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Treatment of Acid Hydrolysis of a 1900 Large-Scale Composite Artwork by the Artist Roberto Sebastian Matta: Comparison between Traditional and Innovative Deacidifying Methodologies

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Abstract: This work was carried out for a master's degree thesis concerning the conservation of a contemporary artwork made by the surrealist artist Roberto Sebastian Matta. The artwork is a large (one central panel 180.3 × 405.1 cm; two side panels 179.1 × 150.6 cm) triptych created in 1974 with pastels on tracing paper adhered onto canvas as a secondary support. After thoroughly studying the execution technique and conservation status of the artwork, several issues arose, including a strong acid hydrolysis of both the paper and canvas supports. We focused our intervention on deacidification treatments by comparing either traditional substances, such as calcium propionate in an alcoholic solution, or more innovative methods, such as a nanostructured calcium hydroxide in isopropyl alcoholic solution. Acid hydrolysis degradation was the most difficult issue to address because of the size of the artwork and for the different sensitivities to aqueous methods of the materials used to make the artwork. For the first time to our knowledge, we used an innovative deacidification method consisting of nanostructured calcium hydroxide particles. This intervention would allow the homogeneous atomization of the deacidifying agent in alcoholic solvents to be safe and effective for the work as a whole.

Keywords: pastel painting; contemporary art; *spolvero* paper; deacidification; nanostructured calcium hydroxide

Citation: Partenzi, I.; Marconi, M.; Vinciguerra, V.; Pelosi, C.; Fontani, N. Treatment of Acid Hydrolysis of a 1900 Large-Scale Composite Artwork by the Artist Roberto Sebastian Matta: Comparison between Traditional and Innovative Deacidifying Methodologies. *Heritage* **2023**, *6*, 2650–2663. https://doi.org/10.3390/heritage6030140

Academic Editors: Andrea Macchia, Fernanda Prestileo and Alexandra Jeberien

Received: 31 January 2023
Revised: 23 February 2023
Accepted: 27 February 2023
Published: 1 March 2023

1. Introduction

Chilean artist Roberto Sebastian Matta (1911, Santiago, Chile, 2002, Civitavecchia, Italy) is one of the most outstanding personalities of the surrealist art movement. Andrè Breton, founder of this group of artists, introduced him to surrealism at the beginning of the 1930s. Matta's paintings are exhibited in the world's most valuable contemporary art collections as London's Tate Modern, the Metropolitan (MET), Museum of Modern Art (MoMA) in New York, and San Francisco Museum of Modern Art. In his latest works, in a phase of overcoming surrealism, Matta devoted himself to the pastel technique. To Matta's late phase and inspiration belongs the triptych. For the victims to win (1974–1975), made up of three separate large paper sheets lined on canvas, consisting of two smaller lateral ones (179.1 × 150.6 cm) and a central one (180.3 × 405.1 cm). The central panel (Figure 1) was investigated with diagnostic techniques in order to understand Matta's creative process, identify painting materials and evaluate the state of conservation of the paint, as well as both paper and canvas support, to properly approach their restoration. The diagnostic study was crucial in understanding the processes of degradation that characterized the state of

conservation of the materials. Such understanding made it possible to elaborate a targeted restoration. In fact, the investigation revealed numerous conservation problems, including a strong acid hydrolysis of both the paper and canvas supports. The restoration, given the severe deterioration of the artwork, the heterogeneous materials employed, and the large dimension, was a challenge for many reasons. It is worth noting that these characteristics precluded the use of most traditional water-based methods, which would have required either a complete immersion or intensive repeated spraying on the artwork. Our in-depth study focused on the deacidification treatment by comparing either traditional substances, such as propylene carbonate in an alcoholic solution, or more innovative methods, such as a nanostructured calcium hydroxide in alcoholic solution, developed by researchers of CSGI (Consorzio Interuniversitario per lo Studio dei Sistemi a Grande Interfase) and the Chemistry Department of the University of Florence. This product is available to conservators under the commercial name of Nanorestore Paper®. Given the excellent outcome following the innovative method of deacidification employed for Matta's artwork, it is now worth taking it into consideration for the restoration of artworks with comparable issues to ours.

Figure 1. The central panel of "For the victims to win" pastels on paper (180.3 × 405.1 cm).

2. Materials and Methods

2.1. Conservation Status of the Artwork

A fundamental step in this work was taking information on the execution technique from direct sources, supported by diagnostic analyses. In particular, the visit to the home and studio of Sebastian Matta in Tarquinia, thanks to the artist's daughter Alisee Matta, gave us the priceless opportunity to access some original painting materials used by Matta in his later production. The visit to the artist's studio in Tarquinia and an interview of one of Matta's collaborators, brought to light the fact that Matta mainly used *spolvero* paper (sketching or tracing paper) to produce his pastel works. This information was confirmed by the Graff C analysis carried out by comparing a sample of paper taken from the artwork with a sample of commercial dusting paper (see below in the Section 3). A further discovery, due to what was found in the artist's studio and to the oral sources, regarded the type of pastels used by Matta. The artist used to employ the famous 'Rembrandt soft pastels' produced by the Dutch company *Talens*. Thanks to diagnostics [1], it was possible to analyze the pastels and discover that they were free of organic binders (wax and oil type), and that they were composed of one part of pigment and one part of kaolin, probably with the addition of a minuscule amount of a gum, such as Arabic, that the analyses were not able to reveal due to very low concentration. This characteristic makes *Rembrandt soft pastels* particularly soft and blendable, more similar to chalk. It is also important to mention the use of gas chromatographic analyses carried out to identify the starch-based adhesive used to ensure adhesion between the dusting paper and the canvas. Overall, the information collected was of fundamental importance not only to understand the underlying reasons of the work's conservation, but also to select a correct intervention

practice. At the time of the transportation of the artwork inside the restoration laboratories of Tuscia University, the painting was in a poor state of conservation due to the unsuitable environmental conditions of the room in which it was preserved and to intrinsic structural factors, such as physico-chemical degradation, which affected the constitutive materials over time. In particular, the *spolvero* paper constituting the primary support of the artwork was suffering the most. This kind of paper is produced by a kraft method and, as it will be explained later, this production method causes the generation of endogenous chemical degradation byproducts leading to the loss of chemical and physical qualities over time. Among the main exogenous factors that contribute to the poor conservation of the paper are: environmental thermo-hygrometric variations, the presence of artificial light sources close to the artwork's surface and exposure to direct sunlight. The acid hydrolysis of the *spolvero* paper and canvas was caused and accelerated by the synergy of the aforementioned factors. A severe acidification of the canvas made of vegetal fibers like the ones observed in Matta's artwork, seems to have occurred due to migration of acid substances from paper to canvas, carried by moisture, due to condensation phenomena on the supports, or because of the percolation of rainwater, an accident occurred in the exhibition hall. Other degradation causes are the probable oxidation and photo-oxidation phenomena leading to the weakening of both the paper and canvas; these are well detectable as a visible yellowing of the paper support and correspond to areas more sensitive to mechanical stress. Several small and medium-sized tears were also observable. A graphic representation of acidification and humidity stains on the artwork are shown in Figures 2 and 3. The joint action of acid hydrolysis and oxidation caused the breakdown of the cellulose polymer and the consequent lowering of the level of polymerization of the paper. This together with the mechanical stresses suffered by the artwork due to several transportations during its conservation history were responsible for the lacerations and tears of the paper support. Most of the conservation issues were also due to the execution technique employed by the artist, such as the use of heterogeneous materials, such as *spolvero* paper and canvas, which have a different response to environmental thermos-hygrometric variations.

Figure 2. Recto of the painting. Digital representation of humidity stains (in yellow) on paper support and concentrated more in the right portion of the central panel.

Considering the execution technique and state of preservation, we reasoned that the artwork would have been seriously affected by aqueous solvents applied either directly on the canvas or in nebulized form. In contrast, alcoholic solvents were tolerated but under a nebulized application only. Consequently, we decided to use an alternative non-aqueous and nebulized solvent, which proved to be effective and safe. To efficiently approach such a complex conservation case, several research and preliminary tests on samples were conducted in the restoration project.

Figure 3. Recto of the painting. Digital representation of acidification (shades of green) of the paper support, more intense in the lower portion of the panel.

2.2. Graff-C Analysis

Graff C was used to characterize the cellulose fibers of the work's primary paper support. By consulting bibliographical sources, we learned that the paper used by the artist was a kraft-type *spolvero* paper. To confirm this hypothesis, we ran a comparative analysis by treating with a Graff C reagent a commercial *spolvero* paper sample, and a sample of artwork's paper. The Graff C staining test was prepared and used according to the guidance reported in the specific ISO standard (ISO 9184-4:1990, Paper, board and pulps. Fiber furnish analysis. Part 2: staining guide). The reagent, over the course of a few minutes, made the fibers colorful, allowing their chemical nature characterization. For the interpretation of the results, we consulted the colorimetric parameters reported in the relevant regulations (ISO 9184-4:1990). The coloured samples, following the application of the reagent, were observed using the Dino-Lite Special digital optical microscope lighting (Physical characteristics: 1.3 megapixel CMOS sensor (1280 × 1024). Illumination LED 390–400 nm. Magnifications 10–70×, 200×) by acquiring images at 100× and 200×.

2.3. Pyrolysis Coupled with Mass Spectrometry (py-GC/MS)

Analytical pyrolysis coupled with a gas chromatography–mass spectrometry system (Py-GC-MS) is a micro-destructive technique widely used for the study of natural and synthetic polymers used in art [2]. This technique, when applied to polymeric substances, allows their structural and chemical characterization. The byproducts of controlled pyrolysis are a mixture of volatile compounds originating from the thermal degradation of the polymer, in an inert atmosphere. Polymeric substances, once introduced inside the heated furnace of the pyrolysis instrument and thermally decomposed, are directly sent to a separation system, the gas chromatograph (GC), coupled to an analytical identification system, such as the mass spectrometer (MS). The identification of pyrolysis by products is based on the retention times of the volatile products of pyrolysis and on the comparison of their mass spectra with reference databases [3]. Therefore, from the reading of the resulting pyrogram, it is possible to determine, quantitatively and qualitatively, the monomers constituting the polymer itself, and to identify the nature of the starting polymer. The purpose of our analysis was to identify the type of adhesive used to line the paper of the artwork to the canvas. In order to take an analytical sample of the liner adhesive, it was necessary to remove the paper to which this was glued. In order to limit the invasiveness of the analysis, the samples to be analyzed were taken in small quantities (2.5 µg approx). The investigation was carried out with a pyrolysis unit equipped with a micro furnace coupled to a gas chromatograph–mass spectrometer system (GC-MS), with pyrolysis temperature set at 600 °C. The instrumental conditions under which the analysis was carried out were: Pyrojector II pyrolytic unit (SGE, Italy) with a micro-furnace coupled to the gas chromatograph–mass spectrometer system GC-MS QP5050A (Shimadzu, Japan) equipped with a Restek

Rtx-1701 column (30 m × 0.25 µm); pyrolysis temperature at 600 °C; pyrolysis interface temperature at 180 °C and the injector temperature at 250 °C. GC column temperature programme: initial temperature of 45 °C, maintained for 4 min, increased to 280 °C (by 4 °C/min) for 3 min; total gas flow He at 38 cm/s.The mass spectra were recorded under the following conditions: electron ionization at 70 eV; scan interval at 35–500 u.m.a. at a frequency of 0.8 scan/s.

2.4. pH Measurements

Acid hydrolysis was one of the main causes of degradation affecting the triptych "For the Victims to Win". To evaluate the substrate acidification, pH measurements were carried out with a portable pH meter (Hanna Instrument HI 8424 with an accuracy of 0.1 unit). The contact electrode was placed on the artwork's surface, previously wetted with one drop of demineralized water. This solvent dissolves the acidic groups inside the paper and allows the instrument to accurately detect the amount of H+ ions present within the chains of cellulose. However, as the addition of water can eventually provoke stains and discoloration, we kept pH measurements to a minimum number (n = 3). In addition, considering the large size of the work, we spaced pH measurements out to obtain a representative range of pH of the entire central panel of the triptych. The three points chosen were located bottom left, top center and bottom right. pH measurements were subsequently repeated in two points on the verso of the artwork with the same criteria followed on the recto.

2.5. Deacidification Treatment: Test Planning on Samples

After having considered different methodologies for the deacidification of the paper and canvas materials, we decided to compare nano calcium hydroxide particles, developed by the researchers of CSGI and the Chemistry Department of the University of Florence, with the widely used solution of calcium propionate, for the treatment of paper support of the artwork. As mentioned above, due to the structural and chemical peculiarities of the artwork, both mixtures (nanoparticles vs. calcium propionate) used were dispersed in solvent, trying to limit, as much as possible, the use of water, preferring alcoholic solvents delivered by spraying. Spray delivery was adopted to avoid contact stress, which is harmful to the substrates. Before proceeding with the application of both mixtures on the original work, compatibility tests were carried out on ad hoc samples, with the aim to obtain insight on the interaction between the deacidifying products and the artwork constituent materials. In addition, the preliminary tests on samples aimed at providing useful indications about the efficacy of the two different treatments. The samples used for the preliminary tests were made to faithfully reproduce the artwork's painting technique and its current state of conservation (see Section 2.5 below).

2.6. Samples: Preparation and Characteristics

The samples were prepared according to the test phase they were allocated, aiming at making them homogeneous, not only in terms of construction technique but also in terms of degradation characteristics. Acid hydrolysis degradation was difficult to simulate by artificial aging, as it is driven by numerous degradation factors, including thermo-hygrometric stress. A first set of samples was realized reproducing the painting technique of the artwork (Figure 4) (dusting paper adhered with starch on canvas and having chromatic backgrounds made with 'Rembrandt soft pastel') and artificially aged in a UV chamber. This group of samples was not affected by acid hydrolysis, but only by oxidative degradation. For this reason, on this latter type of samples, the effectiveness test with the deacidifying mixtures was only colorimetric.

Figure 4. A first set of samples reproducing the painting technique of the artwork.

A second set of samples (Figure 5) was realized to reproduce an acid degradation comparable to the one found on Matta's painting, and having a similar stratigraphy. These samples consisted of a type of old paper and cloth naturally aged; they had a different origin than Matta's materials but similar physico-chemical characteristics. The type of paper used to make these samples was, like *spolvero* paper, an uncoated western paper with a grammage (90/100 g/m^2) slightly lower than that of *spolvero* paper (110 g/m^2). The canvas used to produce the samples was a natural fiber, like the one used for the original artwork. Each sample was analyzed before and after treatment with the different mixtures.

Figure 5. Set of samples realized to test deacidification protocols on Sebastian Matta's painting.

2.7. Accelerated UV Aging

The samples of Set-1 were subjected to accelerated aging inside a UV irradiation chamber for a time of around three weeks. The UV aging performed on the samples was carried out inside a closed chamber irradiated with UVC lamps, Philips TUV model 36 WATT mercury vapor discharge. The artwork was carried out between 1974 and 1975, so to date, it is approximately 50 years old. To simulate solar aging of such a duration requires three weeks in an accelerated aging chamber. ISO 5630-7:2014, "Paper and board Accelerated aging", Part 7: exposure to light.

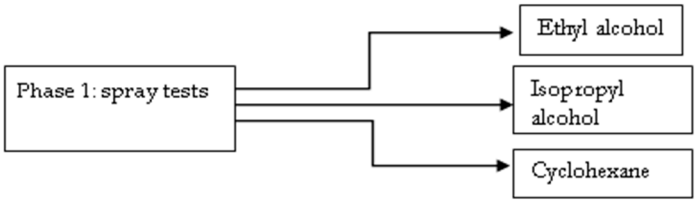
2.8. Tests of Solvents and Deacidifying Mixtures on Samples

The tests on samples were split into two phases.

(1) First phase: identification of the organic solvent capable of conveying the deacidifying agent during application by spraying.

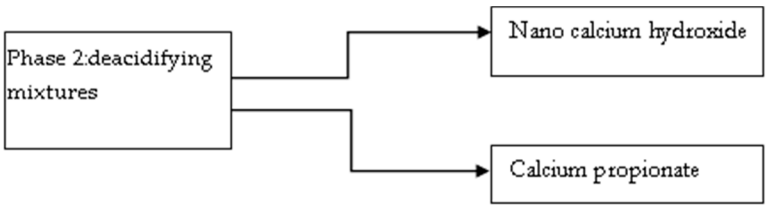
The solvent(s) suitable to be used to solubilise the agents for the deacidification were identified by swabbing them directly on the original artwork (and not onto samples). The initial swab tests, performed on the smallest possible areas, showed that ethyl alcohol and isopropyl alcohol were able to solubilize the pastel colors, unlike cyclohexane. However, as the penetration of solvents could be different between treatments applied directly, by brush or swab, on one hand, from penetration achieved by atomization on the other, we carried out tests with the same solvents by spraying them on the samples. These latter tests

were performed on each sample by atomizing an amount between 10 mL and 20 mL with a nebulizer, on an area of 168 cm^2. Considering the size of the samples, a generous amount of solvent was used to better challenge their safety towards the painting materials. After completely drying, none of the solvents tested was found to be harmful to the constituent materials of the samples, following direct observation and colorimetric analysis. None of the solvents tested, being extremely volatile, left any trace on the surface of the samples. At the end of these tests, the solvent chosen to be used as a vehicle for deacidifying substances was isopropyl alcohol, whose vapor pressure ensures rapid evaporation. This latter property of isopropyl alcohol guaranteed its usage from any risk to produce swelling of the starch adhesive and from the risk of solubilization of the pastel.



After the results obtained from the first phase, the tests on samples continued with the second phase:

(2) Second phase: the identification of the most effective deacidifying mixture.



The second phase involved the analysis of three different samples for each deacidifying mixture under investigation. On these samples, the effectiveness of the deacidifying mixture was proved by pH measurement. The deacidifying tests were carried out using, for both tested mixtures, the same quantity applied with the same methodology, in order to obtain comparable data following a replicable intervention protocol. The samples were classified into two groups according to the efficacy evaluation, as follows:

Set-1, containing samples that replicate the technique and materials used by the artist, and Set-2, containing samples with similar acid degradation but not exactly made with the same constituent materials. Deacidifying products were applied on the front and back of the samples to work on both supports: paper and canvas. An airbrush was used, combined with a compressor, to spray the mixtures onto the samples, a methodology that will later be used on the original painting. Samples received a direct atomization of 1 mL of product on an area of 168 cm^2; that is, 2 mL per sample (1 mL on the front and 1 mL on the back). After the application of Nanorestore Paper® dispersions, the treated samples were kept for 10–15 days at room temperature and at a relative humidity of about 60%, as indicated in the technical data sheet [4]. Such environmental parameters favor the transformation of unreacted calcium hydroxide into calcium carbonate, which is the alkaline reserve. To make treatments comparable to each other, the samples treated with calcium propionate were also stored for a total of 10–15 days under the same conditions described for nanoparticles.

2.9. Colorimetric Analysis

The pH measurements were accompanied by a campaign of colorimetric analysis carried out on a different group of different samples, reproducing the original execution technique and artificially aged.

Color measurements were carried out on all five different backgrounds of each treated sample: paper, violet, orange, blue and black. In each individual background, measurements were recorded on five different points and three repetitions were carried out on which one, following what is indicated in the reference standard (UNI EN 15886 of 2010: Conservation of Cultural Heritage. Test Methods. Measurement of surface color, UNI, Milan, November 2010) [5]. The recognition of previously measured areas was possible by putting over the sample a transparent mask with holes having the same diameter as the instrument used (6 mm). The collected data set was organized, synthesized and compared by performing mathematical averages. The measurements were repeated on the same areas before and after the treatment. The instrument used was an EOPTIS (EOPTIS s.r.l. 38121 Trento (TN) – ITALY) colorimeter model CLM19x 45°/0. The measurement method used was that of the CIE colorimetric space of 1976 (CIELAB), whose coordinates are L*, a* and b*. These colorimetric coordinates express:—L* (brightness), which represents the "clarity" of the color. The parameter L* can have a minimum value of 0, indicating perfect black, up to a maximum value of 100 for white. —a* indicates the chroma coordinate on the axis from red (a* > 0) to green (a* < 0). —b* indicates the color coordinate on the axis from yellow (b* > 0) to blue (b* < 0). The total color difference ΔE is calculated using the following formula: $\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$. Where ΔL* is the difference between the final and initial value of the parameter L*; Δa* the difference between the final and initial value of a* and Δb* the difference between the final and initial values of b* [6].

3. Results

3.1. Graff C Analysis

The fibers belonging to the original artwork, following the application of the Graff C reagent, turned on a bluish color, typical of the chemical-type paper pulp. Chemical pulps are produced from wood according to two different processes. The first one is the kraft process, which can be applied to any wood species, and is based on the use of alkaline substances such as sodium hydroxide (NaOH) and sodium sulfide (Na_2S) from which the pulp or sulfate pulp is obtained. The second one is the sulphite process, which uses magnesium disulphide ($[Mg(HSO_3)_2]$) or sodium sulphide (Na_2S) in acid solution combined with heat to obtain sulphite or coniferous pulp. Both chemical processes create cellulose pulp that, when analyzed with Graff's reagent C, takes on a dark color ranging from light blue to violet; however, the kraft pulps are distinguished by a darker blue color tending to black. Therefore, our results suggested that the raw material of the paper under investigation was produced by the kraft process, which is normally used to obtain cellulose pulp from hardwood. The commercial *spolvero* paper sample treated with the Graff C reagent (Figure 6) turned the same dark blue color, as observed with the original artwork sample. In addition to the color data, the fibers belonging to the two samples were visually comparable in terms of length and thickness. Overall, both chemical and physical results, confirmed the hypothesis suggested by the literature [7], that *spolvero* paper was actually used by the artist to make the artwork under investigation.

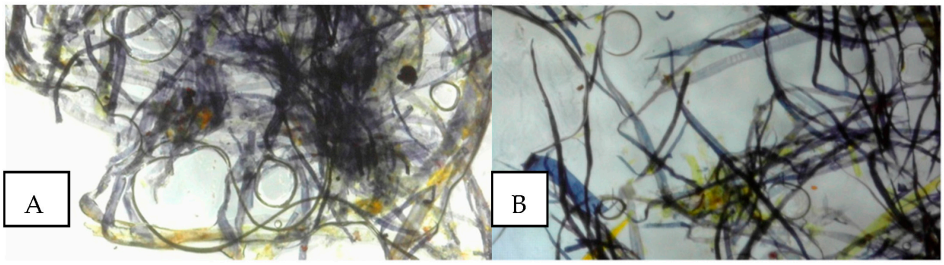


Figure 6. (**A**) sample of the artwork treated with Graff C reagent and (**B**) sample of the commercial *spolvero* paper treated with Graff C reagent. Observed using the Dino-Lite Special digital optical microscope lighting (Physical characteristics: 1.3 megapixel CMOS sensor (1280 × 1024). Illumination LED 390–400 nm. Magnifications 10–70×, 200×) by acquiring images at 200×.

3.2. py-GC/MS Results

Table 1 lists the main compounds detected by the pyrolysis process.

Table 1. Retention time, name and origin of main compounds detected by the pyrolysis process.

Time of Retention (min)	Name	Origin	(%) Paper and Adhesive
1.3	Carbon dioxide	Cellulose	9.2
1.5	Pyruvic aldehyde	Cellulose	8.3
4.5	2-hydroxy butanal	Cellulose	1.7
5.8	2-furaldehyde	Cellulose/starch	10.8
21.8	5-hydroxymethyl-2-furaldehyde	Cellulose/starch	12.2
32.5	Levoglucosan	Cellulose	15.2

Among the most abundant compounds resulting from the analysis of the sample were derivatives of cellulose, with total absence of chemical structures referable to synthetic adhesives. The hypothesis that the adhesive used to glue the paper onto the canvas could have been a starch-type adhesive was confirmed by the particularly relevant presence of certain compounds, such as 2-furaldehyde and 5-hydroxymethyl-furaldehyde, which are molecules typically present in both paper and starch. It is worth noting that starch adhesive contains the same sugar chains as cellulose, although bound with different chemical bonds [8].

3.3. pH Data on the Artwork

The three measurements of pH taken on the paper support, ranged between 4 and 5, as shown in Table 2. Following similar procedures, pH was measured on the verso of the artwork. The results obtained on the canvas show again low pH levels (Table 3), probably caused by the migration over time of the acidic groups from one medium to another.

Table 2. Location and average value of pH measurement points on the recto and verso of Matta's painting.

pH Measurements on the Front		
		
Point of analysis	Area	Values
1. *spolvero* paper	Bottom right	4.47
2. *spolvero* paper	Top center	5.37
3. *spolvero* paper	Bottom left	4.99

Table 3. Location and average value of pH measurement points on the recto and verso of Matta's painting.

pH Measurements on the Back		
		
Point of analysis	Area	Values
1. Canvas	Top right	4.75
2. Canvas	Bottom left	4.26

These low pH values measured on both supports raised a serious concern for the preservation of paper and canvas artifacts.

3.4. Deacidification Treatment: Evaluation of the Results by pH and Color Data

After that, the required period of time needed for the deacidification reactions to take place elapsed; post-treatment measurements and diagnostics were carried out in order to check the effectiveness and conformity of the method with the original materials.

pH measurements on samples were conducted before and after the deacidification treatment. Three measurements were taken on each sample, both on the front and back side, and the average values were compared. With regard to the samples treated with calcium nano-hydroxide dispersions in isopropyl alcohol, the comparison pre- and post-treatment (Figure 7) displayed a clear improvement in the pH values of the supports. Actually, there was an increase of four points of the pH value of the paper support compared to the pre-treatment score, whereas, the pH of the canvas surface increased by two units after the deacidification treatment. A further pH check was run one and a half months after the initial treatment. Figure 7 shows pH measurements at the starting conditions (pre-treatment), intermediate conditions (14 days post-treatment) and final conditions (physico-chemical stabilization, 28 days post-treatment). The data collected showed that the pH value of samples treated with nano calcium hydroxide reached a pH value of 8, then lowered towards neutrality. This lowering of pH could suggest a settling and equilibration of carbonating reactions on the surfaces. On the other hand, the samples treated with calcium propionate solution recorded almost no change in pH conditions, both on the front and back of the samples.

The pH measurements were accompanied by a set of colorimetric analysis (Supplementary Materials SM1) to check if the deacidifying substances had caused any significant color variations on the treated surfaces. Color differences were detected as a variation in (ΔE^*) significantly superior to the indicative value of 3. On the set of samples treated with nano calcium, only one sample showed a significant variation in ΔE^*, whereas of the samples treated with calcium propionate, two suffered a significant variation.

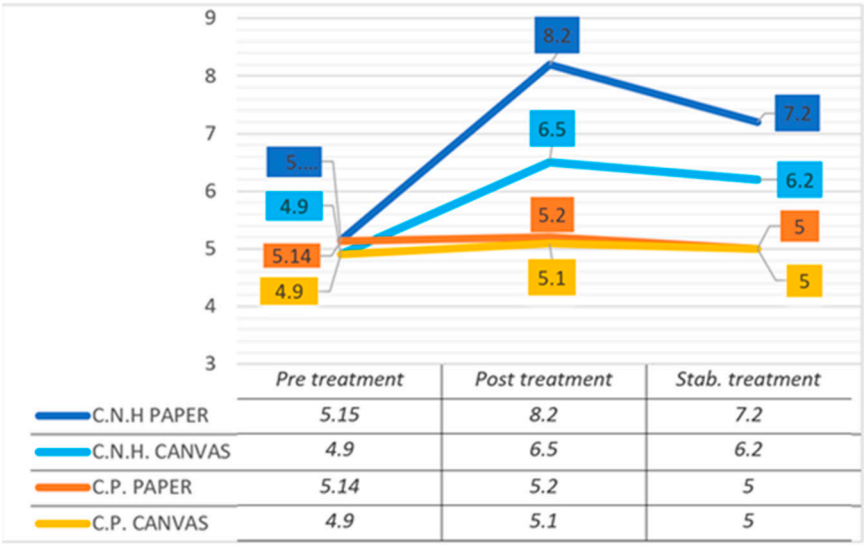


Figure 7. pH changes on samples from starting to final condition. C.N.H. = calcium nano hydroxide and C.P. = calcium propionate. Hanna Instrument HI 8424 with an accuracy of 0.1 unit.

Color measurement was deliberately chosen as a quick and low-cost method to evaluate the effectiveness of the deacidification process because it is a non-invasive method applicable both on the specimens and on the artwork. Color measurement is also recognized, according to the international standard [5], as a reliable and fundamental technique for evaluating the effectiveness of an intervention on works of art, whether it is cleaning, the application of protective agents or other types of treatment. In this sense, there are many publications in the literature that demonstrate how the measurement of color is able to evaluate the effectiveness of a treatment and can also correlate it with the chemical-physical properties of the surfaces [9–18].

At the end of the trial, it was possible to notice that the deacidification method, which produced the best results in terms of pH and colorimetric measurements, was undoubtedly the one with calcium nano-hydroxide in isopropyl alcohol. In contrast, calcium propionate, at an equal weight concentration following the same application methodology, did not produce significant results, leaving the pH of the samples almost entirely unchanged, and slightly modifying the colorimetric parameters.

After the validation on ad hoc samples, the chosen protocol was applied on Matta's masterpiece. The deacidification took place from the starting pH of the paper around 4.9 and from a pH of the canvas support around 4.5 to reach pH neutrality that corresponded to a quantity of Nanorestore Paper® of approx. 68.5 mL/m^2. The quantities for the Nanorestore paper products were calculated on the basis of the information reported in the product data sheets. The needed quantities were calculated based on the size of the object to be treated, the grammage of the paper and the starting pH value of the object. This means that for the entire area of the artwork, which measures 7.3 m^2, approx. 1 L of product had to be used (2 L in total considering both recto and verso). Once applied, a period of 14 days was allowed to elapse for the conversion of calcium hydroxide into carbonate, after that pH was measured again. The pH measurements were carried out around the same areas as the preliminary ones showing, as shown in Figure 8, an increase of almost 1 pH unit on the paper (from 4.9 to 5.5). The canvas support underwent a greater improvement: from an average pH value of 4, to about 7. As the *spolvero* paper did not reach the desired neutral pH values with a single application, it needed a second treatment, carried out on the front side, following the same method as the first one and using the same application parameters. After that, the pH increased from an average of 5.5. to 6.5.

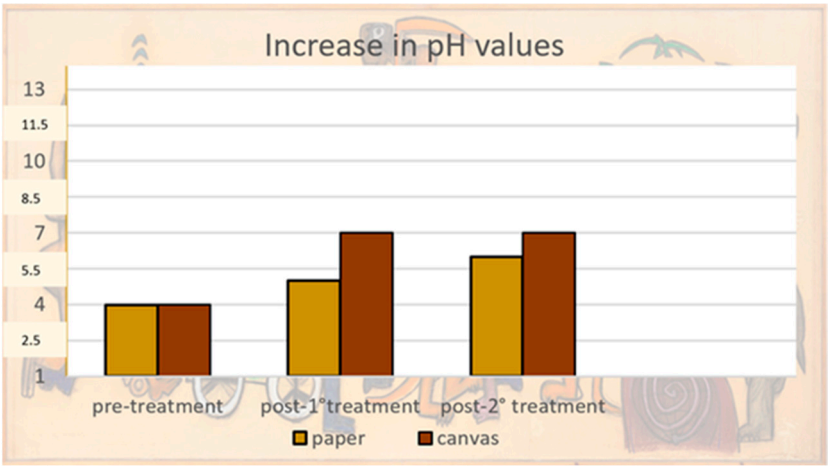


Figure 8. pH changes on the artwork from starting to final condition. Hanna Instrument HI 8424 with an accuracy of 0.1 unit.

4. Discussion

The physical peculiarities and execution technique of this artwork are unusual, and to the best of our knowledge, no published study exists describing a deacidifying intervention on comparable artworks as ours. Such unique characteristics are:

- The large dimensions of the work: one central panel 180.3 × 405.1 cm; two side panels 179.1 × 150.6 cm;
- The different sensitivity to environmental thermo-hygrometric variations shown by the canvas and paper supports of the artwork and the water-solubility of the starch adhesive;
- The limitations on the choice of the deacidifying intervention forced by the constraint existing between the secondary canvas support and the primary paper on which images are drawn in order to avoid structural trauma to the flat work;
- The high level of acidity of the work, detected by pH measurements.

The characteristics described above disallowed the use of most traditional water-based methods, which required complete immersion or repeated spraying on the object. Therefore, we turned to innovative methods allowing the front/back deacidification of the work that was both effective and homogeneous, such as solutions based on nanostructured particles of calcium hydroxide, rather than using the more traditional calcium propionate. We finally discarded sodium propionate, despite its deacidifying efficacy having been studied and used on various media, as well as approved by the Central Institute for the Restoration and Conservation of the Archival and Library Heritage (ICRCPAL). Calcium propionate is, in fact, the most widely used deacidifying agent in Italy on paper and membrane substrates.

Our research, based on experimental data, exploited an innovative deacidification method consisting of nanostructured calcium hydroxide particles studied and developed by the researchers of CSGI and the Chemistry Department of the University of Florence. The reason why nanoparticles performed better than a well-known deacidifying agent in this particular case, can be found in their chemical composition. Firstly, the solvents that were used for the (nano particle) dispersions were able to penetrate into the substrate effectively and quickly, with minimal interaction with the original materials. The organic solvents used for these nano compounds are usually less polar than water and, for this reason, more inert towards certain inks, dyes and substances used for lining [19,20]. In addition to these reasons, the alkaline nanoparticles, which are highly reactive due to their overall high surface area, ensure the effective neutralization of acidity and undergo the conversion of the calcium hydroxide in excess into carbonate, thereby creating an alkaline reservoir useful to counteract incoming acidification processes. Perhaps the most remarkable characteristic of these dispersions is the (low) dimensions of the particles. In

fact, the smaller the particles, the greater their surface area capable of reacting with the external environment. Actually, the average diameter of nanoparticles in dispersions for deacidification ranges from 50 to 300 nm, depending on the synthetic strategy employed to make them. The microparticles present in more traditional mixtures, in contrast, range in size from 1 to 1000 µm [21]. To conclude, the method of calcium nano-hydroxide in isopropanol produced very good results, as it not only allowed pH neutrality to be recovered, but also it operated by respecting the many different characteristics/weaknesses of the artwork. Propionate, in comparison, would have required more product or more intense spraying to produce the same results at the same time. Nevertheless, a difference in the amount of nanoparticle dispersions needed to increase the pH was noted between testing smaller portions compared to treating the entire artwork. We believe this could be attributed to a greater dispersion of the product in the air, which inevitably occurred when treating such a large area by atomisation. Contrary to what happened in the test phase, therefore, on the front, it was necessary to repeat the treatment a second time. The cloth behaved the same as in the sample tests, with no need to repeat the treatment, probably because of a different (better?) absorption index of the fibers. Finally, it is worth mentioning that nanodispersions for deacidification have been appreciated by the scientific community for the preservation of cellulose-based artworks [22]. Several research groups have tested nanoparticles' effectiveness on paper and canvas [23,24], either ancient or contemporary, obtaining excellent results [25].

5. Conclusions

In conclusion, we can affirm that our experimentation succeeded, as the artwork underwent an excellent pH recovery. Here, we have described for the first time an intervention made with an innovative deacidification method based on nanoparticles on an artistic object of very large dimensions, and with severe problems of pastel cohesion; a challenge not addressed by anyone else before this study, to the best of our knowledge.

Finally, we want to remark that the environment where the artwork will be placed, which will surround it should be kept under strict control, as it remains an extremely fragile artwork. In particular, the aspects to be constantly monitored should be light exposure and pH values, which need to be checked.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage6030140/s1, SM1: Comparison Colorimetric Values of the samples.

Author Contributions: Conceptualization, I.P. and N.F.; methodology, N.F., I.P. and M.M.; validation, C.P., N.F. and M.M.; formal analysis, V.V.; investigation, C.P.; resources, I.P.; data curation, I.P. and N.F.; writing—original draft preparation, I.P.; writing—review and editing, I.P.; visualization, I.P.; supervision, N.F., M.M.; project administration, N.F.; All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by CARIVIT foundation, Via Cavour, 67, Viterbo (Italy), and by Comune di Tarquinia, Piazza Giacomo Matteotti, 6, 01016 Tarquinia VT. The APC was funded by participation at the Yococu Special Issue 2022.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank Giorgia Agresti from the University of Tuscia for her collaboration during the pH measurements and lab test and Giovanna Poggi, Rodorico Giorgi and P. Baglioni from CSGI and Chemistry Department of the University of Florence for fruitful discussion.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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