INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE
ISSN: 2067-533X Volume 15, Issue 3, 2024: 1189-1198 www.ijcs.ro
DOI: 10.36868/IJCS.2024.03.03

AN AGAROSE GEL-BASED APPROACH FOR THE REMOVAL OF METALLIC-BASE INK STAIN FROM THE PAPER SURFACES OF A 17TH CENTURY BOOK

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Abstract

Removing ink stains from the pages of ancient and valuable books is a very challenging and sometimes impossible task. Only in some circumstances, restorers are able to improve the appearance of an ink-stained page by lightening the spots using an ink eradicator. This paper reports on an approach for the removal of ink stains from a 17th century book using a combination of two commercial houseware products, the rust remover for textile and bleach. The products were chosen on the basis of their active ingredients such as hydrofluoric acid (HF), which facilitates the removal of metal ions contained in the inks (such as iron and chromium) and sodium hypochlorite (NaClO), known for its whitening abilities. The products were first tested by direct application to one of the several stained pages as a control experiment. The ink stain was successfully removed from the book, but by SEM analysis the page results in a clear detachment of the cellulose fibers from the paper pulp, which reflect a significant change in the paper fine structure. Moreover, the mixing of chemicals occurring during this procedure generated toxic vapors and the entire protocol could only be performed under a chemical fume hood. A new procedure was developed to mitigate these negative effects. Each of the two commercial products was dispersed in a 2% agarose solution shortly before its gelification and the two gels thus obtained were applied consecutively on the surface of the paper to be cleaned. The results showed an effective removal of the ink stain from treated page, avoiding irreparable damage to the paper structure and improving the working conditions of the restorers. Hence, the proposed gel cleaning procedure offers three main advantages: i) a simple and practical tool for effective removal of metallic ink stains from the paper surface; ii) reduction of damage caused by aggressive reagents (HF and NaClO) contained in cleaning products for a better conservation of paper fibers; iii) a great decrease of the risk of accidentally exposing the operators to harmful toxic vapor (produced by accidental mixing of aforementioned chemical reagents).

Keywords*: Ink-stain removal; ICP-MS; Agarose gel-based approach; Cleaning paper; SEM*

Introduction

Cultural heritage is a dynamic and ever-growing asset, which includes a collection of data from the past, objects or cultural traditions that characterize human society, to be preserved and transmitted to future generations. Preserving our cultural heritage through the restoration

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and conservation of art is the best way to take stock of society's progress and pass it on to the future. To this aim, one of the most important and delicate interventions on artifacts is the removal of dirty layers, or non original patinas from previous restorations [1], without affecting the artifact. Hence, one of the major risks in these interventions is the use of invasive procedures that might irreversibly damage the artwork instead of preserving it.

Paper artworks conservation remains a very challenging task and very rare and ancient paper artifacts should be handled only by conservators with extensive experience. The cleaning and conservation of paper artworks is particularly difficult as paper, made from the processing cellulose fibers linked by hydrogen bonds, is an extremely weak material from a mechanical point of view [2, 3]. Scientists constantly research new and better solutions to preserve paper artworks from the unavoidable natural processes of degradation [4-6] and to devise more effective and adequate intervention strategies for the removal of unwanted layers from the original surface [7]. Often a subtle balance between the need to preserve the integrity of artworks and the conservation process required to enhance their aesthetic qualities should be found. In these cases, scientific discussions between experts from different disciplinary fields are essential to define the most effective and least risky restoration treatment for the artworks.

The removal of ink stains from paper is one of the most difficult tasks for restorers. This is demonstrated by the lack of literature on procedures for removing ink stains from paper surfaces. To the best of our knowledge, the reagents and cleaning procedures commonly used by restorers are often either inefficient or too aggressive, causing irreversible damage to the artwork. In recent years, great interest has been given to the development of successful methods for cleaning paper artworks, which at the same time preserve the integrity of its characteristics. In this context, different dry-cleaning techniques are reported in the literature such as mechanical abrasion or laser ablation, wet and hydrogel-based techniques [5, 8, 9]. Wet cleaning methodology by immersion of paper artwork in water is ideally the most effective technique to remove polluted particles, dust and soils deposited on paper surfaces as water can uniformly reach paper artifacts [10]. However, this method often causes inevitable changes in the mechanical and morphological properties of the paper and in addition it could cause the ink fading [10]. Cleaning methodologies based on the application of suitable hydrogel represents a valid alternative to this procedure; due to their retention power and viscosity they reduce the penetration of liquids into the paper sheets, therefore minimizing the disadvantages mentioned before [9, 11, 12]. There are numerous studies reported in the literature on hydrogel-based cleaning techniques for artworks [5, 9, 13-15]. In fact, nowadays gel-based methodologies are widely used as a valid alternative to the classic cleaning methods, responding positively to the conservation requests in the restoration of artworks [3, 9, 16]. In particular, agarose-based hydrogels are commonly applied in the cleaning of artworks because of their great effectiveness and simple application on a variety of substrates, including paper [13, 14, 17]. Unfortunately, little is known about the cleaning procedures for the removal of ink stain from paper.

In this study we developed a reliable procedure to remove an ink stain from the paper surface of a 17th century book while preserving the integrity of the artwork. Figure 1 shows the book object of this case study and the extent of its damage. In fact (Fig. 1b), shows that several pages of the book are decorated with large black spots, probably caused by the accidental dripping of ink in the upper right corner of the book. The proposed cleaning methodology is based on the use of two household products, rust remover for textiles and bleach, selected on the basis of the chemical properties of their constituents. These products were dispersed in an agarose gel matrix to minimize their penetration in paper fibers thus avoiding side-effects during cleaning treatments. The rust remover and bleach are very common household products and even if they are potentially dangerous for health, both by inhalation and by contact, wearing suitable safety devices, such as gloves and operating in an open and well-ventilated workplace, drastically reduces the danger. In addition, the proposed strategy aims to reduce the risk of exposure to toxic vapors. In fact, the rust remover contains diluted hydrofluoric acid <7% which, when mixed with bleach (containing sodium hypochlorite <5%), releases dangerous

toxic vapors. For this reason, extreme care is required in handling the aforementioned products, always wearing protective gloves and absolutely avoiding their direct mixing.

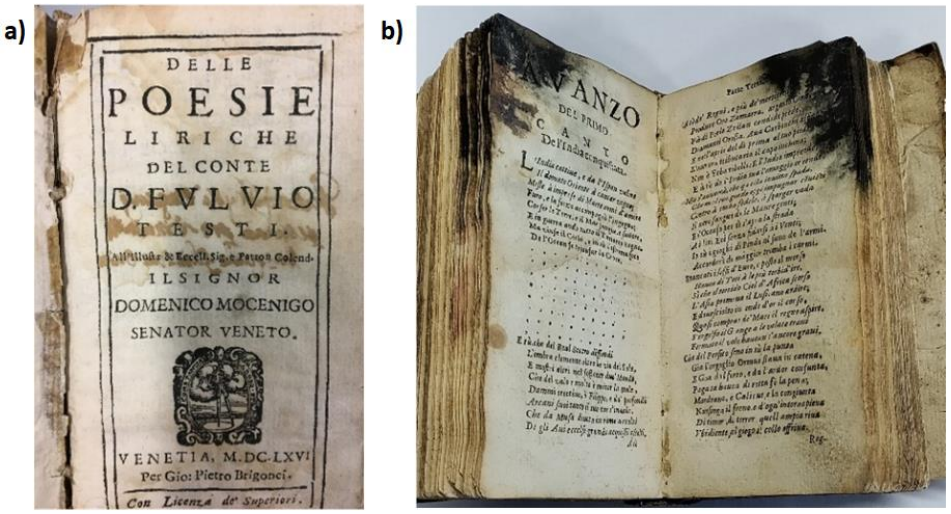

Fig. 1. a) Top page of the 17th century book used for this case study; b) Ink-stain to be removed on several pages.

Experimental part

Materials

17th century Book entitled "Delle Poesie Liriche del conte D. Fulvio" was provided by restorers from "Il Bulino Restauro" (Fig.1).

Nitric acid 68% and hydrogen peroxide 30% were purchased from Romil (Cambridge, UK). Agarose was provided by Sigma. Antirust for cloth "Leva Ruggine (R)" containing among other excipients hydrofluoric acid (HF) < 7% and bleach stain remover "Alba Candegina" containing among other excipients sodium hypochlorite (NaClO) < 5% were purchased in a local houseware store.

Materials and methods

Metals extraction for inductively coupled plasma mass spectrometry (ICP-MS) analysis

About 3x3mm of stained paper sample was excised from a corner of a stained page and from a clean page as a control. The two samples were subjected to mineralization procedure as follows: paper samples were accurately weighed into glass tubes. Concentrated nitric acid (7.0mL) and hydrogen peroxide (1.0mL) were added to each sample. The reaction was conducted for 3.5h at 90°C. After the hydrolysis, the solution was filtered on 0.45µm Millex filter (Millipore, Merck, MA, USA) and diluted to 25mL with milli-Q water. 5mL of the solution was transferred into an ICP-MS vial for the analysis.

ICP-MS analysis

In this case, the technique was performed on an Agilent 7700 ICP-MS instrument (Agilent Technologies Santa Clara, CA, USA) equipped with a frequency-matching radio frequency (RF) generator and 3rd generation Octapole Reaction System (ORS3) operating with helium gas in ORF. The following parameters were used: RF power: 1550W, plasma gas flow: 14L/min; carrier gas flow: 0.99L/min; He gas flow: 4.3mL/min. 103Rh isotope was used as an internal standard (final concentration: 50µg/L). Metals concentrations have been measured with three replicates and the average values were reported in Table 1.

Direct application of cleaning commercial products on paper stained by restorer

5.0mL of “Leva Ruggine(R)” (antirust solution) was directly applied to the surface of one of the ink-stained pages of the book. The excess of product was eliminated after 1 minute. After washing the page with distilled water, 5.0mL of bleach solution were applied for 1 minute. The excess of product was eliminated and the page was washed with distilled water. The procedure was carried out under a chemical hood to avoid exposure to the vapors generated by the mix of the two solutions.

Agarose gel-based approach

The hydrogel was prepared by adding agarose powder (2g) to deionized water (0.1L). The resulting dispersions were heated by microwave oven at 600W until complete hydration. The agarose-based hydrogel (just called gel for simplicity from now on) was cooled down and just before its solidification the antirust solution was added in a ratio gel:antirust 50:50, then 1ml of final gel solution (antirust-gel) was immediately applied for 1 min on stained paper surface with a small brush. The gel was mechanically removed from the surface of the paper with the help of a soft spatula, after which it was rinsed thoroughly with distilled water-gel 50:50. In the same way bleach solution was mixed in gel in a ratio of 50:50 and 1ml of final gel solution (bleach-gel) was applied for 1.0min and easily removed as described before. After careful paper rinsing, these two cleaning steps were repeated twice. Last, the page has been washed with distilled water and left to dry at room temperature.

Scanning Electron Microscopy (SEM) analysis

SEM images, at different magnification, were acquired with a field electron and ion (FEI) Nova NanoSEM450 using an accelerating voltage of 5kV by collecting secondary electrons (SE) with an everhart-thornley detector (ETD) .

Three samples of about 3x3mm of papers were excised from the page treated with chemicals in solution (SEM_Sol), the one treated with agarose-gel solution (SEM_Agarose) and the untreated page (SEM_Ctrl) as control. The samples were coated with a thin layer (5-7nm) of gold-palladium alloy before imaging by using a Denton Vacuum Desk V sputter coater.

Results and discussion

Composition of ink stain by ICP-MS analysis

The composition of inks is variable depending on the historical period and the region of preparation. Inks can be divided in three main groups, carbon-based, metallic-gallic and mixed inks, according to their components [18]. Before carrying out any cleaning procedure on an ink-stained paper artwork, the nature of the ink itself should be thoroughly investigated in order to choose the best cleaning solution. The 17th century book, object of this study, was heavily damaged by ink stains in many pages. As an example, figure 2 shows the ink-stain on one of the pages before any cleaning treatment. To confirm the ink type, a very small portion of the stained page (indicated by the blue box in figure 2) was excised, extracted in acidic conditions and subjected to metal analysis by ICP-MS (see methods paragraph) [19-21].

The metal analysis results are summarized in Table 1. The high concentration of Fe(II) and Cr(II) ions suggest that the nature of the analysed ink stain was type iron-containing chrome-logwood ink [21]. The other metals detected are impurities present in minimum percentage (lower 10% of the total composition) and are commonly found in metallic inks [22, 23]. Fe(II) and Cr(II) cations are only used in the preparation of Gallic inks, when they are stabilized as hardly soluble systems in the form of colloidal microdispersions, and after writing, over time, these cations pass into higher oxidized states, in the form of Fe(III) and Cr(III), very stable, but which creates an acidic environment that affects the paper support, So, the analysis of an old ink, it can contain Fe(II) and Fe(III) in addition to the soluble gel cation, with a conversion rate not easy to determine, for these reasons in table 1 it would be indicated to write Fe(II,III), respectively Cr(II,III).

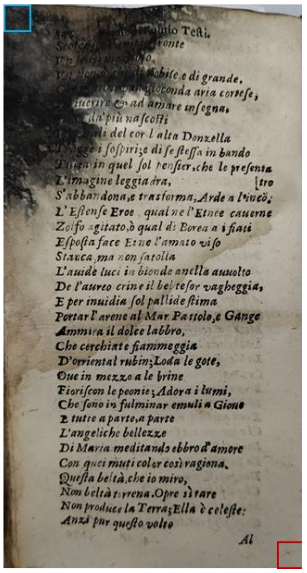

Fig. 1. Ink-stained page without cleaning treatment. The two squares of few millimetres indicated by the blue and red boxes were excised from the book to perform respectively the ICP-MS and SEM analysis.

Table 1. Inkblot metal composition by ICP-MS analysis

Metal	Concentration (µg/L)			RSD %	Percentage (%)
	Rep1	Rep2	Rep3		
Cr(II,III)	1763.00	1917.38	1716.26	1.05	45.7
Fe(II,III)	1587.621	1644.68	1719.102	0.66	42.1
Zn(II)	306.30	298.17	232.35	0.41	7.1
Si(IV)	71.94	74.03	57.55	0.09	1.7
Cd(II)	68.71	70.15	62.77	0.04	1.7
Cu(II)	43.40	43.84	54.75	0.06	1.2
Ni(II)	10.05	10.51	8.81	0.01	0.2
Mn(II)	8.07	8.85	7.92	0.00	0.2
V(V)	1.90	1.91	1.72	0.00	0.1

Once the nature of the ink to be removed was defined, an appropriate procedure for cleaning the stains without damaging the paper was designed. For effective removal of ink stain, two commonly available household products, antirust solution containing hydrofluoric acid (HF <7%) and bleach solution containing sodium hypochlorite (NaClO < 5%) were selected. The reducing acid solution (antirust) would destabilize the iron and chromium complexes whereas the basic solution (bleach) would restore the neutral pH allowing the stain removal from the page.

Ink stain removal by direct application of commercial products

To test the effectiveness of the selected commercial products in cleaning ink spots, a control procedure was carried out by direct application of the products to the surface of the paper as described in the Methods section. The results are shown in figure 3A, in which on the left is shown a reference page (Untreated ctrl), which represents an example of the extent of the stain on all the damaged pages of the book. While figure 3A on the right (Treated_Sol) shows a cleaned page by direct application of selected household products as described in methods section. It is clear that the ink stain has been successfully removed, thus indicating the effectiveness of the commercial products selected for this purpose. However, a simple visual inspection of the paper surface showed that the book was clearly irreversibly damaged with the consistency of the paper significantly degraded to the touch. Moreover, the page number at the

top right was clearly faded. In fact, it is known that oxidation and hydrolysis caused by NaClO and acidic solutions treatment, are the two most common causes of paper degradation [24]. Furthermore, the entire procedure had to be performed in a chemical hood as the mixing of chemicals generated toxic vapors, which are harmful to the environment and the restorers.

Fig. 2. a) On the left the untreated ink-stained page (untreated ctrl) is shown as reference and represent the extent of the stain on all damaged pages. On the right is shown the ink-stained page treated with commercial products by restorer's direct procedure (yreated sol); b) SEM image of the stained paper with chemical in solution (SEM sol) at 200x (upper image) and 500x (lower image) and relative control (SEM ctrl). A few millimetres have been excised (highlighted in red box in figure a) to perform SEM analysis.

A more detailed investigation of paper fiber alteration was performed using scanning electron microscopy (SEM) as described in the methods section. Fig. 3B shows the SEM images of the paper after the direct cleaning procedure (SEM sol) versus the untreated page as control (SEM ctrl). The chemical compounds contained in the commercial products used to remove the ink-stain induced a strong alteration of the morphology of the paper which appears less compact and less homogeneous than that observed in the untreated sample. In Fig. 3B the SEM Sol sample displayed the presence of several voids within the cellulose fibers that are clearly extensively detached from the pulp, confirming the irreversible deterioration of the paper surface. Furthermore, through the direct application of commercial products on the stained page, minimal mixing was inevitable, even if the page was washed with distilled water before applying the second product. Probably the product containing HF (antirust) penetrated

deeply into the paper causing it to accidentally mix with the bleach, thus producing toxic chlorine vapors.

Ink stain removal by agarose gel-based approach

Agarose gel-based methodologies represent a valid approach in the field of artworks conservation as they allow a limited release of the solvent at the interface between the gel and the substrate, limiting the damage to the artwork. Moreover, gel-based methodologies have a high effectiveness on different types of dirt, versatility in removing from different substrates and low cost [25]. In the light of these considerations, a cleaning procedure based on agarose-gel approach was developed. An antirust commercial product was dispersed in agarose gel and applied on the page to be cleaned (see methods section for details). After 1.0min the antirust-gel was easily mechanically removed with a spatula, the page was then treated with a fresh distilled water rinsed gel before the next application of bleach-gel as described in the methods section. Figure 4A shows the result obtained from the cleaning procedure using the agarose gel-based approach; the Treated_Agarose sample is compared with the reference-stained page (untreated ctrl).

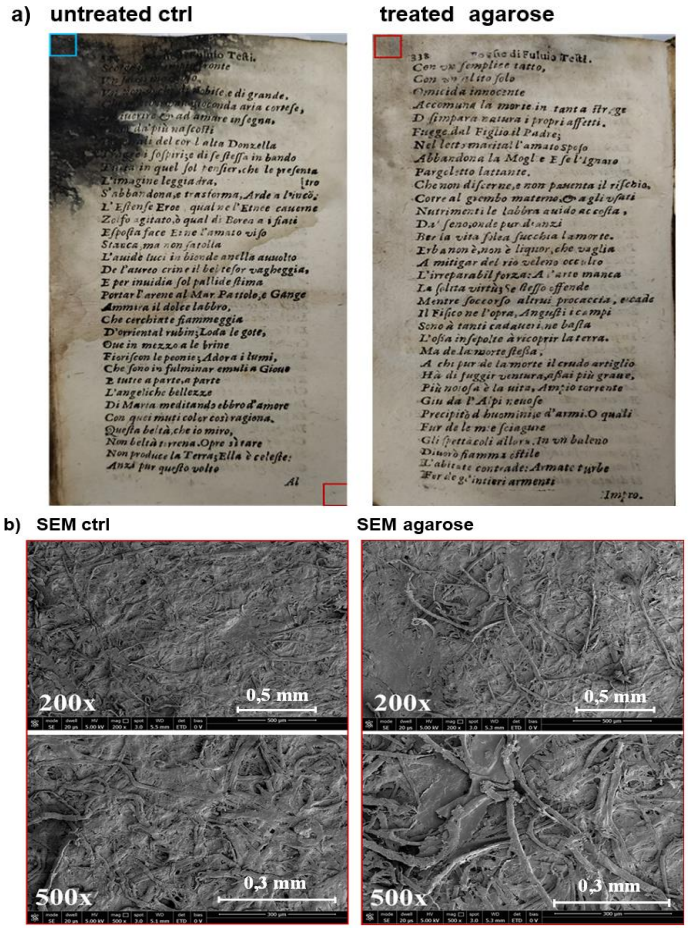

Fig. 3 A) On the left the untreated ink-stained page (untreated ctrl) is shown as reference and represent the extent of the stain on all damaged pages. On the right is shown the ink-stained page treated with agarose gel-based approach (treated agarose). B) On the right is shown the SEM image of the stained paper with agarose gel-based approach (SEM agarose) at 200x (upper image) and 500x (lower image) and relative control (SEM ctrl) on the left panel. A few millimetres have been excised (highlighted in red box in figure A) to perform SEM analysis.

An efficient cleaning of the ink stain was clearly obtained although a much less aggressive approach was adopted.

After gel-based cleaning procedure, the paper does not appear to have sustained structural damage from a visual inspection and the consistency of the paper resulted normal to the touch. These observations were confirmed by the morphological characterization of the treated paper by SEM analyses. The SEM images reported in figure 4B, collected at different magnification, shows the SEM Agarose sample in comparison with the control (untreated ctrl), clearly demonstrating that the agarose gel treatment preserved the nature of the paper structure with the cellulose fibers appearing uniform, homogeneous and compact, confirming the advantages of the "gentle" treatment. The viscosity of the gel prevented the total penetration of chemical substances into the surface of the paper thus avoiding damage to the cellulose fibers.

The use of chemicals in the agarose gel was also effective from the practical and safety points of view as the gel-based method facilitates the complete removal of the acidic reagent (containing in the antirust product) from the surface of the paper before application of the basic reagent (containing in the bleach product), avoiding the mixing of chemicals and thus the production of toxic vapors.

Conclusions

Removing metallic ink stains from paper surface constitute a severe, often impossible challenge for restorers. The use of protocols that use aggressive chemical reagents is commonly avoided as they cause serious damage to the paper structure. In this case study we successfully demonstrated the removal of a wide ink stain from a 17th century book. The proposed procedure, based on the dispersion of commercial products within an agarose gel, produced an effective improvement in cleaning the artwork object of our study under different aspects. The agarose gel-based approach retained the same stain removal efficiency as obtained by the direct application of the commercial cleaning products on the paper. However, the severe alteration of the physical and morphological properties of the paper observed followed the application of the products in solution were avoided. In fact, macroscopic (visual investigation and perceived to the touch) and microscopic investigations (SEM images) of the paper following agarose hydrogel procedure showed respectively a normal texture of the paper to the touch and a more homogeneous distribution of the fibers in the pulp of the paper compared to the treatment in solution. Finally, the application of the agarose gel matrix improves a crucial aspect concerning the reduction of the risk of inhalation of toxic vapors released by the accidental mixing of chemical reagents contained in the commercial products used in this study.

In conclusion, in this study we showed that the approach based on the use of cleaning products already available on the market dispersed in agarose gel was useful to remove the ink stains from the paper surfaces, obtaining a perfect balance between effective cleaning of the pages and preservation of their structural properties with a net reduction of health risks. Furthermore, this methodology is very versatile and could be adopted in future by restorers with any chemical reagent usually needed for the cleaning of artifacts, bringing a clear improvement in the working conditions of the restorer and preserving the artworks from the damage caused by aggressive chemical products.

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Received: February 20, 2024
Accepted: August 15, 2024