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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.

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 (DPv), 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.

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