/L.

Transmission electron microscopy (TEM) was performed using a JEOL JEM3010 operating at a 300 kV acceleration voltage, point to point resolution 0.17 nm at Scherzer defocus. For the preparation of TEM samples, the dispersion was diluted to 0.25 g/L, that is an appropriate concentration to obtain systems homogenously distributed on a holey carbon Cu-grid.

To evaluate the stability of the nanoparticles dispersion, turbidimetry measurements were performed with a Varian Cary 100 Bio spectrophotometer, equipped with a Peltier Multi-block; the absorbance of the sample at 650 nm was measured as a function of time. Absorbance was assumed proportional to the system turbidity: the decrease of absorbance over time is due to particles settling. Measurements were carried out at 25 °C, using sealed quartz cuvettes with an optical path of 0.5 cm.

3.3. Compatibility test

Preliminary compatibility test were conducted using calcium hydroxide nanoparticles dispersion in cyclohexane on samples featuring Bic Cristal blue ink. A drop of dispersion was placed on samples and a video of the evaporation of the solvent was acquired using a Canon EOS 60D equipped with a Canon EF 100 mm f/2.8 Macro lens. Screenshots were extracted from the video at different time from the drop deposition. A similar test was conducted on the same sample, acquiring microscopic pictures using a Reichert Zatopan optical microscopy equipped with a Nikon digital Sight DS-Fi2 camera.
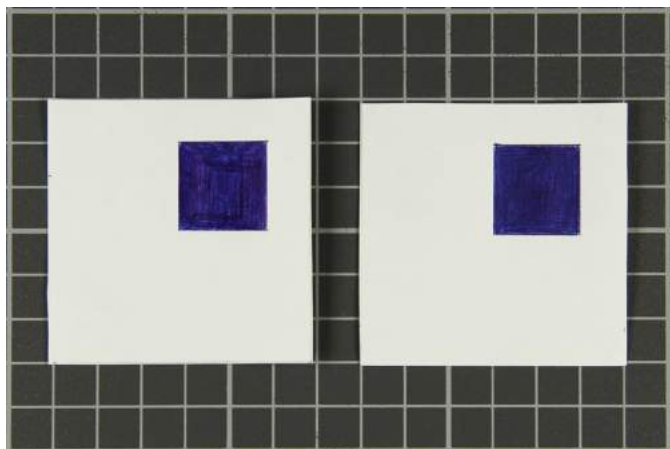
Fig. 1. Mockups prepared on acidic paper using Bic Cristal blue ballpoint pen. Untreated sample (left) and deacidified sample (right) before the artificial aging. Squares on the background measure 1 cm^2.

3.4. Mockups preparation and characterization

Acidic paper (paper grammage 90 g/cm^2) was used for preparing square-shaped samples (12 cm^2). Paper is composed of 70% hardwood bleached pulp, 30% softwood bleached pulp and 20% pulp-filling agent kaolin OT80. Acidity is due to the presence of an acidic resinous sizing (Sacocell 309 aluminum sulphate). On each sample, a square of 4 cm^2 was drawn in a corner using Bic Cristal blue ballpoint pen (see Fig. 1). As can be seen from pictures, due to the thin pen tip, the inked layer is not homogenous.

For the pH measurements of mockups, 125 mg of sample, preconditioned at 25 °C and 50% for two days, was weighted, cut in small pieces (about 9 mm^2) and placed inside screw top vials. 9 mL of ultrapure water (having a resistivity of 16 MΩ·cm) was added inside each vial, which was subsequently sealed, in order to avoid the solubilization of CO_2 from air into the extracting water. The 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).

The thermal behavior of paper samples was studied using a SDT Q600 TA Instrument, operating between 25 and 500 °C at a heating rate of 10 °C/min under nitrogen flow (100 mL/min). For each measurement, about 5 mg of sample was placed inside an aluminum pan and analyzed. From the thermal curves, the pyrolysis temperature (Tp), defined as the maximum of the weight loss derivative, was recorded and used as an indicator of the conservation conditions of the sample [27–29]. Tp experimental error is ± 1 °C.

Viscosimetric determinations of the degree of polymerization (DP) were performed to evaluate mockups resistance to aging [30]. In order to minimize the influence of different standards and techniques used for DP determination [31,32], data are presented in terms of scissions per initial cellulose chain (S^*):

$$S^* = DP_o/DP_t - 1$$

where DP_o is the degree of polymerization at time zero, and DP_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 DPv, due to the fact that polydispersity cannot be assessed by viscosimetric determination [33]. Nevertheless, in the present work, the comparison of S values calculated from DPv can be considered fully acceptable, because the experimental data refer to homologous series of samples. The error bars reported in Fig. 8 are calculated from the experimental error of DPv measurements (± 50 units).

Reflectance spectra were acquired using a Lambda 35 UV-VIS spectrophotometer, working in a λ range of 400–700 nm (with 1 nm of resolution), equipped with an integrating sphere having a circular sampling spot (diameter = 1.5 cm). Colorimetric coordinates were extracted from reflectance spectra using standard illuminant D65 and a standard observer at 10° (CIE 1964). The color difference between samples can be expressed in terms of the ΔE^* parameter, calculated from the colorimetric coordinates and L^*, a^*, and b^*, following the CIEDE2000 definition [34].

For what concerns uninked paper, six reflectance spectra were acquired for each sample. The error bars reported in Fig. 6 are calculated from the experimental error of colorimetric measurements (± 0.5 units). A single spectrum was acquired on inked portion of the samples.

3.5. Mockups deacidification

Each mockup was deacidified with a total amount of 12 mL of calcium hydroxide nanoparticles dispersion in cyclohexane at a concentration of 1 g/L (6 mL on each side). The dispersion was sprayed on the samples using an airbrush (nozzle diameter 0.3 mm), connected to a compressor, set at 1 bar. During the application, the distance between the sample, which was mounted on a vertical support, and the airbrush was 10 cm. Each application consisted of the spraying of 1 mL on each side. Multiple applications were carried out until the chosen amount of dispersion to be applied was reached. Deacidified samples were then left at 50% RH for 14 days, time needed for calcium hydroxide excess to turn into carbonate.

3.6. Mockups aging

In order to accelerate the degradation of cellulose, samples were artificially aged in strong hydrothermal conditions. Samples (about 4 g) were placed in a sealed vessel (5 L), which was put in an oven set at 80 °C. Inside the sealed vessel, the humidity was kept at 75% using a sodium chloride saturated aqueous solution. Sample pH, DPv and Tp, as well as the colorimetric coordinates were monitored during the aging.

3.7. Drawings deacidification and characterization

Stefano Arienti's *Picasso* is a collection of 100 drawings on paper realized in 1989. Each drawing has, on the verso side, a xerography of a page coming from the catalogue of the exhibition entitled *Picasso. La grande grafica. 1904–1971*, which took place in Florence in 1986 [35]. On the recto side, Arienti's interpretation of Picasso xerography can be found. Arienti individually elaborated each xerography with crumples, pyrography, burns, scorches, sewing machine holes, pinholes, red wire and other techniques. For instance, it has been recently shown by FT-IR measurements, that he used heated lemon juice in several of the *Picasso*'s drawings [36]. Each drawing measures 42 cm × 29.7 cm. The paper grammage is 70 g/cm^2 and the pulp-filling agent is kaolin.

In this paper, we will focus on drawing number 53, composed on the verso by the xerography of the famous Picasso's lithography *Paloma et sa poupée sur fond noir*. The drawing, which was slightly acidic (pH = 4.8), was treated with 60 mL (30 mL on each side) of calcium hydroxide nanoparticles in cyclohexane at a concentration of 1 g/L. With the aim of evaluating the changes due to the application of the here proposed deacidification method, reflectance transformation imaging (RTI) was used before and after the treatment.

A Nikon digital single-lens reflex camera (D800) equipped with a AF Micro-Nikkor 60 mm f/2.8D lens was fixed on a tripod above the drawing. A Nikon SB 910 Speedlight flash was used as the moveable light source. During the highlight RTI sequence, 48 photographs
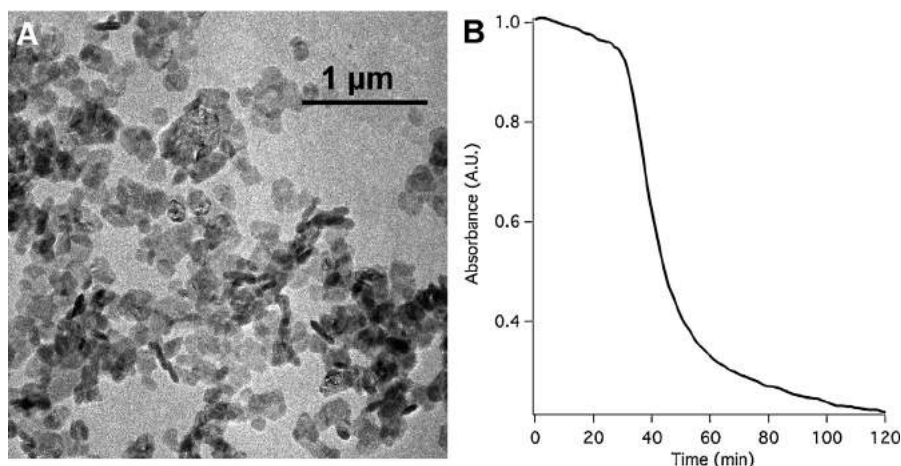
Fig. 2. A. TEM image of Ca(OH)$_2$ nanoparticles used for the preparation of the deacidifying dispersion in cyclohexane. B. Normalized absorbance at 650 nm as a function of time for calcium hydroxide nanoparticles dispersion in cyclohexane. It is worth noting that for application purposes, a stability of about 30 minutes is definitely satisfactory.

are taken, moving the handheld flash around the object along the surface of a "virtual light dome", whose size is defined by a fixed distance. RTIBuilder and RTIviewer were used to process the data and obtained the corresponding RTI pictures.

4. Results and discussion

The lack of established conservation methodologies compatible with techniques and media used by contemporary artists makes the conservation of contemporary art a major challenge for conservators. Two are the main aspects that should be taken into account before proposing a new conservation method for cellulose-based artworks: contemporary writing fluids, including inks of ballpoint and rollerball pens, felt-tips and markers are very sensitive to polar solvents, traditionally used in paper conservation. This aspect is also of fundamental importance in the conservation of contemporary archival documents and manuscripts. In addition to that, the paradigmatic shift in contemporary art in which paper has moved from being a support, to becoming the heart of autonomous works, imposes the preservation of paper topography. As a matter of fact, perforation, burning, folding, twisting, and creasing of paper are used by artist, such as Simon Schubert, Kiki Smith and Stefano Arienti, to create their own art, expressing their feelings or communicating a message.

Therefore, the conservation of contemporary art and archival materials requires an update of the conventional methods, aimed at formulating inert, efficient and compatible advanced solutions. The here proposed deacidification methods, based on calcium hydroxide nanoparticles dispersed in cyclohexane, is designed to overcome the limit of the available conservation procedure, providing a compatible and efficient way to hamper cellulose degradation.

The usage of calcium hydroxide nanoparticles for the deacidification and the pH control of cellulose-based artworks was proposed for the first time about 15 years ago [13]. Since then, research efforts have been devoted to the refinement of synthetic procedures, with the aim of tailoring physico-chemical particles characteristics to different case studies, including paper [13,16,17], iron gall inked manuscripts [18,19] and archeological wood [21,22]. The efficacy of these systems in hampering cellulose degradation has been assessed in several studies [37–40]. Recent updates about calcium hydroxide for deacidification purposes include the preparation of nanoparticles from calcium metal and n-propanol, using a solvothermal process [17]. One of the most interesting features of these nanoparticles is that they can be dispersed in cyclohexane. Cyclohexane was chosen as a dispersing agent for nanoparticles because is a colorless and volatile solvent, traditionally used by

easel paintings conservators mainly for cleaning interventions. As it will be shown later, cyclohexane displays a good compatibility with both inks and paper.

Calcium hydroxide nanoparticles from solvothermal reaction in n-propanol consist of small hexagonal platelets, having a diameter between 100 and 400 nm and a thickness of about 20–30 nm, as shown in Fig. 2A. Hexagonal platelets, with a high degree of ordering, are typical of Portlandite, which is the crystalline form of calcium hydroxide. The crystallinity of calcium hydroxide nanoparticles has been confirmed by XRD measurements conducted on dried powder [17]. Dried calcium hydroxide nanoparticles were dispersed in cyclohexane using an ultrasonic bath. The system, at a concentration of 1 g/L, is stable for more than 30 minutes (see Fig. 2B). For deacidification purposes, such stability is definitely adequate. Moreover, even after a few months, nanoparticles can be easily re-dispersed by gently shaking the dispersion, because no permanent aggregation or flocculation of particles takes place after settling. It is worth noting that the delivery conditions of dispersion during the deacidification treatment (i.e. sprayed as a aerosol on paper) are quite far from the ones used for the characterization of nanoparticles here reported. This means that coupling/clustering of nanoparticles within the cellulose fibers cannot be excluded. However, the absence of a stabilizer in the system makes this non-polar dispersion completely compatible with the original material, without introducing surfactant within the support. It has been shown that the presence of surfactants or other stabilizer could reduce reactivity of particles, creating a too alkaline environment that could be risky for cellulose fibers [41]. Moreover, surfactant interaction and degradation are in most cases unknown, recommending the use of deacidifying agents free from surfactants for the deacidification of works of art.

In Fig. 3, results of a preliminary test on the compatibility between cyclohexane nanoparticles dispersion and Bic Cristal blue ink are reported. Considering the materials heterogeneity of modern and contemporary artworks, preliminary tests should always be performed prior to application on real case studies [42]. After the dispersion's application, paper and ink turn darker, as a result of the wetting of the substrate. In about 15 seconds, the solvent is almost completely evaporated and no bleeding or leaching of the ink can be optically detected. Moreover, no white veil formation, due to the presence of nanoparticles, is observed after the evaporation of the solvent. Optical microscopy pictures were acquired in order to check possible changes in inked fibers after the application of the deacidifying formulation. In Fig. 4, the pictures acquired before and after the deposition of nanoparticles dispersion are reported.
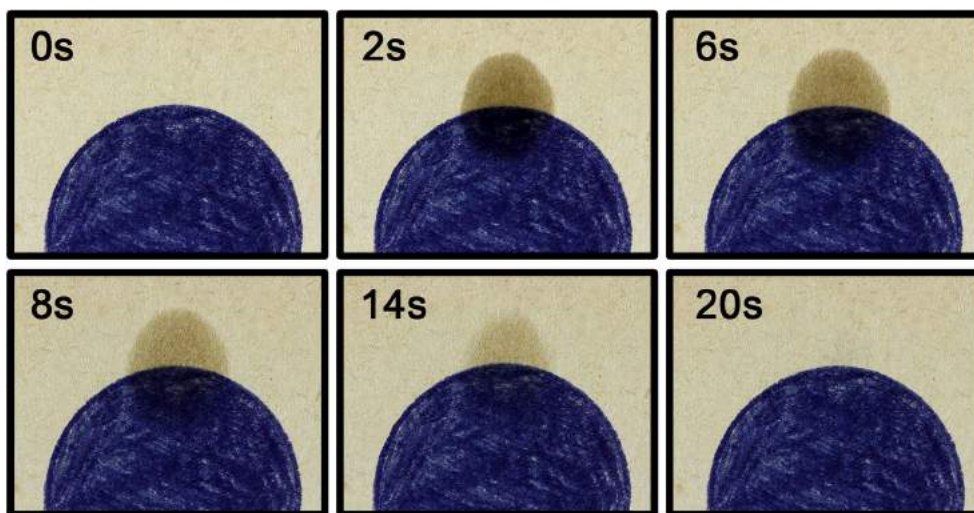
Fig. 3. The effect of a drop of calcium hydroxide nanoparticles in cyclohexane on a mockup prepared using acidic paper and Bic Cristal blue ink. No bleeding or leaching of ink occurred.
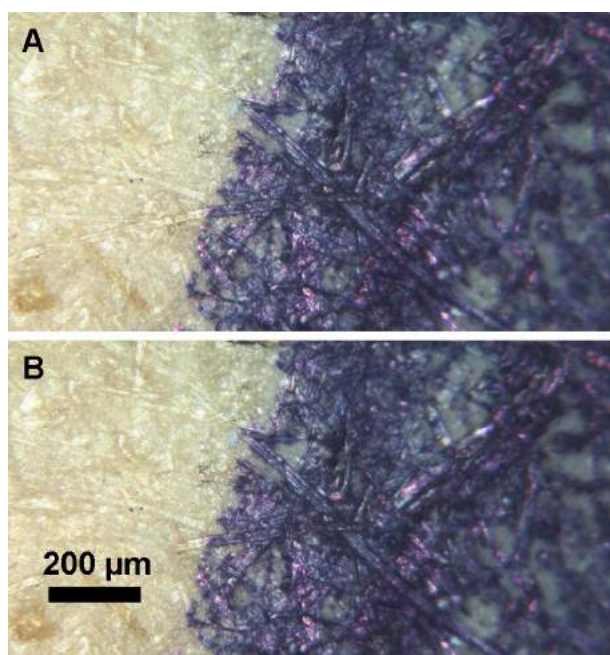

Fig. 4. Optical microscopy pictures taken before (A) and after (B) the application of calcium hydroxide nanoparticles in cyclohexane on acidic paper featuring Bic Cristal blue ink. No difference due to the application can be seen.

Fig. 5. ΔE^* of paper as a function of aging time for untreated (black triangles) and deacidified (grey circles) samples.

The heterogeneous distribution of ink within cellulose fibers is evident: uninked spots can be seen on the right side of both pictures. It is interesting to note that at the microscopic scale the blue dye has a significant purple hue. This is not surprising considering that around 80% of blue and black inks contain the polymethylated Basic Violet 3 and its homologues [43]. After evaporation of dispersion, the visual aspect of the sample is the same as before the application, including the purple hue and the uninked spots.

After preliminary tests, half of the prepared mockups were deacidified and then aged at 80 °C and 75% RH, together with the remaining acidic samples, in order to exacerbate the difference between untreated and treated systems.

The starting pH of acidic support (pH = 4.6) was raised to 7.5 after the application of the deacidifying dispersion. In Fig. 1, a comparison between an untreated sample (left) and a deacidified mockup (right) before the artificial aging is reported. The ΔE^* measured
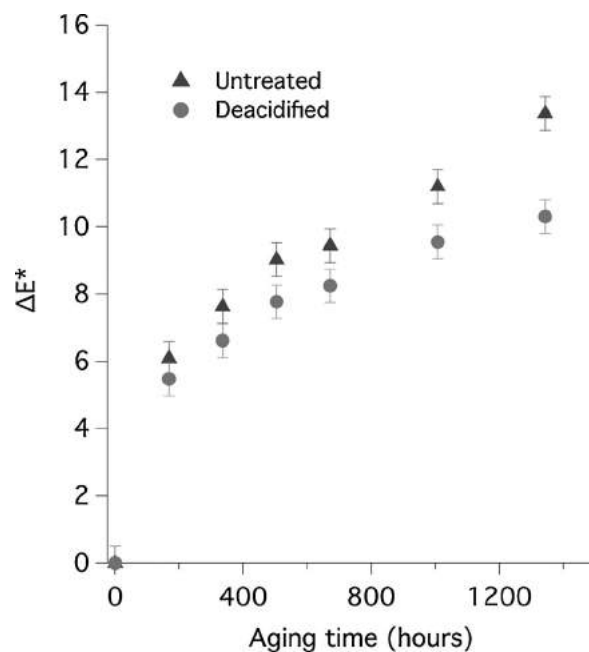
after the application of calcium hydroxide nanoparticles dispersion was 0.65, close to the experimental error.

Colorimetric coordinates were monitored upon artificial aging. The corresponding ΔE^* of paper are reported in Fig. 5, as a function of aging time. During the aging, the ΔE^* of paper in untreated sample increased constantly, reaching a final value of about 13 units after 1344 hours. It is worth noting that a ΔE^* higher than 2 units makes the color difference perceivable by the naked eye [44]. ΔE^* of deacidified sample follows a different trend. As a matter of fact, at the end of the aging ΔE^* of deacidified sample is 10. Therefore, color changes in paper were hampered by the deacidification treatment of about one forth. The color difference of the inked zones at the end of the aging has been reduced of about 60% by the deacidification treatment, meaning that the treatment seems also to hamper the color changes of the blue dye.

As shown by colorimetric measurements, at the end of the aging, the visual aspect of samples is significantly different, as can be seen
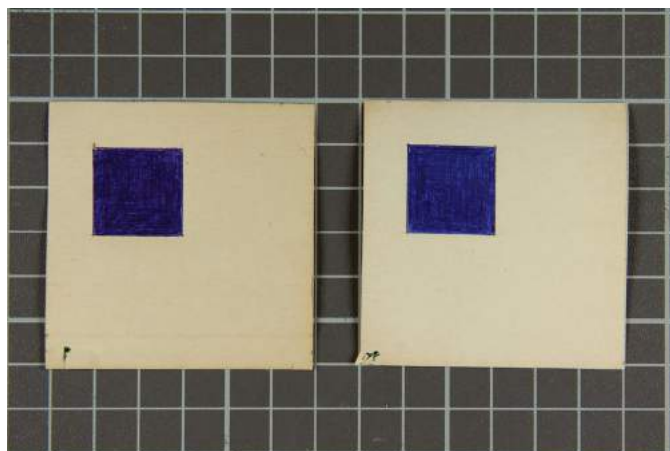
Fig. 6. Untreated sample (left) and deacidified sample (right) after 8 weeks (1344 hours) of artificial aging. The color difference of paper and ink is evident. Squares on the background measures 1 cm^2.

in Fig. 6. In particular, the untreated sample (on the left) is darker and yellower than the deacidified mockup (on the right). Oxidation, that is usually responsible for the yellowing of paper, is interconnected with acid-catalyzed hydrolysis. Therefore, the different behavior of samples can be ascribed to the hampering of cellulose degradation induced by the presence of alkaline nanoparticles on the treated sample.

The evaluation of protective action arising from the deacidifying treatment was also assessed by cellulose DPv in mockups, which was monitored upon artificial aging using viscosimetric measurement. From these data, the scissions per initial cellulose chain (S^*) were calculated and presented in Fig. 7A.

Despite the fact that starting DPv of untreated and deacidified samples were similar (DPv = 600), upon aging the degradation of acidic mockup occurred at a higher rate than the neutralized sample. In particular the difference in S^* between samples increased with time, as it occurred for the colorimetric coordinates.

The benefits arising from the application of calcium hydroxide nanoparticles were also confirmed by thermogravimetric analyses. From DTG curves, the pyrolysis temperature of cellulose (Tp), defined as the maximum of the weight loss derivative, is obtained and used as an indicator of the conservation conditions of paper. Higher Tp values correspond to samples showing greater resistance to thermal degradation [27–29]. In Fig. 7B, thermal curves of untreated and deacidified mockups at the end of the aging (8 weeks)

are reported. The treated sample displays a significant increase of about 20 °C in Tp with respect to the untreated mockup. Neutralization of acidity prevents acidity from favoring the dehydration of cellulose, which is the first step of the thermal degradation process [1]. It has been also hypothesized that the interaction between bivalent ions and carboxylate groups of cellulose creates a network of interactions through the deacidified cellulose chains, increasing cellulose resistance to thermal degradation [45,46].

The positive outcomes of the tests conducted on mockups opened the way for the deacidification of a series of drawings belonging to a private collection.

Stefano Arienti is an Italian contemporary artist whose art is inspired by the Arte Povera and Conceptual movements. Arienti utilizes and manipulates everyday materials, experimenting original techniques and methods. He lets the viewer into his world ruled by the apparent repetitiveness and childlike simplicity in his work by folding, perforating or burning paper, erasing texts and images, tracing photographs and patterns.

With the artwork *Picasso*, Arienti rehashed a catalogue about the graphic art of Picasso, which was the artist that more than others revolutionized the techniques of artistic expression. Arienti's *Picasso* is a collection of 100 drawings on paper realized in 1989. Each drawing is created on the backside of a xerography of the graphic work of Pablo Picasso. Arienti individually elaborated each xerography with crumples, pyrography, burns, scorches, sewing machine holes, pinholes, red wire and heated lemon juice. He created a structure on each drawing by changing the topography and morphology of paper, which is not only a support but also the body of the artwork.

The drawing number 53 is composed on the verso of the xerography of the famous Picasso's lithography *Paloma et sa poupée sur fond noir* as shown in Fig. 8. This drawing has a complex nature and carries four medias and techniques: xerography, crumples, pinholes and burns. It clearly shows that the artist's approach and working methodology is one of taking away rather than putting down. As a matter of fact, Arienti uses very simple processes, reduced to essential, to slight gestures. He destroys, manipulates and transforms common materials; in doing so, he emphasizes the potential of images but also the power of the manipulating gesture.

The drawing number 53, which was slightly acidic (pH = 4.8), was treated with 60 mL (30 mL on each side) of calcium hydroxide nanoparticles in cyclohexane at a concentration of 1 g/L. With the aim of evaluating the changes due to the application of the here proposed deacidification method, Reflectance Transformation Imaging (RTI) was used before and after the treatment.
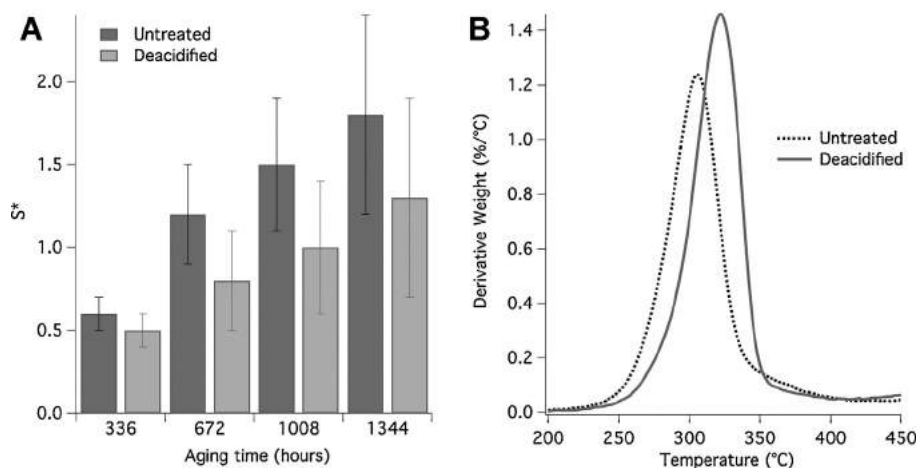

Fig. 7. A. Scission per initial cellulose chains (S^*) of untreated and deacidified samples as a function of the aging time. B. Comparison between DTG curves of untreated and deacidified mockups at the end of the aging.

Fig. 8. Recto and verso of Arienti's drawing number 53 belonging to the Picasso artwork. Diffuse light photographs.

RTI is a computational photographic method used to capture the surface shape and color of an object, permitting the re-lighting of it from any direction. One of the most interesting features of RTI is the mathematical enhancement of object surface shape and color attributes, which are not disclosed under direct examination.

RTI images are obtained shooting multiple digital photos using a stationary camera and a moving light source, whose position is known and controllable. In this way, images display the same subject with different highlights and shadows. The elaboration of these images via software creates a model of the object, and allows an interactive re-light of the artworks, enhancing its shape and topography.

In recent years, the use of reflectance transformation imaging is diffusing in the Cultural Heritage field [47–51]. For what concerns Arienti's drawings, RTI was chosen for the non-invasive evaluation of changes in paper topography due to the application of the proposed deacidification method.

Several image processing algorithms can be used to highlight particular information; for instance, diffuse gain, which is the artificial variation of the diffuse reflectance properties of each pixel, varies contrast between neighboring pixels. As can be seen in Fig. 9, paper of drawing 53 is not plain, but has a complex surface topography due to a deliberate crumpling of the paper followed by an accurate perforation and a final burn.

Fig. 9. Recto and verso of Arienti's drawing number 53 belonging to the artwork Picasso. RTI diffuse gain photographs.
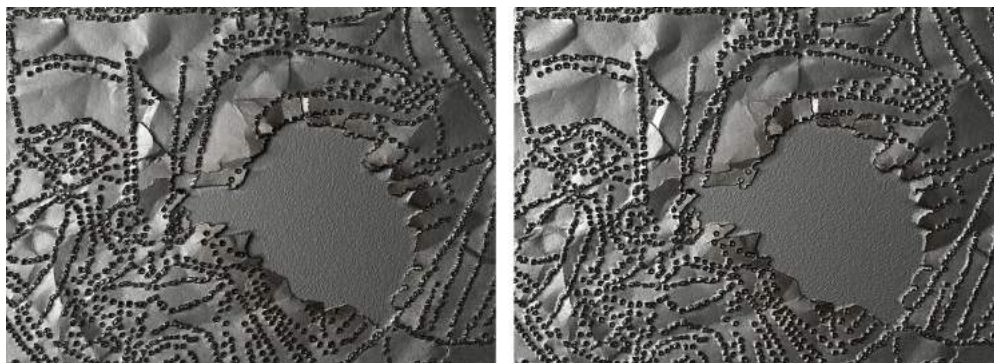
Fig. 10. Detailed views of Arienti's drawing number 53. RTI specular enhancement photographs. On the right, the drawing before the treatment. On the left, the same detail after the application of calcium hydroxide nanoparticles dispersed in cyclohexane. No changes of the drawing 3D topography due to the deacidification intervention are present.

Paper morphology is even more evident in Fig. 10, where specular enhancement was used to make the artworks artificially shiny using a specular shading method. Pictures show a detailed view of the hole due to the burning of the support and of the several pinholes that draw the contours of Paloma's silhouette. The comparison between pictures taken before (on the left) and after the treatment (on the right) shows that, even around the burn, where paper fragments are fragile and delicate, the original shape and topography of the support is safeguarded. This is due to the chemical nature of cyclohexane, which does not interact with hydroxyl groups of the supramolecular structure of cellulose fibers, being a non-polar solvent. Moreover, due to the high volatility of cyclohexane, contact time between solvent and paper is very short, making possible interactions even less probable.

5. Conclusions

Some contemporary media, such as pressure sensitive adhesives, ballpoint and rollerball pens, felt-tips and markers are sensitive to polar solvent, such as water and short-chain alcohols. In addition to that, starting from the middle of 20th century, paper has been used as the heart of autonomous works, at time torn, burnt, folded, perforated, twisted or creased, making the preservation of paper topography fundamental.

Despite the fact that techniques and media have changed in the last century, paper still displays the same conservation issues, being usually acidic and prone to degradation, making a deacidification treatment mandatory.

A dispersion of calcium hydroxide nanoparticles in cyclohexane has been obtained starting from particles synthesized via a solvothermal reaction in *n*-propanol. This formulation overcomes some of the limit of traditional deacidification methodologies, which can be rarely applied on contemporary artworks, drawings and archival materials. In fact, the nanoparticles carrier is compatible with some inks and materials of contemporary arts and, being a non-polar solvent, allows the preservation of original artworks topography.

The new formulation for the pH control was tested on mock-ups prepared using acidic paper and a commercial ballpoint pen, i.e., Bic Crystal blue. Untreated and neutralized samples were aged at high temperature and humidity to exacerbate cellulose degradation. After 8 weeks of aging, the beneficial effect of the application of calcium hydroxide nanoparticles was evident: deacidified samples were more resilient to aging, showing lower cellulose depolymerization and less color changes with respect to untreated mockups. These evidences were also confirmed by DTG measurements, from which the resistance of cellulose to thermal degradation can be obtained.

The calcium hydroxide nanoparticles dispersion in cyclohexane was then tested on contemporary drawings of Stefano Arienti, belonging to a private collection. Reflectance transforming imaging was used to evaluate the changes in paper topography as a result of the deacidification intervention. Comparison between pictures taken before and after the treatment clearly shows that, even around burns, where paper fragments are fragile and delicate, the original shape and topography of the support is safeguarded.

It can be concluded that this stabilizer-free non-polar dispersion, based on calcium hydroxide in cyclohexane, could represent a promising tool for the conservation of some contemporary artworks and drawings on paper, as well as for several archival documents, whose preservation is largely unexplored.

Acknowledgements

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