Article: It All Comes Out in the Wash . . . or Does It? A Comparative Study of Washing Treatments on a Group of 18th-Century Engravings
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It All Comes Out in the Wash . . . or Does It? A Comparative Study of Washing Treatments on a Group of 18th-Century Engravings

INTRODUCTION

A 33-piece collection of 18th- and 19th-century plates depicting the Slave Coast of Africa was acquired by the African and Middle Eastern Division of the Library of Congress in 2017. The collection comprises Italian, Dutch, French, and English engravings and etchings from contemporary travel books by Moore, Middleton, Marchais, Barbot, Banks, and Smith. The black-and-white prints on antique laid paper were generally in fair to good condition; however, they had localized staining and tide lines, and overall discoloration and localized staining that detracted from the image, as well as tears and losses that needed to be addressed prior to exhibition.

EXPERIMENTAL DESIGN

In consultation with curatorial staff, conservators chose to adopt a multiyear approach to the treatment of the collection and selected a representative set of nine prints for the first phase. Taking into consideration that all of the prints required wet treatment to reduce staining and discoloration prior to exhibition, curatorial and conservation staff decided to treat the collection in phases over several years.

Recently, the paper conservation community has investigated polysaccharide gel treatments, introduced by Italian conservators Sotgiu and Iannuccelli (2010), and pH- and conductivity-adjusted solutions, such as those pioneered by Wolbers (n.d.). Chelators can be incorporated into the adjusted solutions to increase the efficiency of cleaning. Conservators at the Library of Congress have begun investigating the advantages of gels and adjusted chelating solutions in the treatment of items in the library's collections. The planned treatment offered a good opportunity to perform a comparative study of different washing methodologies. For this project, the research team chose to compare three washing techniques: (1) on a rigid polysaccharide gel, (2) in adjusted chelating solutions, and (3) by traditional immersion in pH-adjusted water. The set of 9 prints was divided into groupings of three that were similar in condition and appearance (fig. 1). Each print within each group was assigned one of the three different washing methods. The goal was to evaluate and compare the methods, based on change in the appearance of the prints after treatment, ease of use, and time involved for each treatment protocol. In addition, if one method consistently outperformed the others, in terms of the preceding criteria, the team would consider applying this "best" protocol for treatment of the other 24 prints in the collection.

Digital photodocumentation of the prints in normal and raking illumination and UVA-induced visible (UV-vis) fluorescence was completed before, during, and after treatment. Consistency in capture and processing of digital documentation photographs was identified as crucial from the beginning. Images of the three print groups were captured in the same shot to limit variables of lighting and relative placement. Standardized practices for processing those images were followed carefully. However, assessing treatment changes using photographs of nearly white paper is often difficult, especially if changes are subtle, making visual assessment somewhat subjective.

Quantification of color difference is important for any color-based research. To obtain objective, measurable data on the colorimetry of our prints, CIELAB brightness measurements were taken with a Brightimeter and compared with reflectance spectroscopy color measurements using a fiber optic spectrometer. TAPPI standards for measuring brightness specify the use of a Brightimeter. Brightimeter measurements typically require weighting objects to improve conditions of measurement through full, even contact of the instrument with the object. Fiber optic reflectance spectrometry (FORS) presented an alternative to Brightimeter readings because it offers a noncontact, noninvasive method of gathering color values. FORS gathers spectra from 350 to 2500 nm, offering the opportunity to observe the effects of washing treatments in the full range of the spectrum, from UV to infrared.

Several randomly selected prints were measured with both the Brightimeter and FORS. Consistency in color

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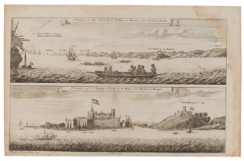
	Rigid Gel	Adjusted Chelating Solutions	Conditioned Water
Group 1	1.1  "Africa"	1.2  "Plan of James Island in the Gambia, 1732"	1.3  "Negro Women in different dresses"
Group 2	2.1  "Animals and Birds of Africa"	2.2  "Cape de Verde Camels and Lions of Africa"	2.3  "A Pholey Town"
Group 3	3.1  "Prospect of the European Factories at Xavier"	3.2  "Prospect of the Coast from El Mina to Mowri"	3.3  "Procession to the temple of the Great Snake"

Fig. 1. Assignment of prints to groups and methods.

measurements was ensured with overlay templates, created by punching 9-mm-diameter holes in translucent paper with an arch punch. During the Brightimeter measurements, the sheet was positioned on the instrument recto side up, with a light weight to ensure good contact (fig. 2). During the FORS measurements, all spectra were normalized to a white standard. The measurement probe was fixed and the print was positioned beneath it, so there was no contact between the probe and the print (fig. 3). The readings taken with the Brightimeter and with the FORS were found to be within comparable range, so the FORS data were used for the remainder of the study. Nine readings were taken from each print: three from blank areas in the image, three from the more discolored margins of the print, and three from the verso. The readings were averaged together to obtain a more representative value for each print.

Fig. 2. Brightimeter measurement of Print 2.2.

TREATMENT

Prior to treatment, the prints were surface cleaned, the paper was tested for permeability with water, and the printing ink was tested for friability and solubility in ethanol and water. All nine prints were humidified in Gore-Tex envelopes for 1 hour to 1 hour 30 minutes and misted recto and verso with a 50:50 mixture of ethanol and deionized water prior to washing.

RIGID POLYSACCHARIDE GEL PROCEDURE

Preparation of Cast Sheets of 2% Gellan Gum

To make an evenly dispersed, fairly thick gel, 20g of gellan gum powder was slowly stirred into 1 L of a 0.4-g/L calcium acetate solution. The solution was cooked in an 1100-watt microwave on the highest power for successive short intervals. A silicone floppy lid was used to contain the hot solution in the glass beaker during cooking. After each interval, the oven door was opened to observe the solution. By the end of the final interval, the solution was bubbling from the bottom of the beaker. The solution was poured into an aluminum half-sheet pan, on a level surface, to cool. The gel cooled completely in about 15 minutes. To remove the gel from the casting pan, the edges were loosened with a nonstick spatula. Polyester film and a rigid board, cut to the size of the gel sheet, were placed on the top of the gel, then the gel was flipped out of the casting pan. A layer of lightweight *hanji* (Korean handmade paper) was selected to act as a barrier layer between the print and the gel surface in this washing method. Because the paper does not have a strong grain direction, it was expected to expand evenly when wetted out.

Washing on 2% Gellan Gum

The three prints selected for gel washing and their barrier papers were humidified together and wet out separately. The barrier paper was brushed onto the gel and then the print was placed on top of the *hanji*, recto facing up. Transparent

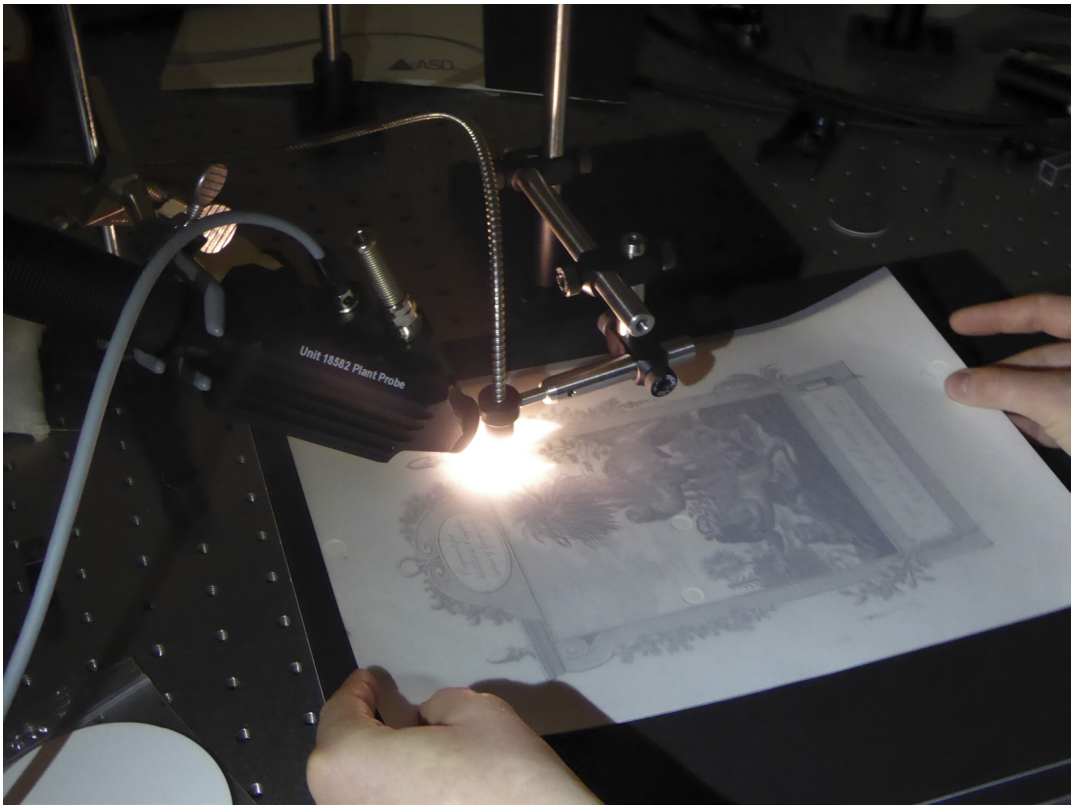


Fig. 3. FORS measurement of Print 2.2.

polyester film was placed on the print, and the package was lightly brushed to ensure good contact between the print, the barrier paper, and the gel. Two felts were placed on top of the gel/print package to provide light, even weight across the surface. The package was checked at intervals to monitor the progress of washing.

For the first print washed, the gel was noticeably discolored in the contact area after 2 hours. The print was placed on a fresh gel sheet, without a barrier layer, for an additional 1 hour 15 minutes. No discoloration was observed in the second gel sheet, so the print was removed and placed between polyester web and felts to dry. The second gel sheet seemed unnecessary, so the remaining two prints were washed on only one gel sheet, but otherwise the procedure was the same as that for the first print.

The gel sheets were examined after the washing and found to be quite yellow. Under UVA radiation, areas of discoloration products, a ghost image of the print, and the laid and chain lines of the paper were visible (fig. 4). A cross section of the gel used to wash Print 1.1 demonstrated that the products from the more degraded areas penetrated deeper into the gel, mainly in a vertical direction (fig. 5).

ADJUSTED CHELATING SOLUTION PROCEDURE

Preparation of Solutions and Agarose Plugs for Testing

Richard Wolbers developed treatment protocols using the principles of conductivity, pH, and chelation to clean paintings, and recently began applying the methods to works on paper. The protocols are based on (1) measuring the pH and conductivity of the paper requiring treatment by using agarose plugs and (2) determining the most effective of six cleaning solutions to use for treatment by comparing the results of local application of solution-infused agarose plugs.

For testing purposes, 100 mL each of six different adjusted chelating solutions were prepared according to recipes from Wolbers (fig. 6). A 4% w/v agarose sheet was prepared by adding agarose powder slowly to deionized water, then heating to 198°F while stirring constantly. The resulting solution was poured into a sterilized petri dish to set. Plugs were punched from the agarose sheet with a 4-mm dermal punch, cleaned after each use with ethanol. The punched plugs were infused in the adjusted chelating solutions overnight.

Fig. 4. Gel sheet used to wash Print 1.1 under UVA radiation (left) with Print 1.1 after treatment (right).

Measuring pH and Conductivity with Agarose Plugs

Blank agarose plugs were placed on three areas of each print to determine the pH and conductivity of the paper. All plugs were handled with sterilized plastic tweezers and were blotted first onto filter paper to remove excess moisture. Once placed on the print, the plugs were covered with polyester film to prevent drying. The plugs remained in place for 5 minutes and were then placed on the sensors of the pH and conductivity meters to obtain measurements.

Stained areas outside of the plate mark on each print were identified to test with the six solution-infused plugs. Considering that Prints 1.2 and 3.2 had significant staining, additional areas within the stains were tested as well. After 5 minutes in contact with the prints, the plugs were tested for conductivity and pH. When dry, test areas were examined and documented in both normal illumination and longwave UV (365 nm). Based on the results of the tests, solution D was selected for Prints 3.2 and 1.2, whereas solution C was selected for Print 2.2. In each case, these solutions cleaned the staining and discoloration more effectively than the others.

Calculation for Preparing the Bath

The following are steps for calculating the solutions for the adjusted baths:

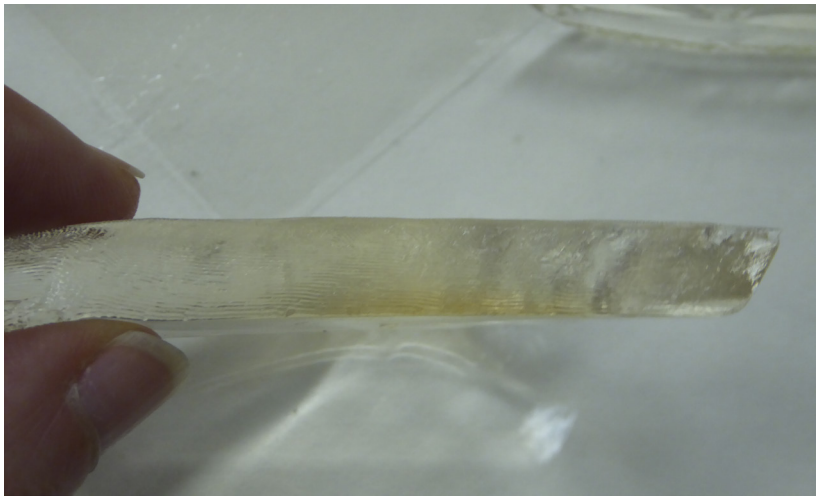


Fig. 5. Cross section of gel sheet used to wash Print 1.1. The bottom edge was the side in contact with the print.

Adjusted Chelating Solutions	Recipe
Solution A	100ml H_2O (distilled) 0.5g Citric Acid Adjust pH to 6.0 with 50% w/v 1M NaOH solution
Solution B	100ml H_2O (distilled) 0.5g Citric Acid 0.5g Tetrasodium Borate Adjust pH to 8.0 with 50% w/v 1M NaOH solution
Solution C	100ml H_2O (distilled) 0.5g DTPA (diethylenetriamine pentaacetic acid) 0.5g Citric Acid Adjust pH to 6.0 with 50% w/v 1M NaOH solution
Solution D	100ml H_2O (distilled) 0.5g DTPA 0.5g Tetrasodium Borate Adjust pH to 8.0 with 50% w/v 1M NaOH solution
Solution E	100ml H_2O (distilled) 0.5g Disodium EDTA (ethylenediaminetetraacetic acid) 0.5g Citric Acid Adjust pH to 6.0 with 50% w/v 1M NaOH solution
Solution F	100ml H_2O (distilled) 0.5g Disodium EDTA 0.5g Tetrasodium Borate Adjust pH to 8.0 with 50% w/v 1M NaOH solution

Fig. 6. Adjusted chelating solutions.

1. Determine the average conductivity of the paper.
2. Measure the conductivity of the solution that is most effective for cleaning the paper.
3. Divide the conductivity of the adjusted chelating solution by the average conductivity of the paper.
4. The resulting number, plus 1, is the total parts of the treatment solution.
5. Divide 1000 mL by the total parts of solution to determine the isotonic value for the paper.
6. For a hypertonic solution, multiply the isotonic value by 5 to 10. Wolbers recommends no more than 10x.
7. The resulting number is the milliliters of solution per liter for the washing treatment.
8. Using the total volume of each bath, as well as the number of baths anticipated, determine the amounts of adjusted chelating solution and deionized water needed to prepare washing baths.

Sample calculation:

Average conductivity of Print 3.2 300 μS
Conductivity of Solution D 2800 μS
2800 μS / 300 μS = 9.3
9:1 = 10 parts
1000 mL/10 parts = 100 mL/L (isotonic value)
100 mL × 5 (hypertonic) = 500 mL of solution D per 1 L
(500 mL of solution D + 500 mL of deionized water = 1 L of washing bath)
2 L bath × 2 baths = 4 L total
Needed = 2 L solution D and 2 L of deionized water

The same method of calculation was used to determine that 555 mL of solution D per liter of wash bath volume were needed for Print 1.2. Because of the similarity in the calculated values for Prints 1.2 and 3.2, the values were adjusted slightly to increase the efficiency of treatment by washing both prints in the same bath.

Washing in Adjusted Chelating Solutions

Print 2.2 was washed in three successive 20-minute baths of solution C (a mixture of water, diethylenetriamine pentacetic acid, and citric acid adjusted to pH 6) until no discoloration remained in the wash water. It was rinsed in a bath of deionized water adjusted to pH 6 with calcium hydroxide, then in a second bath adjusted to pH 7.5. Wolbers recommends rinsing in calcium acetate. Future treatments at the library will follow his methodology.

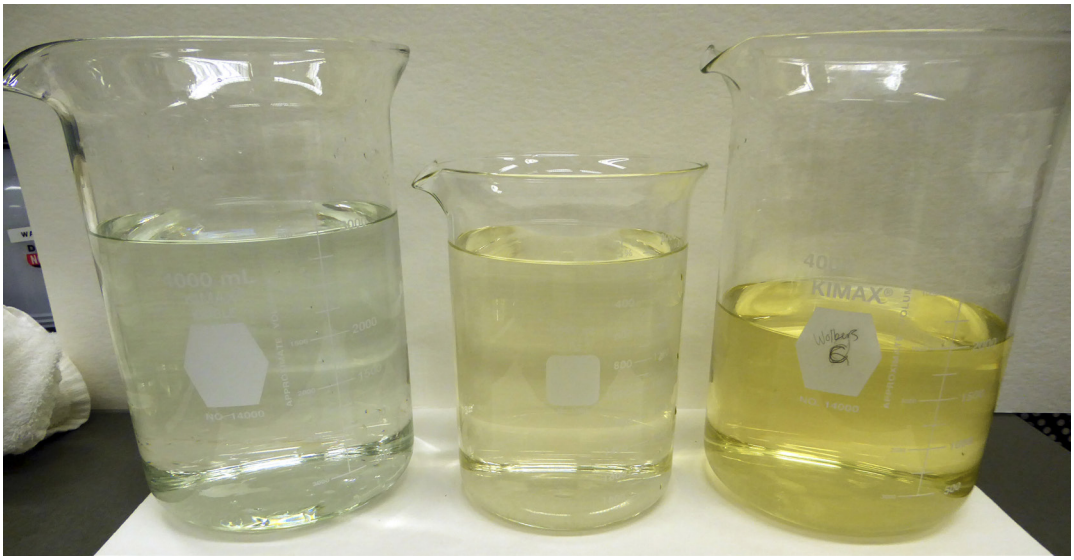


Fig. 7. Water collected from Solution D bath (right), first rinse bath (center), and second rinse bath (left).

Prints 1.2 and 3.2 were washed together in two successive 20-minute baths of solution D (a mixture of water, diethylenetriamine pentacetic acid, and tetrasodium borate adjusted to pH 8). Although slight discoloration remained in the water after the second bath, it was decided to move the prints to a rinse bath of pH 7.2 due to the alkalinity of the solution relative to the starting pH of the prints. A second rinse bath of pH 7 followed the first. Discoloration was visible in the water collected from the successive treatment baths (fig. 7). All three prints were removed from the baths, blotted, and placed between polyester web and felts to dry.

TRADITIONAL IMMERSION WASHING PROCEDURE

Deionized water adjusted to pH 7.5 with saturated calcium hydroxide solution was prepared, and the prints were washed in three successive 2 L baths for 20 minutes. As no discoloration was visible in the last bath, the prints were removed, blotted, and placed between polyester web and felts to dry.

RESULTS

After treatment, the set of nine prints improved in visual appearance: overall discoloration and localized staining were noticeably reduced (fig. 8). This was due to the removal of water-soluble degradation products and may include some loss of sizing. Gelatin sizing has a yellow fluorescence response when irradiated with UVA. The UV-vis photographs taken before treatment show yellow fluorescence, which is absent after treatment, and may indicate that sizing was removed during treatment.

Within each group of prints that were treated with the three different washing methodologies, perceivable visual differences were subtle. This was expected and indicated the necessity for objective color measurements of the papers to determine if any observable trends were present.

The visual differences are corroborated by color data collected using FORS. The total color change, or the ΔE, was calculated using the CIE2000 equation. ΔE values less than 1 represent changes in color that are considered imperceptible to the human eye. Values between 1 and 2 can be picked up by a discerning eye, and values above 2 are perceived as a noticeable change in color. All of the treated prints have ΔE values greater than 2. The ΔE values within each washing method vary considerably, but within each print group, the results are comparable. Recalling that the prints were grouped according to similarity of condition becomes helpful when comparing the performance of each washing method on prints in the same group. Occasionally, one method performs better within a group, but no methodology stands out as superior overall.

Most conservators are familiar with the shift in paper tone that can occur after an aqueous treatment. The study also considered specific color shifts, along the L* a* b* axes for each washing method. After treatment, the a* measurements shifted slightly away from red and toward green, and the b* measurements shifted away from yellow and toward blue.

All L* values increased along the L* axis or became whiter. The increase in luminance is replicated in the shift in the reflectance spectra of the paper captured with FORS (fig. 9). The spectrum is representative of the majority of prints in the set. The shift higher on the graph indicates an increase in reflectance after washing, which corresponds with the visually discernible lightening usually observed in the paper.

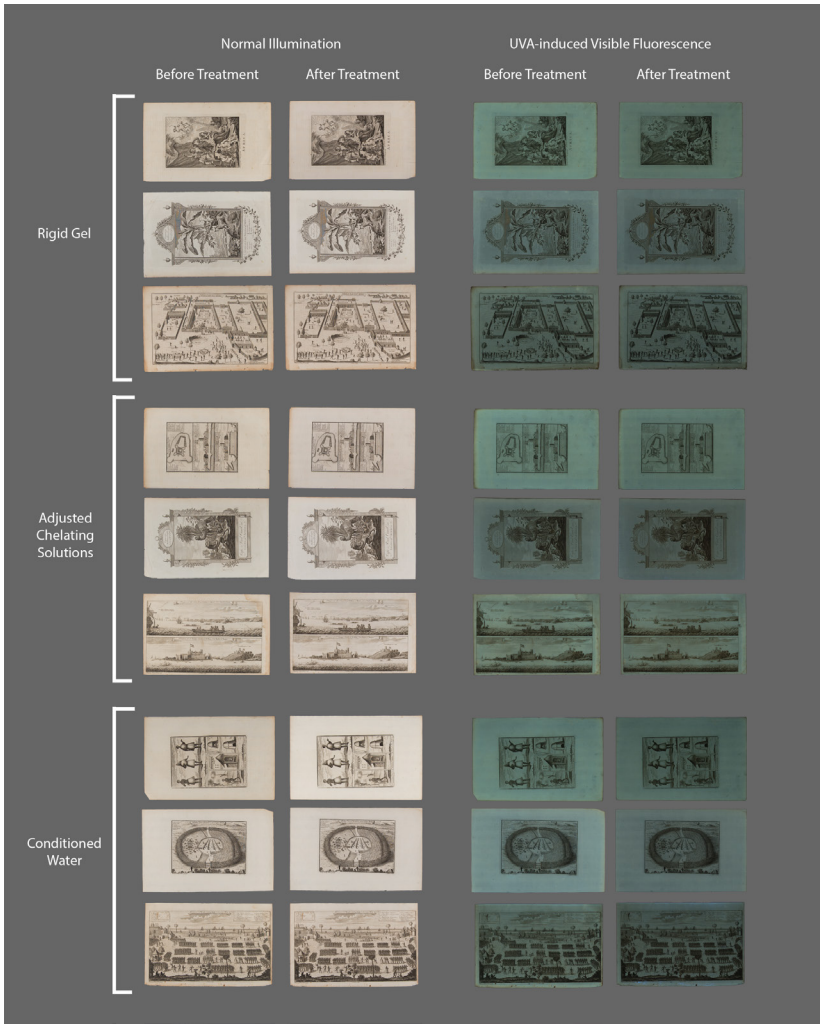


Fig. 8. All prints before and after treatment in normal illumination and UV-vis fluorescence.

All of the prints had increased luminance after treatment. At first glance, the results within each method seem quite variable, as one might expect for different papers. However, similarities within each grouping of prints were also noted. Group 1 prints showed the smallest variation in ΔE values for all areas of the papers, and the measurements are most consistent across all of the treatment methods compared with Groups 2 and 3. Group 2 readings indicate that in three out of four paper locations, the adjusted chelating solution method resulted in higher ΔE, correlating to more brightening as a result of the treatment. In Group 3, the results are the opposite of Group 2, with rigid gel and traditional immersion washing yielding significantly higher values than the adjusted chelating solutions. The reason for the differences between the prints in Groups 2 and 3 is not clear.

Testing the paper with agarose plugs, both for pH and conductivity measurements of the paper and for determining the most effective adjusted chelating solution, resulted in visible tide lines that appeared as yellow fluorescence in UV

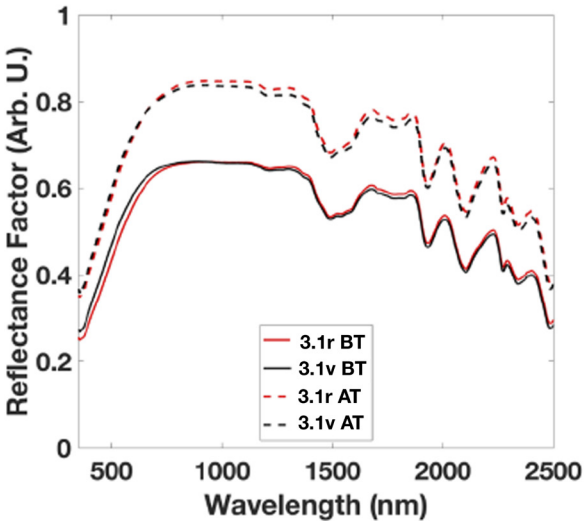


Fig. 9. Representative FORS spectrum of Print 3.1.

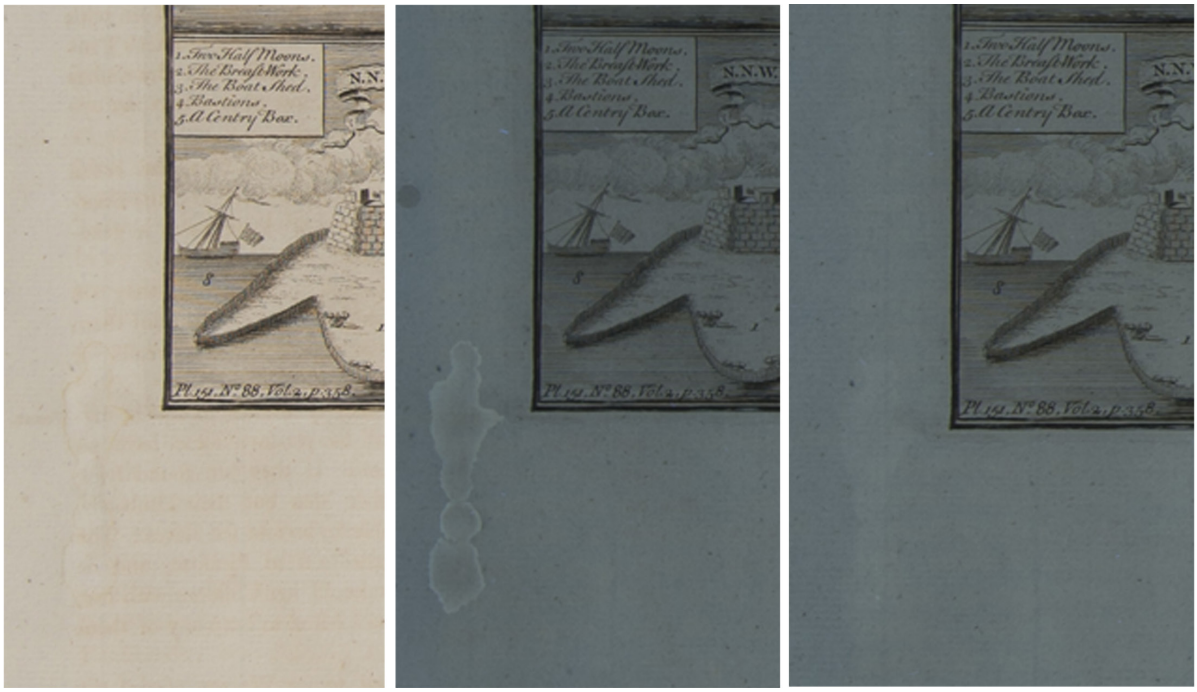


Fig. 10. Left to right: Area of testing under normal illumination after testing, UV-vis fluorescence after testing, and UV-vis fluorescence after treatment.

radiation (fig. 10). The test-induced tide lines continued to fluoresce after treatment, although they were much reduced.

CONCLUSION

Based on this study, FORS is a viable noninvasive, noncontact colorimetry method for paper, comparable with results obtained by a Brightimeter. All three washing methods are effective in improving paper brightness, and one technique may be more effective than another, depending on the paper properties and condition. Compared with traditional immersion washing, the methods of capillary washing on a rigid polysaccharide gel or in an adjusted chelating solution are significantly more time consuming and require considerably more materials and equipment.

Making a rigid gel is not difficult, but familiarity with the cooking power of the microwave is helpful. Once the gel is made up, this method of washing is fairly straightforward. The gel sheets can be prepared in advance but should be checked for microbial growth before use. A longwave UV light source may be helpful in checking gel sheets for fluorescence indicative of some types of mold. Considering that there are no baths of water to pH adjust, this method does not require the use of a sink. The size of the artwork is a consideration and may be a limiting factor.

Washing by immersion in adjusted chelating solutions requires more time and materials than the other two methods. Each test solution must be prepared and adjusted to the correct pH, agarose plugs must be prepared and infused overnight, and, after testing has occurred, the treatment bath must be calculated and prepared. Safe handling, storage, and disposal of some chemical components of the solutions is a consideration. The post-treatment tide lines and fluorescence associated with testing sites for adjusted chelating solutions warrant more investigation as they relate to long-term differential aging of the paper substrate.

The benefits and drawbacks of each washing method become important when only subtle differences are achieved. In some circumstances, the gel or adjusted chelating solution methods may be worth the extra resources, such as for sensitive media and/or delicate paper that cannot be immersed or washed on a suction table, or for staining that includes tide lines.

This study is preliminary, with the limitation imposed by variability in each historical print and does not allow for true comparison between them. A follow-up study of washing methodologies might include only one type of paper.

ACKNOWLEDGMENTS

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FURTHER READING

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SOURCES OF MATERIALS

Chartham Translucent Paper
Hollinger Metal Edge
9401 Northeast Dr.
Fredericksburg, VA 22408
800-634-0491

Brightimeter Micro S-5
Technidyne
100 Quality Ave.
New Albany, NY 47150
812-948-2884

Fiber Optic Reflectance Spectrometer (FORS): FieldSpec4
Malvern Panalytical
Grovewood Rd.
Malvern, WR14 IXZ
United Kingdom

pH and Conductivity Meters: LAQUAtwin pH Model B713; SO10 and LAQUAtwin Conductivity Model B-771; SO70
Horiba
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Clifton Park, NY 12065
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Vinyl Eraser, Grated
William Minter Bookbinding
4364 Woodbury Pike
Woodbury, PA 16695

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CP Kelco US, Inc.
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Calcium Acetate, Calcium Oxide
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81 Wyman St.
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Silicone Floppy Lid (Charles Viancin)
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1101 S. Joyce St., Ste. B-20
Arlington, VA 22202
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Aluminum Half-Sheet Pan (interior surface 16.25 × 11.25 × 1 in.)
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Hanji (Korean handmade paper, *cham dak* fiber, 2005, 14 g^2, wooden drying boards)
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