Application of Mg(OH)₂ Nanosheets for Conservation and Restoration of Precious Documents and Cultural Archives

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Magnesium hydroxide (Mg(OH)₂) nanosheets were explored as an effective material for the restoration and conservation of paper-based cultural archives and compared with the commonly used Ca(OH)₂ nanoparticles. The $(Mg(OH)_2)$ nanosheets were applied to filter paper as a reference, as well as to new and old paper samples. The effectiveness of Mg(OH)₂ nanosheets was evaluated by (i) a pH test of the surface and the bulk extracts, (ii) measuring the alkaline reserve and correlating it with the enhancement in life expectancy, and (iii) in terms of mechanical strength. The alkaline reserve test indicated an increase in the alkaline buffer, which resulted in markedly reduced acidic content of the samples. It was inferred from the improved properties that Mg(OH)₂ nanosheets coated the paper as a lamination sheet and protected it as the first line of defense against acidic environmental attack. Moreover, its presence within the paper acted as an alkaline reserve and also as reinforcement in the form of an inorganic nanosheet. The results suggest that the nanosheets are an innovative, compatible, and efficient material for the consolidation and restoration of old and new paper samples.

Keywords: Magnesium hydroxide nanosheets; Preservation; Restoration; Heritage; Alkaline reserve; Microwaves

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INTRODUCTION

Preserving cultural heritage is crucial to understanding a country's past, as it provides a unique window into the history and the culture of a nation. The preservation and restoration of cultural heritage objects that are in danger of being lost from a variety of factors, such as environmental degradation, adds to the overall value of the global human culture and helps to keep it alive for future generations. Books and other documents are some of the most important legacy for a nation. Millions of important books at libraries are deteriorating, and their aging makes them too fragile to handle. Glances at literature suggest that efforts have been made to take preventive and preservative measures for the conservation and restoration of such precious documents.

The primary cause of paper deterioration is the presence and development of acidic content during manufacturing and aging. The acidic content attacks the cellulose fibers in the paper and depolymerizes them through an acid-catalyzed hydrolysis process. Other factors, such as oxidation, varying or extreme temperatures and humidity, exposure to light,

air pollutants in the storage areas, and the amount of use, also play a significant role in the deterioration of books.

One of the strategies for dealing with the acid book preservation problem is the deacidification of papers with suitable materials (Baty et al. 2010). Such materials may neutralize acid content and also deposit an alkaline buffer that acts as a reserve to neutralize any acids that may form later during service life. Weak bases, such as bicarbonates, carbonates, various oxides, some hydroxides, and amines, are often used to de-acidify papers. Other bases used for this purpose have been listed by Cedzova et al. (2006), including barium hydroxide, alkaline oxides, gaseous hexamethylenetetramine, gaseous morpholine, methyl magnesium carbonate, diethyl zinc, magnesium oxide, zinc carbonate, sodium carbonate, amine compounds, ammonia, carbonated ethoxy magnesium-methoxy poly ethoxide, organic aluminum carbonate, ethyl magnesium carbonate, dibutyl magnesium, tetra butyl titanate, and alkoxides of alkaline earth metals. Compounds such as magnesium methyl carbonate and methyl-methoxy magnesium carbonate have been used as solvent-soluble carbonates (Kelly 1976). Calcium hydroxide (Ca(OH)₂) has been widely used for deacidification (Williams 1994; Kolar and Novak 1996; Kolar et al. 1998). Giorgi et al. (2005b) noted that once Ca(OH)₂ particles are deposited on paper, they react with CO₂ from the air and form CaCO₃, resulting in surface deposition of insoluble CaCO₃. A saturated aqueous solution of Ca(OH)₂, diluted 1:1 with deionized water, is normally employed to prevent precipitation of CaCO₃ before the calcium hydroxide penetrates the fiber network. Other researchers (Guerra et al. 1995, 1998; Giorgi et al. 2002) have reported the effective use of an aqueous Ca(OH)₂ suspension in combination with a strengthening agent, such as methyl cellulose. Although calcium hydroxide has been explored extensively, the direct use of its aqueous solution is limited because of its low solubility (1.3 g/L). The dispersion of lime in water has been explored as a way to increase the lime concentration. However, water dispersions of commercially available Ca(OH)₂ have not been found effective because of the large particle sizes (Sequeira et al. 2006) and fast sedimentation rates, in addition to producing a white glaze over the surfaces that not only damages the cellular structure but also reduces the mechanical strength of the paper. Some other studies report that both aqueous and non-aqueous suspensions of Ca(OH)₂ have been found effective for deacidification (Salvadori and Dei 2001; Dei and Salvadori 2006).

Magnesium hydroxide nanoparticles have also attracted strong interest because of their high-performance applications and controllable morphology (Kim et al. 2013a,b). Generally, Mg(OH)₂ is obtained by reaction of a magnesium salt with an alkaline solution (Cherkezova-Zheleva et al. 2008). Mg(OH)₂ can also be obtained through a hydrothermal reaction of metal Mg powder (Jin et al. 2008; An et al. 2010), or commercial bulk magnesium oxide crystals (Yu et al. 2004). The literature suggests that Mg(OH)₂ products with various morphological nanostructures, such as needles, lamellae, wires, rods, tubes, and flower-like crystals, have been obtained via various synthesis methods (Ding et al. 2001a,b; Henrist et al. 2003) and have been utilized for various applications. Preparation of flower-shaped aggregates of $Mg(OH)_2$ has been reported using a hydrothermal method (Lv et al. 2004). Morphological control of Mg(OH)₂ nanocrystals is usually achieved through surfactant templating routes (Sharma et al. 2004; Dei and Salvadori 2006). The research groups of Baglioni and Giorgi (Giorgi et al. 2005a; Baglioni et al. 2009) in their separate studies synthesized magnesium hydroxide nanoparticles and evaluated their use for paper conservation. Stefanis and Panayiotou (2008, 2010) deacidified paper with microand nanoparticulate dispersions of $Ca(OH)_2$ or $Mg(OH)_2$. Synthesis of $Mg(OH)_2$ nanosheets has been achieved by controlling the precipitation process of a dissolved Mg²⁺

solution (Wu *et al.* 2008; Yang *et al.* 2008) or disaggregation of bulk brucite particles into thin $Mg(OH)_2$ nanosheets without a dissolution-recrystallization process (Pang *et al.* 2011). However, the use of $Mg(OH)_2$ nanosheets for the conservation and restoration of cultural heritage items has not been reported to date.

In addition to synthesizing particles of the desired morphology for paper conservation, their dispersion is another major issue. It has been found that with an increase in the size of particles, their effectiveness as a preservation or rehabilitation material is significantly reduced because of poor dispersion (El-Sayed 2001). Researchers have also highlighted concerns about the mechanisms and rates of equilibration within paper when large particles are deposited. The dispersion issues can be improved by reducing the average size of the consolidating particles to the sub-micrometric scale. Dispersions of nano-sized particles in non-aqueous solvents produce kinetically stable systems and solve most of the associated problems. This also helps to achieve a deeper penetration of the dispersion, better stability, and to avoid the formation of white glaze on the treated surface (Salvadori and Dei 2001).

Keeping in view the unique nanosheet morphology of the Mg(OH)₂ particles, their moderate basic nature, and the issues associated with the application of nanoparticles as conservation and restoration treatment materials, it is anticipated that the nanosheet morphology Mg(OH)₂ is worth exploring because of their ability to overcome the hurdles associated with other prevailing treatment processes. Furthermore, it is expected that coating with nanosheets to act like a lamination sheet on the surface of the paper would protect it as the first line of defense against any acidic attack on the outside. In addition, deposition of these nanosheet structures inside the paper would not only enhance the strength of paper as nano-sized reinforcement but also would counteract any acid generated within the paper by degradation during its service life. Thus, Mg(OH)₂ nanosheets were (Hafezi *et al.* 2014)) and applied to both new and 100-year-old paper samples to evaluate their effectiveness. The same paper samples were also treated with Ca(OH)₂ nanoparticles, and a comparative assessment is presented to highlight the peculiarities of the Mg(OH)₂ nanosheet treatment.

EXPERIMENTAL

Materials

Calcium nitrate (Ca(NO₃)₂; Labchem, Zelienople, USA, 98% purity), magnesium sulfate (MgSO₄; medical grade, Labchem, Zelienople, PA, USA, 99% purity), and sodium hydroxide (NaOH; Sigma-Aldrich, St. Louis, MO, USA) were used as received and without further purification. Distilled water and pure ethanol were used in all the preparations. Filter paper (WhatmanTM 1441-055 Grade 41, Capitol Scientific, Inc., Austin, TX) manufactured from 100% cellulose and containing no additives was used in the study as a reference. Old paper from a book published approximately 100 years ago, new paper manufactured in the last 2 to 5 years, and environmentally aged newspapers were also used.

Synthesis of magnesium hydroxide nanosheets

The $Mg(OH)_2$ nanosheets were prepared by the microwave-assisted reduction of metal sulfate using sodium hydroxide (NaOH) as the reducing agent at an appropriate pH and microwave radiation dose, a method reported earlier (Hafezi *et al.* 2014) and the

authors' group (Saoud *et al.* 2014). $Mg(OH)_2$ was synthesized using a microwave assisted irradiation method. The method was based on the reduction of metal sulfate using cetyltrimethylammonium bromide (CTAB) as a directing agent and NaOH as reducing agent and subjected to microwave irradiation. The resultant $Mg(OH)_2$ nano-sheets were obtained by wet homogeneous precipitation in the presence of dispersant surfactant (CTAB) with a pH between 8 and 10 according to the following reaction:

$$MgSO_4 + 2NaOH \rightarrow (MgOH)_2 + Na_2SO_4$$
(1)

In a typical synthesis, 5 g of magnesium sulfate (MgSO₄, medical Grade, Bell, sons &, UK: Labchem, 99%), is dissolved in 100 mL of DI water. The solution then added to 1% solution of cetyltrimethylammonium bromide (CTAB, Sigma Aldrich, 99%) surfactant in 250 mL of DI water and ethanol with (1:1 ratio) in a reaction flask. The solution is kept under vigorous stirring while 1M NaOH solution is being added drop-wise to the solution. Then, the solution is transformed into translucent white color. After that, the solution is subsequently placed in a microwave chemical reactor (MCR-3), operated at a power of 266 W, for 10 to 15 minutes and is removed upon the onset of boiling. The content is allowed to cool down to ambient temperature to form a gel-like structure. Finally, the precipitated particles are filtered and collected after washing thoroughly several times with distilled water and ethanol. The dried powder samples are heated at temperatures ($\geq 300^{\circ}$ C) to remove the CTAB.

The prepared nanosheets (15 g/L) were dispersed in pure ethanol, or its aqueous mixture, and were sprayed on the sample paper sheets. The treatment was also applied to the acidified surface of the Whatman filter paper. This was done by soaking the paper first in a sulfuric acid solution (pH 2.5), after which it was deacidified by soaking it in alcoholic dispersions of Ca(OH)₂ and Mg(OH)₂ nanoparticles. The treatment was evaluated by measuring the surface and bulk pH value of the samples. A deacidification treatment was also applied naturally and to the artificially aged (by hydrothermal aging; 90 °C) paper samples. The filter paper was aged by dipping it in a dilute solution of an H₂SO₄ acid with a pH of approximately 3.0. The filter paper, after drying, was kept for 1 to 6 h in an oven set at 90 °C and 80% humidity. The surface pH value was measured after every hour.

Methods

Alkaline reserve test

An approximately 1-mg piece of the dry sample paper was chosen. It was placed in approximately 25 mL of water in a 125-mL Erlenmeyer flask. A volume of 20 mL of standardized 0.1 N HCl was pipetted into the flask and boiled for approximately 1 min. After cooling down to room temperature, three drops of methyl red indicator were added. The alkaline reserve value was measured as per the standard procedure reported in TAPPI T553 om-10 (2010).

Characterization

X-ray diffraction (XRD) of the nanoparticles used in this study was recorded using a Rigaku MiniFlex600 (Rigaku Corporation, Wilmington, MA; CuK α radiation, wavelength = 1.54 Å), operated at 40 kV and 15 mA. High-resolution transmission electron microscopy (HRTEM; JEOL JEM-2100F, JEOL Ltd., Peabody, MA) was used for the morphological and crystallographic characterization of the nanoparticles. Scanning electron microscope (SEM) images were obtained with a Hitachi SU-70 SEM (Hitachi Co., Chula Vista, CA) operated at an accelerating voltage of 5 keV. For tensile testing, an Insight 30 was used with a 100 N load cell and at an extension rate of 2 mm min⁻¹ (Donggun JiaTesting Equipment Co., Ltd., Hong Kong). The sample was cut into strips 10 mm wide and 80 mm in length. The pH was measured either by taking extracts from the samples and dipping a temperature-compensated pH electrode into the extract, or by using a pH marker pen that provided quick surface pH measurements.

RESULTS AND DISCUSSION

XRD Analysis

Figure 1 shows XRD patterns of $Ca(OH)_2$ and $Mg(OH)_2$ nanoparticles used in this study. The XRD pattern was consistent with the standard patterns of crystalline $Ca(OH)_2$ and $Mg(OH)_2$ nanoparticles. The data reported in Fig. 1 and explained elsewhere (Ihara *et al.* 2015; Mohammadi and Moghaddas 2015) suggest successful preparation of the desired materials that were used for the preservation of paper in this study.



Fig. 1. XRD patterns of Ca(OH)₂ and Mg(OH)₂ nanoparticles

SEM Analysis

Figure 2 shows SEM micrographs of Ca(OH)₂ and Mg(OH)₂ nanoparticles synthesized in this study. The micrographs clearly show the highly porous structure of Mg(OH)₂ as compared with Ca(OH)₂. Further details were explored through HRTEM measurements. The HRTEM micrographs of Mg(OH)₂ nanosheets shown in Fig. 3 clearly show that Mg(OH)₂ particles have a unique highly porous structure with particle sizes of < 20 nm, which resulted from nanosheets instead of particles. The thickness of these sheets was in the range of a few nanometers, whereas other planar dimensions were in the range of a few hundred nanometers. The Brunauer-Emmet-Teller (BET) surface area and nitrogen adsorption/desorption measurements of these Mg(OH)₂ nanoparticles showed a surface area of 80.3 m²/g. The morphology was revealed *via* HRTEM analysis, and the patterns dynamic selected area electron diffraction (SAED) and the BET surface area suggested that Mg(OH)₂ was composed of nanosheets with a unique packing structure that gave a highly porous nanostructure to the material.



Fig. 2. SEM micrographs of Ca(OH)₂ and Mg(OH)₂



Fig. 3. HRTEM micrographs of (a) $Mg(OH)_2$ nanosheets showing the lateral dimension of submicron size and with a with thickness of 1 nm to 2 nm, (b) micrograph of a selected area of few single nanosheets with its dynamic SAED pattern as shown in (c) and (d)

Effect of Solvents

It is well known that most of the group II metal hydroxides have a high pH value when dissolved in water, whereas the same is low when dissolved in alcohols. The values of pH on both extremes were not desirable in the deacidification treatment, as they may have initiated the degradation process. It is known that paper with a neutral or mild alkaline pH deteriorates more slowly than paper with a low pH value (*i.e.*, higher acidic content). The hydroxide with a high pH value in aqueous solution damages the cellular fabric of the archives being treated. Thus, such a solvent is desired that does not cause noticeable damage and, hence, a reduction in the strength. The pH measurement was conducted to quantify the effectiveness of the prepared material in three different solvents namely ethanol, propanol, and distilled water. Figure 4 is the graphical representation of the pHe value of solutions of Ca(OH)2 and Mg(OH)2 in these solvents according to ASTM D6423 method (ASTM D6423-99, 199). It is evident that both hydroxides yielded high a pH value, $(Ca(OH)_2 = 10.2 \text{ and } Mg(OH)_2 = 11.4)$ when dissolved in water. The pH value of these materials showed a similar behavior in ethanol and propanol, where the values were noticeably lower and were closer to neutral pH values. The results indicated that ethanol was the most suitable solvent compared to distilled water and propanol. Furthermore, lower boiling points of ethanol ensured faster drying at a lower temperature. The fast evaporation rate also shortened the time consumed for the preservation treatment. The solvent's effect on the pH value of the treated Whitman filter paper was also explored.



Fig. 4. Effect on the pH value of solutions of Ca(OH)2 and Mg(OH)2 in different solvents

It is known that water as a medium of suspension produces detrimental effects on the mechanical strength and stability of the paper sample by greatly reducing their strength and stiffness to nearly 10% of the original strength. In contrast, the alcoholic suspension can be safely applied due to the negligible loss it produces in mechanical properties during the

treatment process. The other benefits of alcoholic suspension include that it is environmentally friendly, volatile in nature, and low in toxicity in comparison with other solvents of equal volatility. The surface tension of alcohols is adequately low, which ensures optimal wetting, penetration, and loading of the dispersions within the porous structure of the paper samples or other porous materials. The fine mist of the suspension was sprayed using a spray gun. This application strategy also produced a uniform thin layer on the nanosheets overall surface that was like laminating the paper. Keeping all the positive aspects of ethanol in view, it was chosen as a medium for dispersion of nanomaterials for the subsequent experiments.



Fig. 5. Measured pH values as a function of number of hours after the treatment with both bases; (a) cold extracts, (b) hot extracts



Fig. 6. Surface pH of papers treated with nanoparticles: (a) filter paper; (b) 100-year-old paper

The effect of nanomaterials on the filter paper samples and the old paper sample was studied by measuring the surface pH value of the samples. The data obtained are depicted in Fig. 6, whereas actual images of the tested samples are shown in Figs. 7 and 8.



Fig. 7. pH measurement with pH marker pen on the surface of filter paper treated with Ca(OH)₂ nanoparticles and Mg(OH)₂ nanosheets

It was clear from the trend of the plots that for the filter paper sample, which was composed of pure cellulose, the pH value was 7 before the application of nanomaterials. However, it shifted to 12 for both hydroxides.

Contrarily, the pH value for the old paper sample remained at approximately 2.5 and rose to 8.5 for calcium hydroxide and to 10.5 for magnesium hydroxide nanosheet-treated samples. This data clearly showed the relatively better effectiveness of nanosheets due to their larger surfaces in combating the acidic content present in the old paper, whereas stabilization in the pH value around its maximum was indicative of its pure cellulosic nature.

The applied treatment of the nanomaterials and nanosheets on the paper samples fought against the acidic content, and the remaining alkalinity served as an alkaline reserve to provide protection from further attack by acids during its future life. It is known that for a paper to have a life expectancy of at least 100 years it must have an alkaline reserve of 2% or more (or it should be > 400 mmol/kg for a life expectancy of 500 to 1,000 years, depending on the nature of the paper).

The ISO 10716 (1994) test standard was adopted to determine the amount of alkali reserve. Figure 9 illustrates that by applying only 0.1 g of the nanomaterials, nearly 11 and 15 times higher values were obtained (compared to 400 mmol/kg) for the filter paper treated with Ca(OH)₂ nanoparticles and Mg(OH)₂ nanosheets suspensions, respectively. However, the Mg(OH)₂ nanosheets treatment to the old paper sample yielded more than double the value of Ca(OH)₂ nanoparticles.

It is important to note that if -242 mmol/kg was taken as zero, then the nanosheets alkaline reserve of 130 mmol/kg was equivalent to 372 mmol/kg, and this is close to the value that may be required for a life expectancy of at least 500 years (Bukovský 2005). Thus, it may be concluded that the Mg(OH)₂ nanosheet treatment provided far better results than Ca(OH)₂ nanoparticles.





Fig. 8. pH measurement of reference old paper and old paper treated with Ca(OH)₂ nanoparticles and Mg(OH)₂ nanosheets



Fig. 9. Comparison between the alkaline reserve tests performed on (a) Whatman filter paper and (b) 100-year-old paper

Mechanical Strength Test

The mechanical strength of the samples is another important aspect of evaluating the effectiveness of the treatment. Both the filter and old paper samples were tested before and after the application of the treatment. The tensile and fracture strength of the samples were preformed using an Insight 30 tensile testing machine. The sample lengths were between 15 to 21 mm, sample widths 4 to 5 mm, and thicknesses of *ca*. 0.13 mm. The test is done by ramping the strain on a sample with a constant rate and measure stress. The young's modulus is then calculated from the stress/strain graph in the linear region.

The fracture strength of the samples is shown in Fig. 10 (a, b). A reduction in the fracture strength was observed in the case of the filter paper sample treated with $Ca(OH)_2$ nanoparticles, whereas a large increase was noted in the samples treated with $Mg(OH)_2$ nanosheets. The $Ca(OH)_2$ nanoparticles seems to have made the paper brittle, which resulted in declining strength values, whereas the $Mg(OH)_2$ nanosheets treatment enhanced the mechanical strength by making the paper a nanocomposite-like structure that was reinforced with high-strength inorganic nanosheets.



Fig. 10. Comparison of fracture strength of the samples treated with $Ca(OH)_2$ nanoparticles and $Mg(OH)_2$ nanosheets; (a) filter paper samples and (b) 100-year-old paper sample

The nanosheet morphology improved the strength by occupying the spaces within the bulk of the paper that supported the fibrous strands. The strength improvement for the old paper sample was observed for both hydroxide treatments and resulted in similar improvement. In the case of the old paper, the competing factors were the acidic content present in the paper and the contribution of particles or sheets as a physical entity present in the fibrous structure of the paper. A major portion of the applied particles or sheets was consumed in fighting the acidic content and the little that remained contributed to mechanical strength.



Fig. 11. Comparison of mechanical strength of the old paper before, after coating with Mg(OH)₂ nanosheets.

Also, the mechanical strength of the paper before and after coating with $Mg(OH)_2$ nanosheets were measured, and the results are shown in Fig. 11. The results show that the sample treated with $Mg(OH)_2$ had the highest value of Young's modulus of *ca.* 6 GPa, followed by the untreated sample *ca.* 2.5 GPa, as shown in Table. 1.

 Table 1. Mechanical Strength of the Old Paper Before and After Treatment with Mg(OH)2 Nanosheets

Sample	Maximum Stress at Breaking point (MPa)	Maximum Strain at Breaking point (%)	Young's Modulus (GPa)
Control (uncoated)	20.3	1.05	2.488
Treated Paper (coated with Mg(OH) ₂	21.73	1.25	6.5

Finally, it can be seen clearly that the alkali Mg(OH) treatment of old paper significantly increased the tensile strength and modulus of the paper. However, the tensile strain of the paper increased after the treatment.

Future Direction

After demonstrating the effectiveness of $Mg(OH)_2$ nanosheets treatment in paper deacidification, it is crucial to test the long-term preservation of paper and to assess the possible deterioration of paper over an extended period. Even though it is impossible to simulate the natural aging of the paper and predict the exact lifetime of the paper in the laboratory, it is crucial to obtain a reliable measure to evaluate the stability and performance of the $Mg(OH)_2$ nanosheets treatment.

An aggressive aging procedure should be applied to reveal the role of the nanosheets toward the conservation and restoration of old paper samples within a short time. Also, mechanical and other relevant tests should be performed on the treated sample to have a clear idea about the stability and reproducibility of the paper after the treatment. Accelerated aging tests are needed to measure the stability to model the long-term degradation processes before and after deacidification treatments with $Mg(OH)_2$ nanosheets. Mechanical properties of treated paper can be measured using a very sensitive indicator such as folding endurance to determine the paper breakage upon aging which could be observed before the change in the stretch or tensile strength.

To have precise results of the performance of $Mg(OH)_2$ nanosheets treatment, we will perform a series of experiment to study the mechanical properties of the untreated and treated papers before after the accelerated aging test. The results will be consolidated and presented in the form of a future publication.

CONCLUSIONS

Prepared $Mg(OH)_2$ nanosheets were tested for their effectiveness as a material for the conservation of paper-based cultural heritage documents by comparing them with the known Ca(OH)₂ nanoparticle treatment. The Mg(OH)₂ nanosheets' effectiveness was evaluated by performing surface and bulk pH tests, measuring the alkaline reserve and correlating it with the enhancement in life expectancy, and mechanical strength measurements. The confirmation of the composition and morphology of the materials was tested using XRD, SEM, and HRTEM.

- 1. The data confirmed nanosheets morphology with a thickness < 5 nm and a unique packing structure that gave a highly porous nanostructure to the material.
- 2. Ethanol was found as the best solvent for the dispersion and application of these materials.
- 3. The pH measurements, alkaline reserve tests, and mechanical properties provided insight into the effectiveness of Mg(OH)₂ nanosheets in comparison with Ca(OH)₂ nanoparticles.
- 4. It was concluded that the Mg(OH)₂ nanosheets treatment acted as a lamination sheet and protected it as the first line of defense against acidic environmental attack, whereas its presence within the paper acted as an alkaline reserve and also as reinforcement in the form of an inorganic nanosheets.

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REFERENCES CITED

- An, D. M., Ding, X. F., Wang, Z. C., and Liu, Y. H. (2010). "Synthesis of ordered arrays of magnesium hydroxide nanoparticles *via* a simple method," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 356(1-3), 28-31. DOI: 10.1016/j.colsurfa.2009.12.027
- ASTM D6423-99. 199. Standard Test Method for Determination of pHe of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol (Ed75-Ed85), ASTM International,. West Conshohocken, PA.
- Baglioni, P., Giorgi, R., and Poggi, G. (2009). "Hydroxide nanoparticles for deacidification of paper and waterlogged wood," *Abstracts of Papers of the American Chemical Society* 237, 1155. DOI: 10.1021/la1030944
- Baty, J. W., Maitland, C. L., Minter, W., Hubbe, M. A., and Jordan-Mowery, S. K.
 (2010). "Deacidification for the conservation and preservation of paper-based works: A review," *BioResources* 5(3), 1955-2023. DOI: 10.15376/biores.5.3.1955-2023
- Bukovský, V. (2005). "The analysis of alkaline reserve in paper after deacidification," *Restaurator* 26(4), 265-275. DOI: 10.1515/REST.2005.265
- Cedzova, M., Gallova, I., and Katuscak, S. (2006). "Patents for paper deacidification," *Restaurator-International Journal for the Preservation of Library and Archival Material* 27(1), 35-45. DOI: 10.1515/rest.2006.35
- Cherkezova-Zheleva, Z. P., Paneva, D. G., Manova, E. D., Kunev, B. N., Petkova, V. A., and Mitov, I. G. (2008). "Mechanochemical synthesis of layered double hydroxides," *Journal of the Balkan Tribological Association* 14(4), 508-513.
- Dei, L., and Salvadori, B. (2006). "Nanotechnology in cultural heritage conservation: Nanometric slaked lime saves architectonic and artistic surfaces from decay," *Journal of Cultural Heritage* 7(2), 110-115. DOI: 10.1016/j.culher.2006.02.001
- Ding, Y., Zhang, G. T., Wu, H., Hai, B., Wang, L. B., and Qian, Y. T. (2001a).
 "Nanoscale magnesium hydroxide and magnesium oxide powders: Control over size, shape, and structure *via* hydrothermal synthesis," *Chemistry of Materials* 13(2), 435-440. DOI: 10.1021/cm000607e
- Ding, Y., Zhao, H. Z., Sun, Y. G., Zhang, G. T., Wu, H., and Qian, Y. T. (2001b). "Superstructured magnesium hydroxide sulfate hydrate fibres - Photoluminescence study," *International Journal of Inorganic Materials* 3(2), 151-156. DOI: 10.1016/s1466-6049(00)00105-7
- El-Sayed, M. A. (2001). "Some interesting properties of metals confined in time and nanometer space of different shapes," *Accounts of Chemical Research* 34(4), 257-264. DOI: 10.1021/ar960016n
- Giorgi, R., Bozzi, C., Dei, L. G., Gabbiani, C., Ninham, B. W., and Baglioni, P. (2005a).
 "Nanoparticles of Mg(OH)₂: Synthesis and application to paper conservation," *Langmuir* 21(18), 8495-8501. DOI: 10.1021/la050564m

- Giorgi, R., Chelazzi, D., and Baglioni, P. (2005b). "Nanoparticles of calcium hydroxide for wood conservation. The deacidification of the vasa warship," *Langmuir* 21(23), 10743-10748. DOI: 10.1021/la0506731
- Giorgi, R., Dei, L., Ceccato, M., Schettino, C., and Baglioni, P. (2002).
 "Nanotechnologies for conservation of cultural heritage: Paper and canvas deacidification," *Langmuir* 18(21), 8198-8203. DOI: 10.1021/la025964d
- Guerra, R. A., Vives, J. M. G., Monmany, J. M. D., and Garrido, J. F. (1995). "Procedure for simultaneous deacidification and sizing of paper," *Restaurator-International Journal for the Preservation of Library and Archival Material* 16(4), 175-193. DOI: 10.1515/rest.1995.16.4.175
- Guerra, R. A., Vives, J. M. G., Monmany, J. M. D., and Garrido, J. F. (1998). "The effect of aqueous solutions of alkoxypolyethyleneglycols (ALKPG) on the mechanical properties of paper," *Restaurator-International Journal for the Preservation of Library and Archival Material* 19(4), 187-211. DOI: 10.1515/rest.1998.19.4.187
- Hafezi, M., Nadernezhad, A., Mohammadi, M., Barzegar, H., and Mohammadi, H.
 (2014). "Effect of ball milling time on the synthesis of nanocrystalline merwinite via mechanical activation and heat treatment," *International Journal of Materials Research* 105(5), 469-473. DOI: 10.3139/146.111048
- Henrist, C., Mathieu, J. P., Vogels, C., Rulmont, A., and Cloots, R. (2003).
 "Morphological study of magnesium hydroxide nanoparticles precipitated in dilute aqueous solution," *Journal of Crystal Growth* 249(1-2), 321-330. DOI: 10.1016/s0022-0248(02)02068-7
- ISO 10716 (1994). "Paper and board Determination of alkali reserve," International Organization for Standardization, Geneva, Switzerland.
- Jin, D. L., Gu, X. Y., Yu, X. J., Ding, G. S., Zhu, H. L., and Yao, K. H. (2008). "Hydrothermal synthesis and characterization of hexagonal Mg(OH)₂ nano-flake as a flame retardant," *Materials Chemistry and Physics* 112(3), 962-965. DOI: 10.1016/j.matchemphys.2008.07.058
- Kelly Jr., G. B. (1976). "Composition for use in de-acidification of paper," U.S. Patent No. 3939091.
- Kim, S. W., Kim, I., and Moon, D. J. (2013a). "Synthesis and characterization of magnesium oxide supported catalysts with a meso-macropore structure," *Journal of Nanoscience and Nanotechnology* 13(8), 5750-5753. DOI: 10.1166/jnn.2013.7038
- Kim, S. W., Kim, K. D., and Moon, D. J. (2013b). "Shape controlled synthesis of nanostructured magnesium oxide particles in supercritical carbon dioxide with ethanol cosolvent," *Materials Research Bulletin* 48(8), 2817-2823. DOI: 10.1016/j.materresbull.2013.04.019
- Kolar, J., and Novak, G. (1996). "Effect of various deacidification solutions on the stability of cellulose pulps," *Restaurator-International Journal for the Preservation of Library and Archival Material* 17(1), 25-31. DOI: 10.1515/rest.1996.17.1.25
- Kolar, J., Strlic, M., Novak, G., and Pihlar, B. (1998). "Aging and stabilization of alkaline paper," *Journal of Pulp and Paper Science* 24(3), 89-94.
- Lv, J., Qiu, L. Z., and Qu, B. J. (2004). "Controlled synthesis of magnesium hydroxide nanoparticles with different morphological structures and related properties in flame retardant ethylene-vinyl acetate blends," *Nanotechnology* 15(11), 1576-1581. DOI: 10.1088/0957-4484/15/11/035
- Pang, H. C., Ning, G. L., Gong, W. T., Ye, J. W., and Lin, Y. (2011). "Direct synthesis of hexagonal Mg(OH)(2) nanoplates from natural brucite without dissolution

procedure," *Chemical Communications* 47(22), 6317-6319. DOI: 10.1039/c1cc10279f

- Salvadori, B., and Dei, L. (2001). "Synthesis of Ca(OH)₂ nanoparticles from diols," *Langmuir* 17(8), 2371-2374. DOI: 10.1021/la0015967
- Saoud, K. M., Saeed, S., Al-Soubaihi, R. M., and Bertino, M. F. (2014). "Microwave assisted preparation of magnesium hydroxide nano-sheets," *American Journal of Nanomaterials* 2(2), 21-25.
- Sequeira, S., Casanova, C., and Cabrita, E. J. (2006). "Deacidification of paper using dispersions of Ca(OH)₂ nanoparticles in isopropanol. Study of efficiency," *Journal of Cultural Heritage* 7(4), 264-272. DOI: 10.1016/j.culher.2006.04.004
- Sharma, R., McKelvy, M. J., Bearat, H., Chizmeshya, A. V. G., and Carpenter, R. W. (2004). "*In-situ* nanoscale observations of the Mg(OH)₂ dehydroxylation and rehydroxylation mechanisms," *Philosophical Magazine* 84(25-26), 2711-2729. DOI: 10.1080/14786430410001671458
- Stefanis, E., and Panayiotou, C. (2008). "Study of the photochemical stability of paper deacidified with dispersions of Ca(OH)₂ and Mg(OH)₂ nanoparticles in alcohols," *Restaurator-International Journal for the Preservation of Library and Archival Material* 29(2), 125-138. DOI: 10.1515/rest.2008.007
- Stefanis, E., and Panayiotou, C. (2010). "Deacidification of documents containing iron gall ink with dispersions of Ca(OH)₂ and Mg(OH)₂ nanoparticles," *Restaurator-International Journal for the Preservation of Library and Archival Material* 31(1), 19-40. DOI: 10.1515/rest.2010.002
- TAPPI T435-52 (1952). "Hydrogen ion content (pH)," TAPPI Press, Atlanta, GA.
- TAPPI T435 om-02 (2002). "Hydrogen ion concentration (pH) of paper extracts," TAPPI Press, Atlanta, GA.
- TAPPI T553 om-10 (2010). "Alkalinity of paper as calcium carbonate (alkaline reserve of paper)," TAPPI Press, Atlanta, GA.
- Williams, W. (1994). "Mass deacidification of paper A comparative study of existing processes," *Library Journal* 119(4), 126-126.
- Wu, X. F., Hu, G. S., Wang, B. B., and Yang, Y. F. (2008). "Synthesis and characterization of superfine magnesium hydroxide with monodispersity," *Journal of Crystal Growth* 310(2), 457-461. DOI: 10.1016/j.jcrysgro.2007.10.025
- Yang, Y. F., Wu, X. F., Hu, G. S., and Wang, B. B. (2008). "Effects of stearic acid on synthesis of magnesium hydroxide via direct precipitation," *Journal of Crystal Growth* 310(15), 3557-3560. DOI: 10.1016/j.jcrysgro.2008.05.006
- Yu, J. C., Xu, A. W., Zhang, L. Z., Song, R. Q., and Wu, L. (2004). "Synthesis and characterization of porous magnesium hydroxide and oxide nanoplates," *Journal of Physical Chemistry B* 108(1), 64-70. DOI: 10.1021/jp035340w

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