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New Approaches to Cleaning Works of Art on Paper and Photographs

ABSTRACT

During the Fall 2013 semester, second-year graduate students in the Winterthur/University of Delaware Program in Art Conservation completed a course entitled "Conservation Cleaning Methods" led by Professor Richard Wolbers. This course explored approaches to controlled cleaning of works of art and artifacts using gels, microemulsions, and silicone solvents, as well as the optimization of aqueous cleaning systems through pH-adjustment and the addition of chelators, enzymes, and surfactants. This paper discusses two studies undertaken by students specializing in the conservation of works on paper and photographic materials as an extension of this course and in collaboration with scientists and conservators at the Winterthur Museum, Garden & Library to address specific problems within their disciplines.

The first study explored the reduction of foxing stains in paper-based materials utilizing a combined chelator-enzyme solution delivered locally using rigid gels. As the exact nature of foxing remains an area of debate among conservators and scientists, students first demonstrated that the phenomenon related to both metal oxidation and biological growth in paper samples used in this experiment. Foxed samples were subjected to a histological staining protocol to confirm the presence of fungi, and x-ray fluorescence spectroscopy (XRF) was performed to determine the relative metal concentration in affected areas. With the source of foxing established, an experiment was devised to explore the combined and independent treatment effects of the chelator hydroxybenzyl ethylenediamine (HBED), the enzyme chitinase, and the rigid agarose gel. The contribution of each to stain reduction was assessed using colorimetry, semi-quantitative XRF, and visible and ultraviolet photography. The preliminary data collected indicates both the chelator *and* enzyme contribute to improved foxing reduction. This gel-based delivery system, while still experimental, is promising as an effective stain reduction treatment for severely foxed works of art on paper.

The second study explored the use of a silicone solvent to protect the surface of cyanotypes during local gel-based cleaning and as a method for reducing sooty surface grime on the emulsion of fiber-base, gelatin silver developed-out photographs. While silicone solvents have been used successfully in art conservation to protect porous architectural materials during

treatment and consolidation, there are few published findings regarding their use in paper and photograph conservation. The first goal of this study was to determine the residency time of octamethylcyclotetrasiloxane solvent, also known as D4 silicone solvent, in cyanotypes and fiber-base, gelatin silver prints using gas chromatography-mass spectrometry (GC/MS) on expendable samples of photographic papers. The GC/MS results demonstrated that after a 24-hour period, the silicone solvent reaches an undetectable level in the cyanotype paper and is recorded as less than one part per million (0.0001%) in the fiber-base, gelatin silver paper. Results from subsequent cleaning tests showed that D4 was effective in minimizing the formation of visible tidelines on cyanotypes during local gel-based cleaning, and effective in reducing sooty surface grime on the emulsion of fiber-base, gelatin silver prints while minimizing swelling and surface-related damage.

1. INTRODUCTION

During the Fall 2013 semester, second-year graduate fellows in the Winterthur/University of Delaware Program in Art Conservation (WUDPAC) completed an elective course on the cleaning fine art surfaces taught by Richard Wolbers. This course was open to students of all specializations and focused on two fundamental concepts: (1) modification of aqueous solutions to optimize cleaning and (2) controlled delivery of aqueous solutions and solvents during conservation treatment.

Students investigated pH adjustment as well as the addition of chelators, enzymes, and surfactants to modify aqueous cleaning systems. Controlled delivery of cleaning solutions with gels and emulsions was also explored in the context of treating works with sensitive media, minimizing surface manipulation, and reagent clearance. As a product of the course, each student also prepared a cleaning test kit for future use.

While the approaches explored in the cleaning course are regularly applied to the conservation of painted surfaces and objects, their use within paper and photograph conservation is more limited. With half of the students enrolled in the course specializing in the conservation of paper, books,

and photographic materials, there was great opportunity to apply these methodologies to problems specific to these materials and investigate new approaches to their treatment.

This paper discusses the results of two treatment-based experiments undertaken as an extension of this course. The first experiment explores the reduction of foxing stains in paper-based supports with a modified aqueous solution delivered in a rigid gel. The second reviews the use of the silicone solvent D4 as both a volatile masking agent and cleaning solvent in the treatment of photographic prints.

2. INVESTIGATION OF FOXING REDUCTION IN WORKS ON PAPER WITH ENZYMES AND CHELATORS IN AGAROSE GELS

2.1 THE PROBLEM OF FOXING

Foxing is a prevalent problem for paper-based materials in museums, libraries, and private collections; however, the cause of these irregular, rust-colored stains remains an area of debate among conservators. These stains usually appear as a cluster of circular or "snowflake"-shaped brown spots. While some attribute foxing to pigmented compounds associated with fungi and their metabolic processes (Florian 2002), others cite the oxidation of metal particles (Rebrikova and Manturovskaya 2000). Still others believe foxing is a combination of the two (Choi 2007). Both fungal spores and metal inclusions may be inherent to a sheet of paper from its manufacture or introduced at a later date from its surrounding environment. Regardless of source, cellulose in foxed areas exhibits a higher degree of oxidation, lower pH, and greater autofluorescence than unfoxed areas (Bicchieri et al 2001). Traditional approaches to foxing reduction include light bleaching and chemical bleaches such as sodium borohydride and hydrogen peroxide. Experimental treatments involving the use of organic solvents, chelators, enzymes, and lasers are also documented in the literature (Choi 2007; Florian and Purinton 1995; Szczepanowska and Lovett 1992; Szczepanowska and Moomaw. 1994).

2.2 EXPERIMENTAL DESIGN

With this understanding of potential sources of foxing and the history of its treatment in mind, an experiment was designed with the following goals:

- Characterize foxing as a phenomenon related to both biological growth and metal oxidation
- Develop a targeted treatment using an enzyme and chelator to address the fungal and metallic components respectively
- Evaluate the efficacy of this two-pronged approach by comparing the independent and combined effects each reagent.

In this experiment, naturally foxed samples were obtained from adjacent sheets in a mid-19th century book donated to the conservation program for student experiments. The paper is primarily comprised of cotton and bast fibers with a light gelatin size.[1] Chosen for similar foxing damage and for as consistent manufacture as possible, eight adjacent pages were removed from the book for the experiment.

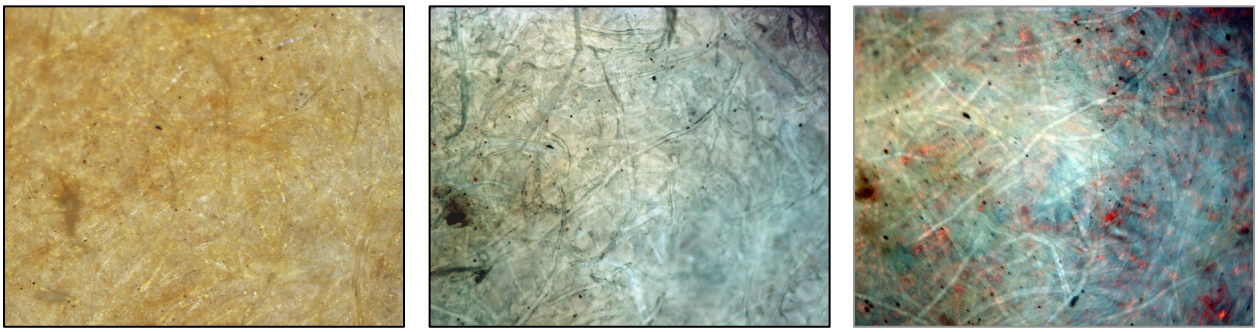
2.2.1 Characterization of Foxing

A fluorescent staining protocol was used to establish the biological component of the foxing present in the paper samples selected for the experiment. A conjugate of wheat germ agglutinin (WGA)-Texas Red® dye was applied to 4-mm punches taken from homogenously foxed areas of the paper samples and mounted to a glass slide.[2] Wheat germ agglutinin is a molecular probe with a strong affinity for chitin, the primary component of fungal cell walls. As this attachment alone does not produce a visible indicator, WGA is typically coupled with a histological stain that fluoresces when exposed to a specific range of electromagnetic radiation. In this experiment, WGA was coupled with the dye Texas Red® and applied in a 1:8 dilution with phosphate buffered saline (PBS) to saturate the samples. Excess conjugate dye solution was wicked away from the samples using a square of blotter. The dye conjugate remained on the

[1] Polarized light microscopy (PLM) was performed to determine the fiber content of the foxed samples. Microchemical spot testing with ninyhdrin yielded a positive result for proteinaceous sizing.
[2] Beva® 371 film was used to mount the punches to a glass microscope slide for staining. The adhesive was activated with gentle heat from a hot plate.

samples for 10 minutes in the dark to prevent degradation of the Texas Red® chromophore. Four rinses of additional PBS were applied the samples to clear any unreacted material.

The stained foxing samples were viewed at 100x using a Nikon Eclipse 80i Normal Light View microscope with Nikon Excite 120 Mercury Lamp and with a Nikon BV-2A Cube (EX 400-440, BA 470nm) engaged. Images were captured using Nikon Act I imaging software. As Texas Red® is excited at ~595nm and emits at 615nm, fluorescence resonance energy transfer (FRET) was used to excite the dye when exposed to near-ultraviolet radiation (400-440nm) and highlight areas where chitin components are located (Life Technologies 2014). In figure 3, red fluorescence confirms the presence of chitin and fungal material in the foxed areas tested.



Figs. 1-3. Foxed sample observed at 100× with Nikon Eclipse 80i fluorescent microscope under visible light (left), near ultraviolet light (center), and near ultraviolet light with wheat germ agglutinin-Texas Red dye conjugate applied (right). Courtesy of Richard Wolbers.

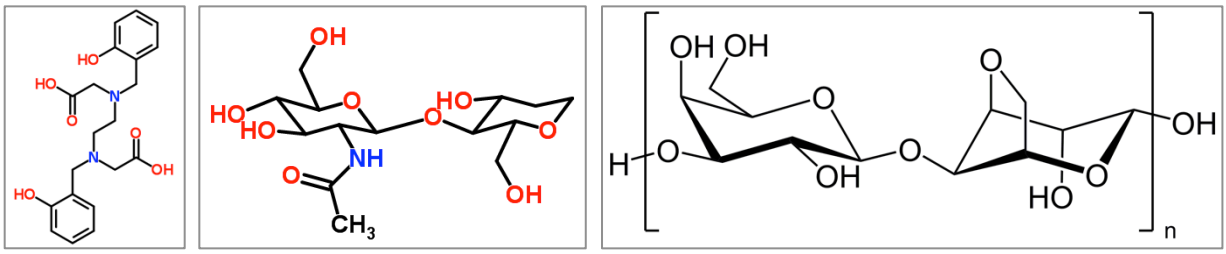
To determine the contribution of metal oxidation to the foxing present, semi-quantitative x-ray fluorescence (XRF) spectroscopy was performed. XRF analysis was performed using a handheld Bruker Tracer III-SD XRF spectrometer with a rhodium tube. The spectrometer has an oblong spot size measuring 0.5cm × 1cm and was fitted with a 25µm Ti/305µm Al filter. The spectrometer was operated at 40 kV high voltage; 9.6 µA anode current; and 60 seconds live time irradiation.

The data collected with the handheld spectrometer was imported into ArtTAX (v.7.5.2.0) software to plot and overlay spectra. By overlaying spectra for foxed and unfoxed areas of a

single sheet, discrepancies in metal concentration were illuminated. In every case, a higher concentration of iron was observed in the foxed areas versus unfoxed areas (fig. 10).

2.2.2 Experimental Enzyme-chelator Gel Treatment

With the presence of fungal material and higher iron concentration established, a targeted treatment was developed to address both factors contributing to the foxing observed in the samples selected for this experiment. The targeted treatment entailed the use of a chelator and an enzyme to address the metal and biological components of the foxing respectively. The chelator and enzyme are prepared in a buffered solution and delivered in a rigid polysaccharide gel block.



Figs. 4-6. Molecular structure of HBED (left); chitin (center); and agarose monomer (right). Courtesy of Wikimedia Commons.

The chelator selected is a N,N'-Di(2-hydroxybenzyl) ethylenediamine-N,N'-diacetic acid, commonly known as HBED (fig. 6). HBED is a potent chelator for iron (III) and other trivalent metal cations, forming highly stable, water-soluble complexes that are readily removed from paper supports. The complex formed between iron (III) and HBED has an exceptionally high stability constant (39.01), remains stable over a broad pH range, and exhibits a distinctive pink color that serves as a convenient indicator for successful iron chelation (Ma et al 1994). HBED also exhibits an additional antioxidant property. Upon binding with HBED, iron (II) is readily oxidized to the extremely stable iron (III)-HBED complex. By chelating iron (II) and facilitating its oxidation to iron (III), HBED halts the Haber Weiss reaction[3] (Samuni et al. 2001).

[3] The Haber Weiss reaction is a redox cycle between iron (II) and iron (III) cations that results in the formation of free hydroxyl radicals that accelerate the oxidative degradation of cellulose. This phenomenon is familiar to conservators from iron gall ink deterioration.

The enzyme selected is chitinase (EC 3.2.1.14). Chitinase is a highly specific enzyme that catalyzes the hydrolysis of chitin, a water-insoluble polysaccharide that makes up the cell walls of fungi (fig 5). This hydrolysis proceeds by cleaving the 1,4-β glycosidic bonds in chitin. While chitin itself is not colored, pigmented compounds including melanins and cartenoids are contained within fungal cell walls and their removal is facilitated by enzymatically breaking down these cellular structures (Singh et al. 2007).

The enzyme-chelator solution is delivered locally to foxed areas in a rigid gel block of agarose (fig. 6). Derived from seaweed, agarose is a purified, polysaccharide polymer that forms a rigid gel. Agarose has been used in art conservation as a poultice material and, as in this study, a means to deliver aqueous solutions and enzymes (Warda et al. 2007; Van Dyke 2004). It was selected for this treatment for several reasons:

- Minimize surface manipulation that can occur with brush application of solutions
- Reduce the quantities of chelator and enzyme needed for effective treatment
- Increase contact time between reagents and foxed areas
- Utilize capillary action of the gel to extract discolored materials rather than drive them through the support.

To evaluate the efficacy of the targeted treatment, an experiment was designed to compare the independent and combined effects of the enzyme, chelator, and gel-delivery system. In addition to the enzyme-chelator—or "hybrid"—gel, three additional gels were prepared: a blank gel with deionized water; a gel that contained only the chelator HBED; and a gel that contained only the enzyme chitinase. These four gels were compared to a direct application of the enzyme-chelator solution by micropipette and a control. Three foxed areas were selected for treatment on each sample.

To determine the effect of treatment duration, each of the five variants was tested at three different time intervals—60 minutes, 90 minutes, and 120 minutes. Including a control that was blotter-washed for 3 hours, this resulted in a total of 16 samples (fig. 7).

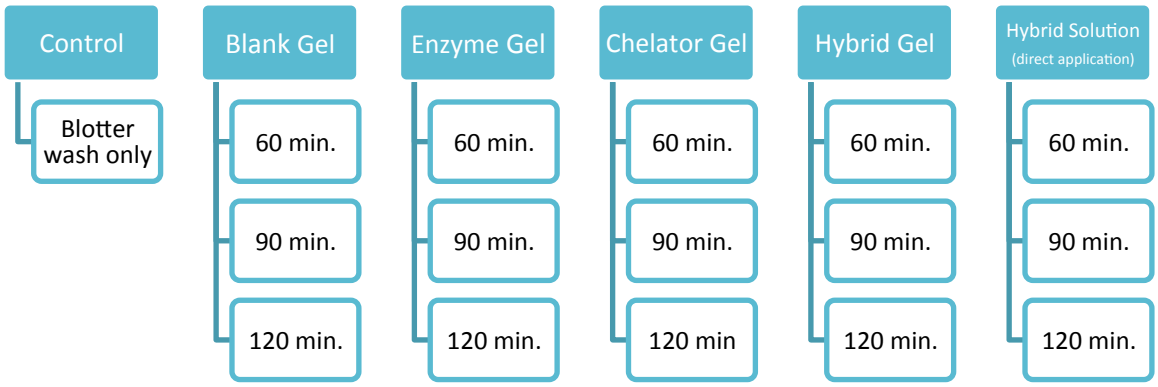


Fig. 7. Diagram of treatment variants and time intervals tested during experiment, yielding a total of 16 samples.

Preliminary experiments performed during the cleaning course informed the development of the enzyme-chelator gel treatment and standard protocols for the extended experiment including methods for uniform gel casting and optimal thickness; application of the gels during blotter washing to prevent tideline formation; and immersion as a final clearance step. As the agarose gels naturally extract water-soluble, degradation products by capillary action, all samples were first blotter washed to remove as much discoloration as possible prior to treatment with the chelator and enzyme gels and solution.

The efficacy of each treatment variation and the effect of treatment duration were assessed using colorimetry, semi-quantitative XRF, and visible and ultraviolet photography. Templates were created for each of the 16 samples to facilitate gel application as well as registration of the colorimeter and XRF unit. Three evenly foxed areas on each sample were selected for treatment and analysis. In addition to the three foxed spots to be treated, colorimetry and XRF data were also recorded for an additional, unfoxed reference spot. This resulted in a total of sixty-four XRF spectra for the 16 samples.

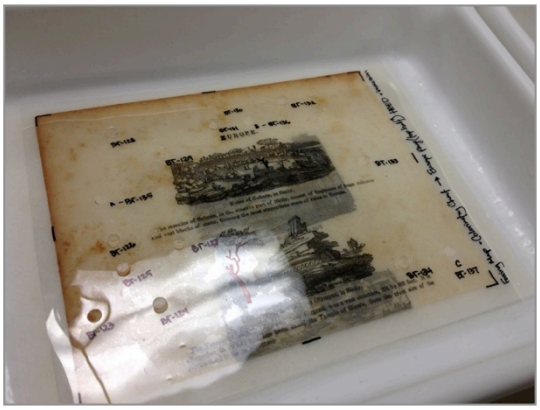


Fig. 8. Template used to facilitate gel placement and instrument registration.

2.3 EXPERIMENTAL

2.3.1 Sample Preparation

Prior to treatment, each of the 16 samples were chamber-humidified for one hour and blotter washed for a total of 3 hours with one blotter change after two hours. After treatment, each sample was immersed in a shallow bath of calcinated filtered tap water (pH 7) and air dried before transfer to a blotter stack where drying continued for 10 days with periodic blotter changes.

2.3.2 Gel and Solution Preparation

Table 1 lists the formulas used to prepare the gels tested in this experiment. All gels were 3% w/v concentration[4], buffered with sodium citrate and adjusted to pH 6 with citric acid. Throughout the experiment, pH measurements were taken using a HORIBA Twin pH Waterproof Compact pH Meter B-212 calibrated with Fisher Scientific SB107-500 Buffer Solution to pH 7.00.

To prepare the gels, the buffer and sodium citrate were first added to the specified volume of deionized water. If HBED was to be incorporated, it was added at this point as well. This mixture was heated and stirred continuously on a hot plate until boiling to ensure complete hydration of the agarose. In enzyme-containing gels, the chitinase was dissolved separately in a small volume of buffered citrate solution. To prevent denaturation of the enzyme, it was added to the agarose mixture when the beaker cooled enough to touch but before the gelation occurred. In the gel and solution preparations outlined in Table 1, the chitinase units of activity were calculated to be 100 units of activity per liter or 0.0141 per gel (Sigma Aldrich 2014).[5]

Gels were cast in disposable, plastic petri dishes from Fisher Scientific to a thickness of 2mm and cut into 3-mm rounds using a disposable biopsy punch with plunger from Miltex. For the direct application treatment variant, 14.1µL of solution was applied to test sites using a

[4] This concentration previously determined to yield a pore size large enough to permit two-way flow of large, enzyme molecules but also small enough to prevent rapid lateral flow of the aqueous cleaning solutions (Wolbers 2013).

[5] Lysing enzymes from Trichoderma harzianum (Sigma Aldrich product no. L1412) containing chitinase with an activity ≥100 unit per gram. This figure was used to calculate the activity units per gel block, which contains 0.01mg of enzyme.

micropipette. This volume was calculated as the solution content of one enzyme-chelator gel block.

Table 1. Gel and Solution Preparations

Treatment	Preparation
Blank Gel (deionized water)	50mL deionized water 1.5g agarose
Chitanase Gel	50mL deionized water 0.25g sodium citrate 0.5g chitinase 1.5g agarose adjusted to pH 6 with citric acid
HBED Gel	50mL deionized water 0.25g sodium citrate 0.25g HBED 1.5g agarose adjusted to pH 6 with citric acid
Hybrid Gel	50mL deionized water 0.25g sodium citrate 0.25g HBED 0.5g chitanase 1.5g agarose adjusted to pH 6 with citric acid
Hybrid Solution (direct application)	50mL deionized water 0.25g sodium citrate 0.25g HBED 0.5g chitinase adjusted to pH 6 with citric acid

2.3.3 Colorimetry

Before and after treatment, a Minolta CR-221 colorimeter with 8-mm spot size was used to collect CIE L*a*b* values for the three sites treated on each sample as well as an additional unfoxed reference spot. The data recorded for the three, treated foxed spots were used to calculate average L*a*b* values and an average delta E value to reflect the color shift observed for each treatment variation.

2.3.4 X-ray Fluorescence Spectroscopy

Semi-quantitative XRF analysis was used to assess the effect of each treatment variation by determining the relative concentration of iron in each of the three sites treated on each sample and the unfoxed reference spot. As described above in **2.2.1 Characterization of Foxing**, a handheld Bruker Tracer III-SD XRF spectrometer with a rhodium tube was used. The spectrometer has an oblong spot size measuring 0.5cm x 1cm and was fitted with a 25µm Ti/305µm Al filter. The spectrometer was operated at 40 kV high voltage; 9.6 µA anode current; and 60 seconds live time irradiation. The data collected with the handheld spectrometer was imported into ArtTAX (v.7.5.2.0) software to plot and overlay before- and after-treatment spectra.

2.3.5 Visible and Ultraviolet Light Photography

All 16 samples were imaged before and after treatment under visible and ultraviolet light using a Nikon D3200 DSLR with Nikkor 18-55mm zoom lens. For ultraviolet photography, Broncolor Mini ultraviolet lamps were used and the camera was fitted with a Promaster 52mm CIR-PL ultraviolet lens filter. All images were processed in Adobe Photoshop and Bridge CS6 according to the specifications outlined in *The AIC Guide to Digital Photography and Conservation Documentation* (Frey and Warda 2008).

2.4 RESULTS

2.4.2 Colorimetry

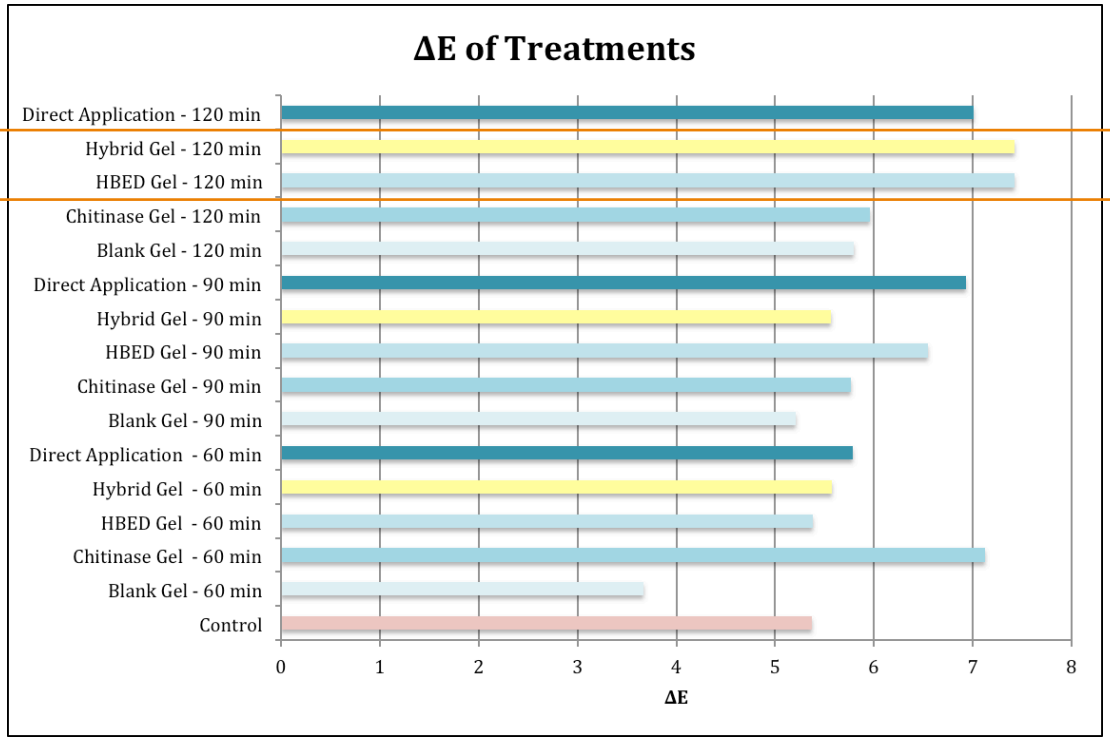


Fig. 9. Graph illustrating the average ΔE values for all treatment variations and durations tested. The orange rectangle highlights that the greatest ΔE values were observed with the hybrid and HBED gels applied for the maximum duration tested, 120 minutes.

2.4.2 X-ray fluorescence Spectroscopy

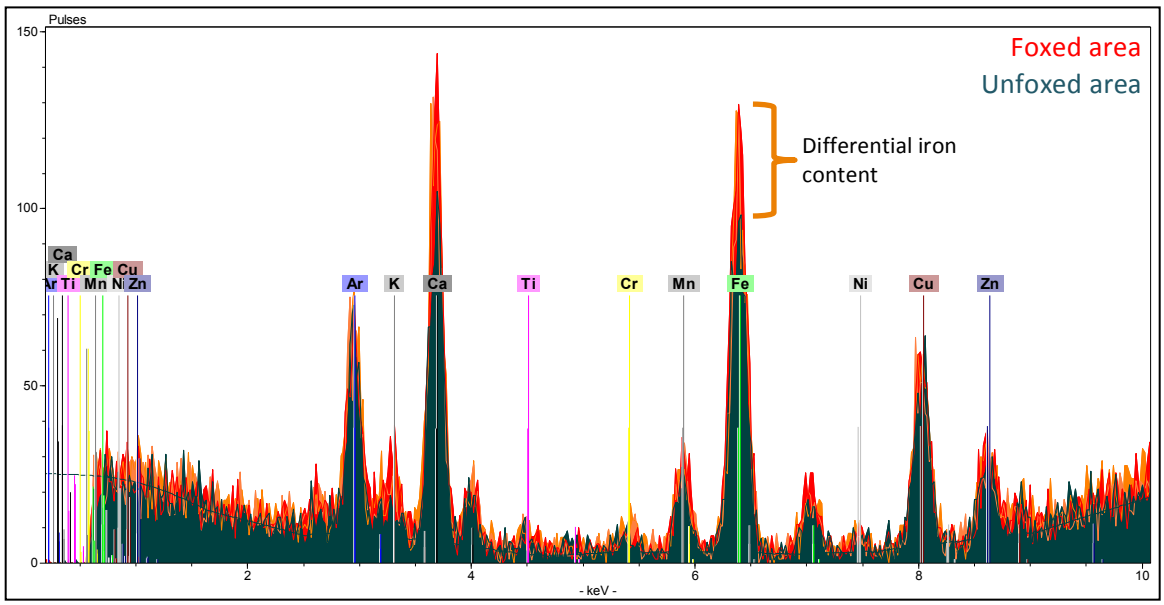


Fig. 10. Before treatment with hybrid enzyme-chelator gel, 120 minutes

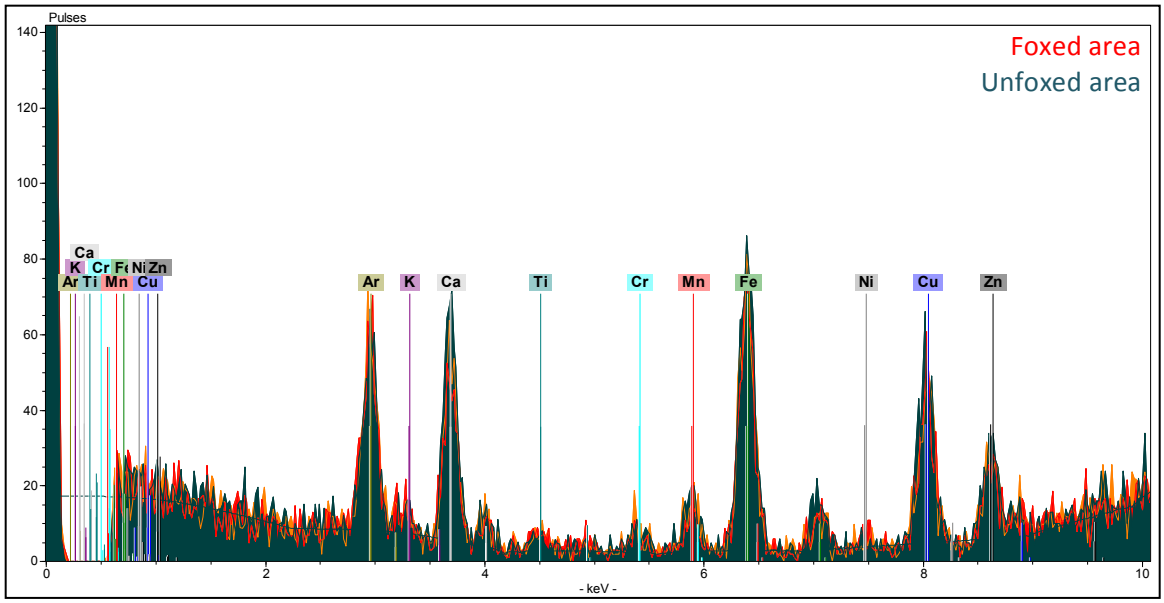


Fig. 11. After treatment with hybrid enzyme-chelator gel, 120 minutes

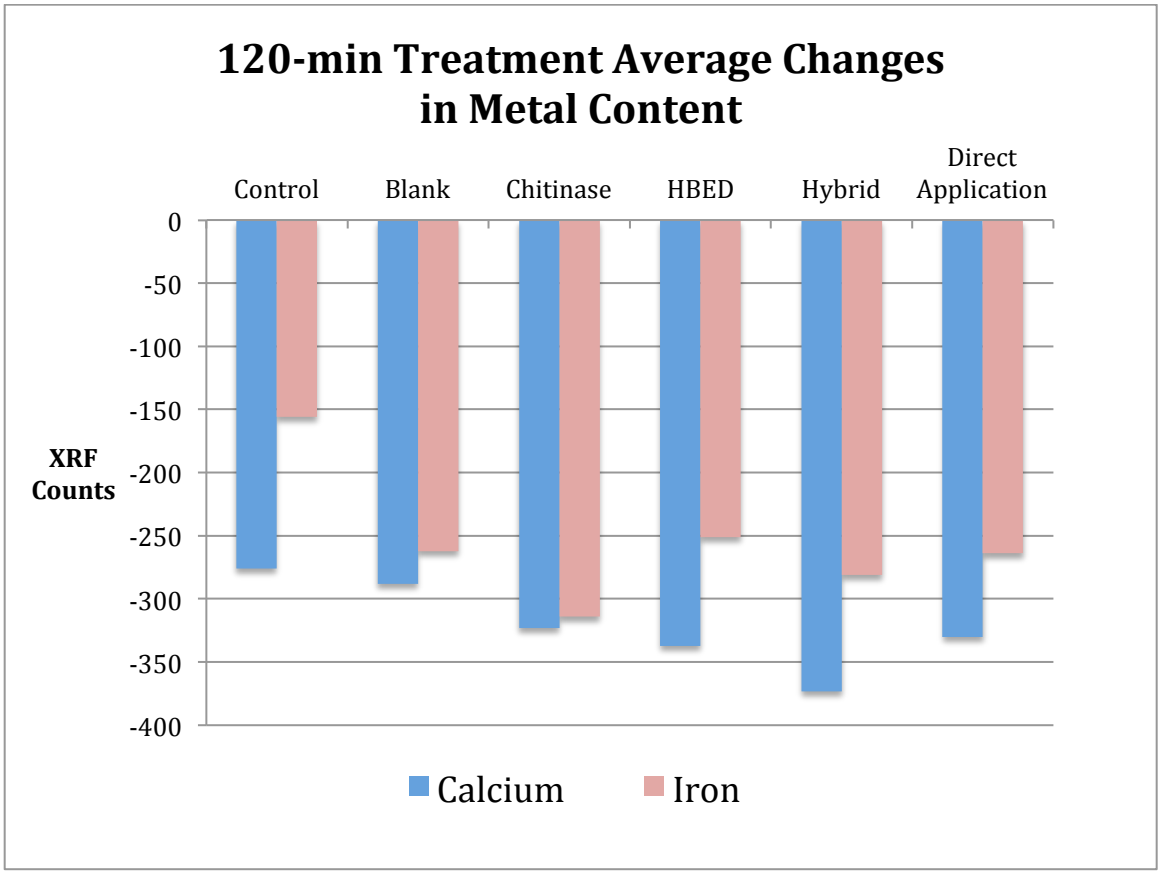


Fig. 12. Graph demonstrating the decrease in calcium and iron concentration observed resulting from each treatment variations for 120 minutes, the maximum duration tested. The values expressed are averages of XRF data collected from the three areas tested on each sample.

2.4.4 Visible and Ultraviolet Photography

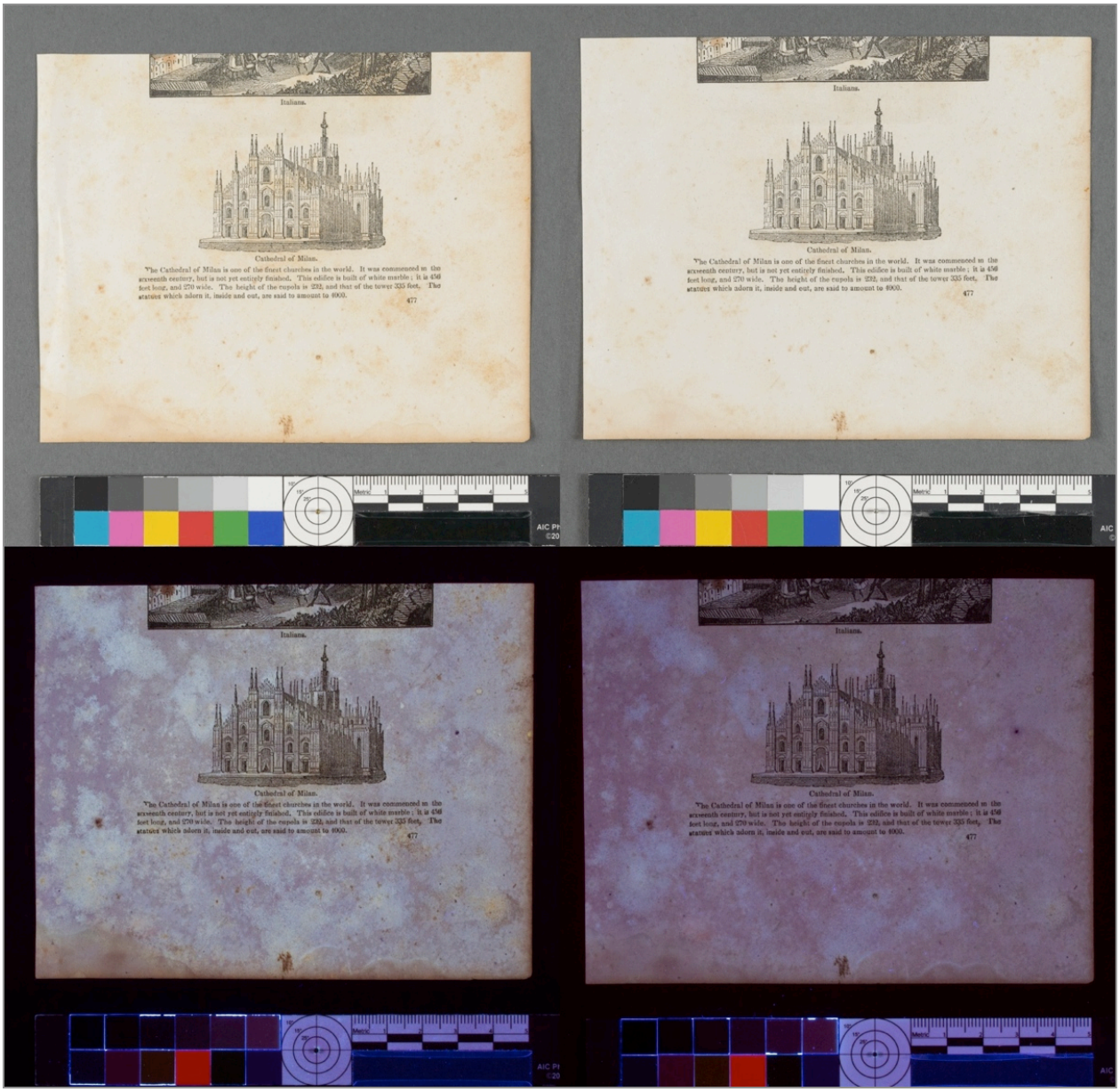


Fig. 13. Sample treated with chitanase-only gel for 120 minutes before treatment in visible light (top-left) and ultraviolet radiation (bottom-left) and after treatment in visible light (top-right) and ultraviolet radiation (bottom-right).

2.5 DISCUSSION

While an effort was made to select consistent samples that were naturally aged, the treated spots undoubtedly vary in metal content, composition of staining materials, and levels of oxidation. Each of these factors impact the performance of the gels and solution tested in this experiment. Accordingly, trends rather than conclusions are drawn from the data collected. These trends are viewed as points of departure for future experiments and continued research.

2.5.1 Colorimetry

Several observations can be made in reviewing the average ΔE values for all 16 samples presented in figure 9. At all treatment durations, the blank gel showed the least color shift suggesting that the chelator and enzyme both contribute to more effective foxing reduction than bathing alone. It was also noted that all treatment variations resulted in lighter, greener, and bluer color shifts as would be expected in any successful bathing or stain reduction treatment. However, the greatest ΔE —7.42—was observed in both the hybrid gel and chelator-only gel applied for 120 minutes, the maximum treatment duration tested.

2.5.2 X-ray Fluorescence Spectroscopy

A comparison of XRF data reveals a decrease in both calcium and iron in all samples after treatment. It is believed that while the decrease in iron content may be attributed to the HBED chelator, the decrease in calcium is a result of the blotter wash or immersion bath clearance protocols. While a decrease in calcium is observed in both the foxed and unfoxed areas in all samples after treatment, a significant decrease in iron is only observed in the foxed areas treated with the HBED and hybrid gels. These trends are evident in the overlaid spectra of foxed and unfoxed areas in the paper sample treated with the hybrid gel for 120 minutes (figs. 10 and 11). Further, the complex HBED forms with calcium has a low stability constant (9.29) relative to that formed with iron (39.01) (L'Eplattenier 1967).

The significant iron loss in the enzyme-only treatment was also observed and may indicate the release of iron-containing materials that are trapped in the cell (Florian 1997). If the iron present is contributing to fungal attachment to the paper, access to the metal cations may be inhibited and the HBED's chelating performance impeded. In this experiment, the hybrid gel performed

only slightly better than the chelator-only gel, but not as well as the enzyme-only gel, perhaps an indication of unanticipated interaction between the chelator and enzyme.

2.5.3 Visible and Ultraviolet Photography

Finally, visible and ultraviolet photodocumentation were completed for all samples before and after treatment. As anticipated, an overall increase in sheet brightness was observed under visible light. Under ultraviolet radiation, an overall decrease in autofluorescence was observed due to removal of oxidized degradation products from the cellulosic support. Further, no increase in autofluorescence or absorption relative to the control was noted as a result of localized treatment, confirming the efficacy of the final immersion bath as a clearance protocol (fig. 13).

2.6 CASE STUDY: TREATMENT OF A LITHOGRAPHIC PRINT

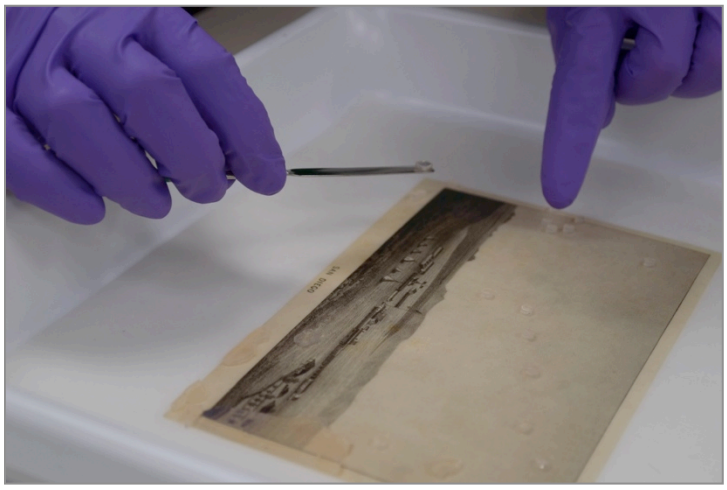


Fig. 14. Placement of hybrid enzyme-chelator gels during treatment

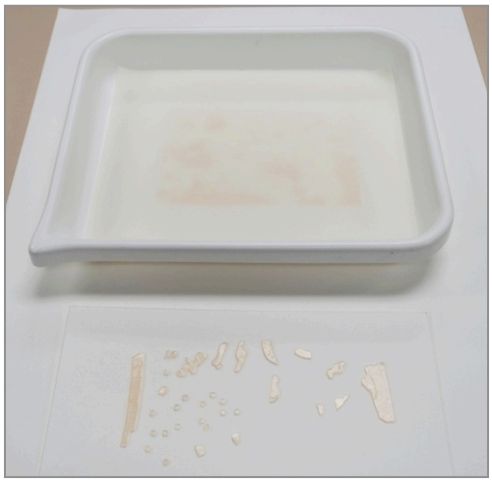


Fig. 15. Pink discoloration in gels and blotter indicate successful iron chelation in treated areas

In light of the positive results of the experimental treatment, a lithographic print was selected from the program's study collection for full treatment using the hybrid enzyme-chelator gel. The print was first dry surface cleaned and attachments and adhesive residues reduced from the verso. Following 30 minutes of humidification, the print was blotter washed for a total duration of three hours. After one hour, the print was transferred to a fresh blotter wash and hybrid gels were applied locally to foxed areas of the print. A template of the foxed areas was

used to cut the hybrid gels to shape. The hybrid gels remained in place for 120 minutes and the print was immersed in a final bath of calcinated, filtered tap water to clear any residual enzyme-chelator solution.

Fig. 16. Before treatment with hybrid enzyme-chelator gel

Fig. 17. After treatment with hybrid enzyme-chelator gel

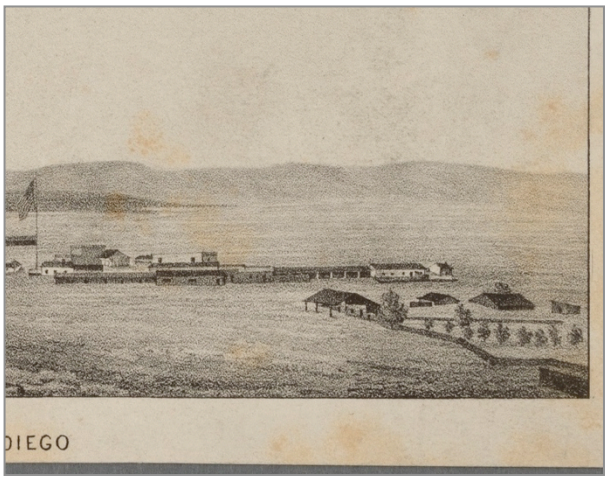


Fig. 18. Bottom-left (detail) before treatment with hybrid enzyme-chelator gel

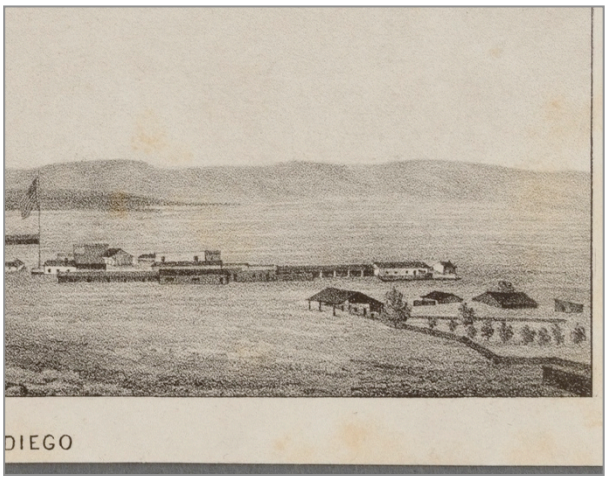


Fig. 19. Bottom-left (detail) after treatment with hybrid enzyme-chelator gel

In comparing the before- and after-treatment documentation of the print, successful and significant reduction of foxing stains in the treated areas is evident (figs. 16-19). While the stain-reduction effects of bathing alone cannot be dismissed, the pink color of the gels and in the blotter indicates that iron was successfully chelated from the foxed areas of the print (fig. 15).

The distinct shapes transferred to the blotter below also confirm that the gel effectively restricted lateral flow of the aqueous cleaning solution.

2.7 CONCLUSIONS AND FUTURE RESEARCH

A review of the experimental results and case study presents several conclusions regarding the targeted, hybrid gel treatment: (1) Colorimetry and XRF data support the hypothesis that both the enzyme and the chelator contribute to improved foxing reduction; (2) Longer application times proved most effective in all treatment variations explored; (3) Gel delivery facilitates local treatment by restricting the lateral flow observed in direct application.

The authors are encouraged by these results and have identified numerous avenues for future research to optimize the proposed treatment and better understand it in the context of traditional stain reduction in works on paper:

- Accelerated aging and long-term effects of treatmnet
- Clearance methods for sensitive media and weakened supports
- Complementary masking techniques
- Comparative study with traditional stain reduction treatments
- Analysis of gels and materials extracted

3. APPLICATIONS OF D4 SILICONE SOLVENT AS A CLEANING AND TEMPORARY MASKING AGENT IN THE CONSERVATION OF PHOTOGRAPHIC MATERIALS

3.1 Specific Challenges in Cleaning Photographic Materials

3.1.1 Water Sensitivity of Cyanotypes

Cyanotypes are relatively abundant in photograph collections, either in the form of cyanotype photographs or as architectural blueprints/drawings. The process was invented in 1842 by Sir John Herschel and the final image material in both of these processes is based on the light sensitivity of iron salts, specifically the chemical reduction of ferric salts (Fe^{3+}) to ferrous salts (Fe^{2+}), to form as a result of oxidation, the blue pigment Prussian blue. The final image is printed directly onto a sensitized paper support without a baryta layer and is thereby a “single layer”

photographic process. Figure 20 outlines the general structure of these types of photographs. Though the process was invented in the 1840s, it did not become widely popular until the latter part of the 19th century, and its unpopularity could be due to its "powerful color" (Ware 1999).

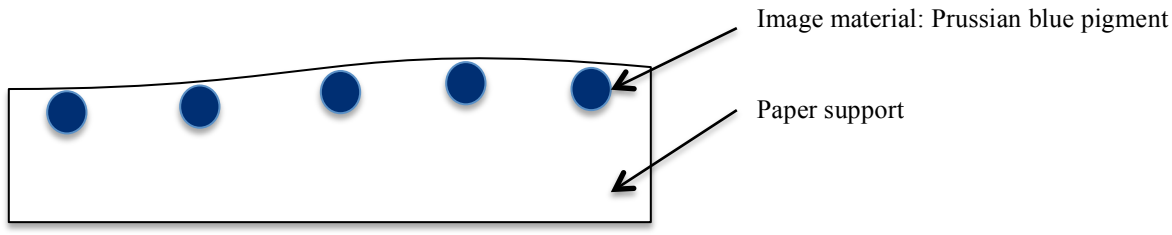


Fig. 20. General stratigraphy of cyanotype photographs

There are three major forms of deterioration unique to this process, fading, bleaching, and dispersing (Ware 1999). Fading, more aptly referred to as photochemical reduction, is the result of exposure to light (visible and ultraviolet radiation), and it manifests as a loss of image density and the product is Prussian white (ferrous ferrocyanide). The remedy for this type of degradation is proper storage and exhibition in low-light environments. Bleaching, or alkaline hydrolysis, varies from fading in that it is the result of contact with alkaline pH and a catalyst – typically water. The resulting products are ferric oxide and ferrocyanide and this type of damage becomes less and less reversible over time. The third type of degradation, dispersion or aqueous peptization, results in the removal or loss of Prussian blue pigment particles. This type of degradation can occur when cyanotypes are washed via immersion, such as in the washing step during initial processing or during a conservation treatment. In experiments performed by Mike Ware, Sarah Wagner, Ian Moor, Angela Moor, and others, a loss of image density as a result of aqueous peptization can occur regardless of the type of water used (neutral pH tap water, deionized water, and distilled water) and age of the cyanotype (Ware 1999). What was noticed in these studies is that immersion in water with an acidic pH (6.0-6.6) resulted in a lowering of the percentage of image density (pigment) loss.

Due to the possibility of peptization, immersion of cyanotypes and blueprints is generally not the approach conservators use for stain reduction on these materials. Instead, conservators opt to use passive bathing methods such as capillary washing with blotter or other absorbent substrates to pull the stains out of the photographic supports. This type of stain reduction, while commonly

accepted in photograph and paper conservation, has its drawbacks in that the staining material is pulled through the support and can, in some cases, result in the formation of new stains. Nonetheless, capillary washing is typically successful in removing water-soluble staining material.

In keeping with the approaches learned from Professor Wolbers in the "Conservation Cleaning Methods" course, the idea of "removing treatment from the object" was attractive. This philosophy is one Professor Wolbers applies in his treatment of paintings and architectural materials. The technique of removing treatment away from the object involves local application of a rigid gel or other poultice material which will pull the staining material into the matrix of the gel or poultice and away from the object's surface rather than through the object, as in capillary washing. While local treatments are often not the first choice of conservators, the author was interested to see if the D4 solvent could be used on cyanotypes as a temporary masking agent or fixative, similar to the use of cyclododecane (Brückle et al 1999; Nichols and Mustalish 2002) during local stain reduction with a rigid gel.

3.1.2 Methods for removing soot from fiber-base, gelatin silver photographs

Fiber-base, gelatin silver photographs are one of the most abundant photographic materials in collections and the process was introduced in the 1880s. Often called silver gelatin developed out prints (DOPs), these materials are laminate in structure and their paper supports are coated with the following materials: a baryta layer (consisting of gelatin and barium sulfate), a gelatin binder and layer of silver image material (often called the "photographic emulsion"), and a protective gelatin overcoat. Figure 21 shows the general layered stratigraphy of these materials. Many collections also possess resin-coated, gelatin silver photographs, however, the area of inquiry for the present study is focused on fiber-base, gelatin silver photographs, which do not have the two layers of resin coating encapsulating their paper support. Although similar in image tonality and structure, resin-coated papers have challenges unique to their structures that fiber-base papers do not.

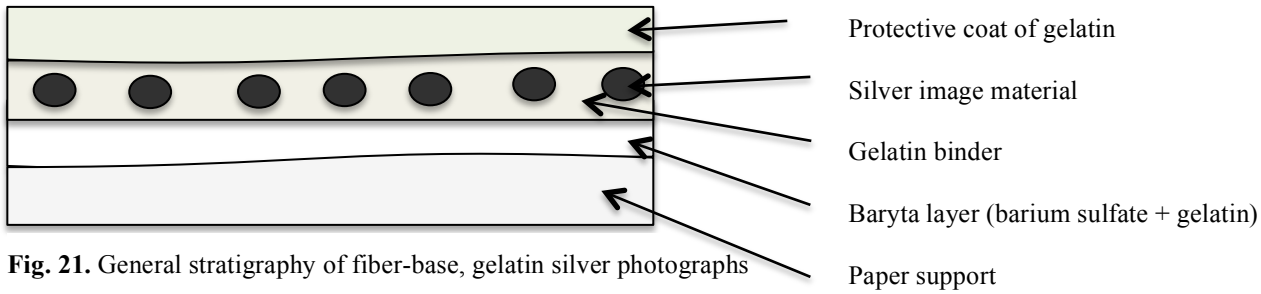


Fig. 21. General stratigraphy of fiber-base, gelatin silver photographs

The types of degradation for these materials varies from image fading as a result of oxidation, and silver mirroring due to pollutants in the environment, both of which are chemical forms of deterioration. Other forms of degradation seen in these materials are surface soiling and physical damage as a result of improper storage, handling, and display. For the purposes of this study, reduction of a specific type of surface soil was the area of interest. These types of photographic materials can come in contact with surface soil bearing a greasy or oily component, such as soot, either from exposure during a fire or accidental contact in some other manner, such as a furnace puff-back. Nonetheless, this soiling material can prove challenging to remove and is often reduced with dry surface cleaning methods such as vulcanized rubber-based chemical soot sponges and cosmetic sponges. More tenacious soot soil can be reduced using an alcohol (isopropanol or ethanol) dampened cotton ball or with a surfactant such as Kodak Photo-Flo 200[6].

While dry methods are typically the first choice for conservators, these specific techniques if not used with care could result in changes in a photograph's surface characteristics. These changes could be an increase or decrease in surface gloss or abrasion, if the surface is particularly sensitive. Conversely, the solvent and aqueous-based approaches to stain reduction could result in swelling or dessication of the gelatin binder layer, which in turn, will also change the appearance of the photograph[7].

[6] Used as a dilute solution of 1 drop Photo-Flo 200 to 100 mL of water.

[7] Swelling the gelatin binder has adverse effects such as: complete loss of material, change in surface gloss or texture. Dessicating the gelatin binder has similar adverse effects. Additionally, swelling or dessicating the binder could result in the soiling material being driven into the binder, making it impossible to reduce or remove.

In some instances, such as the reduction of a stain or tenacious soiling material, swelling of the gelatin binder layer is necessary, and considered acceptable, in order for the binder to release the soiling material and allow it to be reduced/removed. In these cases, the swelling is minimal and controlled to the extent possible. Conservators use this approach with great discernment taking into consideration the needs specific to the object and goals of treatment.

For this treatment challenge, the author was interested to see if the D4 solvent could be used as a solvent-based approach for the reduction of sooty surface soil on fiber-base, gelatin silver photographs, without resulting in any surface alterations or leaving behind residues.

3.2 INTRODUCTION TO D4 SILICONE SOLVENT

3.2.1 Chemical Properties

D4 is a high molecular weight, volatile cyclic siloxane (fig. 22) sold commercially under its INCI name "Cyclomethicone." The solvent is extremely non-polar; has very low surface tension, thus it spreads readily on a porous or non-porous substrate. It is immiscible in water, but can readily form microemulsions with water or another polar solvents and a surfactant. The solvent evaporates slowly, a working property that lends well to use as a masking agent.

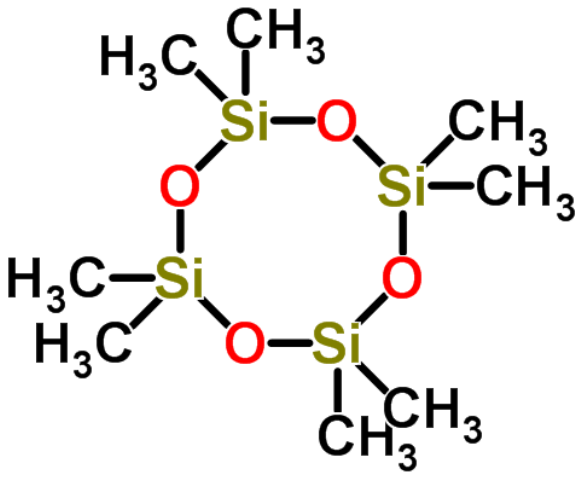


Fig. 22. D4 chemical structure, image courtesy ChemSpider

Regarding health and safety, although D4 is found in many cosmetics and personal care products, it has a moderate toxicity rating of 2 (ChemWatch MSDS for Octamethylcyclotetrasiloxane 2013). It is recommended to use the same personal safety precautions one would use with any solvent, such as working with it in proper ventilation (in the fume hood, for instance) and wearing the appropriate personal protective equipment, such as gloves, and eye protection.

As mentioned above, D4 solvent is sold commercially under the INCI name "cyclomethicone," and depending on the manufacturer, this can be mixture of the D3, D4, D5, D6, and D7 polymers, the ratios of which will vary. Higher molecular weight polymers of this nature will volatilize more slowly, thus a solvent with an equal combination of D4 and D5 will have a slower evaporation rate than one that is primarily D4.

For this study, there was an interest in determining the purity[8] of the solvent, which is imperative in any solvent-based cleaning/treatment system. The fewer impurities in a cleaning system minimize the possibility for interaction with silver image material or adverse long-term effects on an object. In addition, the retention of the solvent in cyanotype and fiber-base, gelatin silver paper samples was also an area of interest.

3.2.2 Current Applications in Art Conservation

While there are no published articles on use of D4 solvent in the conservation of photographic materials, it has been recommended by Professor Wolbers for use in cleaning stone materials and monuments. For these applications its recommended use is as a masking agent to prevent a microemulsion cleaning system from driving into a porous stone structure. In a recent email exchange to the Western Association for Art Conservation (WAAC), conservator Chris Stavroudis described the recipe used by Professor Wolbers to clean the Lincoln Memorial following vandalism (2014). Essentially the stone is saturated with the D4 solvent, which serves as a temporary mask (or "resist" as it was referred to in the email), then the cleaning system, a microemulsion[9], is applied to the area by brush. The cleaning material must be cleared, first by swab to remove any bulk, followed by a final clearance with water. In this situation, the staining material is paint and the microemulsion does not dissolve the paint, but swells it causing it to become trapped in the structure of the gel (Stavroudis 2014).

In paintings conservation, students in the Winterthur/University of Delaware Program in Art Conservation (WUDPAC) have used D4 in microemulsions for cleaning water-sensitive ground layers on murals. (Ford 2013; Hartman 2013). Their approach is similar to how microemusions

[8] Purity in reference to the amount of D4 polymer relative to D5 or other volatile cyclic siloxanes.

[9] 2% xanthan gum gel made with deionized water, citric acid and sodium hydroxide to adjust pH, and benzyl alcohol as the cleaning solvent

are used for cleaning stone, but the D4 is part of the microemulsion and is not used as a temporary masking agent.

In paper conservation, a classmate of the author's, Austin Plann Curley, has published his work on use of D4 solvent as a masking agent to prevent the disruption of water sensitive media during tear mending. Out of the solvents tested (benzyl alcohol and ethanol) Plann Curley found that the D4 was the only solvent that did not disrupt water sensitive media when applied overall, but that it failed to work as a masking agent to hold water-soluble design media in place during a tear mending treatment (2013).

3.3 EXPERIMENTAL DESIGN

3.3.1 Gas Chromatography/Mass Spectrometry

A sample of D4 solvent and ¼-inch samples of cyanotype and fiber-base, gelatin silver papers saturated with D4 solvent were analyzed by gas chromatography/mass spectrometry (GC/MS). Chloroform was the solvent used to extract the volatile products for analysis. Samples are analyzed using the Hewlett-Packard 7820A gas chromatograph equipped with 5975 mass selective detector (MSD) and G4513A automatic liquid injector. The Winterthur SOLVENT method was used with conditions as follows: inlet temperature was 300°C and transfer line temperature to the MSD (SCAN mode) was 300°C. A sample volume (splitless) of 1µL was injected onto a 30m×250µm×0.25µm film thickness HP-5MS column (5% phenyl methyl siloxane at a flow rate of 2.3mL/minute). The oven temperature was held at 55°C for two minutes, then programmed to increase at 10°C/minute to 325°C where it was held for 10.5 minutes for a total run time of 40 minutes. Hexadecane was used as the internal standard.

A sample of D4 solvent was analyzed in order to determine the purity of the solvent. The ¼-inch samples of cyanotype and fiber-base, gelatin silver papers were analyzed to determine the retention time of the solvent in these materials (fig. 23). The samples used in this experiment belonged to the study collection of the author and were deemed appropriate "representative" samples of the cyanotype and fiber-base, gelatin silver processes.

To prepare the paper samples for analysis, each ¼-inch sample was saturated with 2µL of D4 silicone solvent. Following saturation with D4, the first pair of samples (cyanotype and fiber-base, gelatin silver) were immediately placed into small vials containing chloroform. The second and third pairs of samples remained in the fume hood for one hour and 24-hours, respectively, to allow the solvent to volatilize before being placed into small vials containing chloroform. Once placed into the vials the samples were able to undergo analysis in the instrument.

3.3.2 Gravimetric Analysis

Gravimetric analysis is a quantitative analytical technique used to determine the mass of an analyte based on the mass of a solid. In the present experiment, this technique was used in order to support the findings from GC/MS. In analytical chemistry, the general approach is to record the initial weight of a solid containing a volatile material (analyte) to be analyzed. Next the volatile component is removed by volatilization and in some experiments it is collected and weighed. Finally, the solid is weighed again and the difference between the initial weight and final weight are recorded, taking into account the amount of volatile material lost.

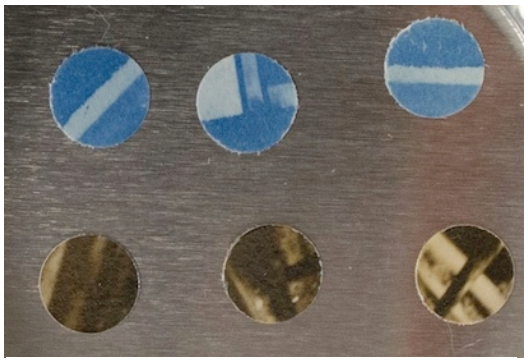


Fig. 23. Detail of quarter-inch cyanotype and fiber-base, gelatin silver paper samples used for py-GC/MS.

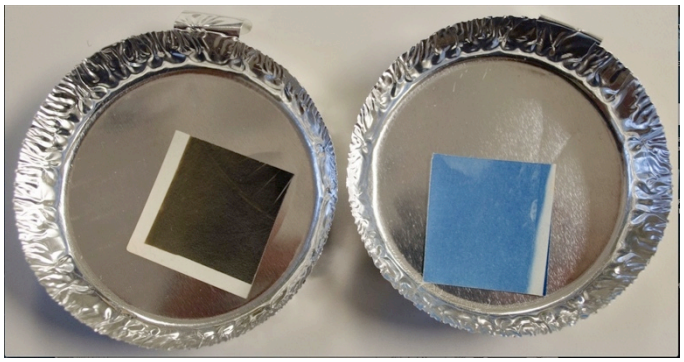


Fig. 24. Detail of one-inch by one-inch cyanotype and fiber-base, gelatin silver paper samples used for gravimetric analysis.

The instrumentation utilized in this portion of the experiment was a Denver Instrument M-220D analytical balance. The experimental approach was to place an empty aluminum weighing boat on the balance and record the weight. Next a 1-inch × 1-inch sample (fig. 24) of either cyanotype or gelatin silver paper was then placed into the weighing boat, and the weight of the weighing boat and paper sample were recorded. The balance was then zeroed. Next the paper sample was

saturated with D4, the amount of solvent used varied between the cyanotype and fiber-base, gelatin silver paper, but the amount applied was enough to visibly saturate the paper sample, as would be done during treatment. The small doors on the balance were closed and the initial weight of the applied solvent was recorded, then the small doors on the balance were opened and the ambient air in the fume hood was allowed to pass over the sample on the balance, in order to encourage the solvent to volatilize. In ten-minute intervals, the doors on the balance would be closed so the air movement could stop and the weight of the sample could equilibrate, and an accurate weight measurement could be recorded. This was done over a period of time, depending on the paper sample, until the balance reading reached 0.0000 or within one-one thousandth of 0.0000 (thus 0.0010).

3.4 RESULTS

3.4.1 Gas Chromatography/Mass Spectrometry

Regarding the purity of the D4 solvent used in this experiment, it was found that the solvent is 99.4% D4 polymer and 0.6% D5 polymer (fig. 25).

GC/MS on the cyanotype paper showed that after 1 hour a trace amount of the solvent was present (figs. 26 and 27), and after 24 hours no D4 solvent was recorded in the sample. For the gelatin silver paper, after 1 hour the sample was readily detected and after 24 hours a trace amount, comparable to that found in the cyanotype paper's 1-hour reading was found. For both, this trace amount is recorded as less than one part per million (0.0001%) compared with the initial amount of 2µL. This indicates for the cyanotype, that after 1 hour, approximately half of the D4 solvent had volatilized, and after 24 hours none was detected. For the fiber-base, gelatin silver paper, after a 24-hour period, approximately half of the D4 solvent had volatilized.

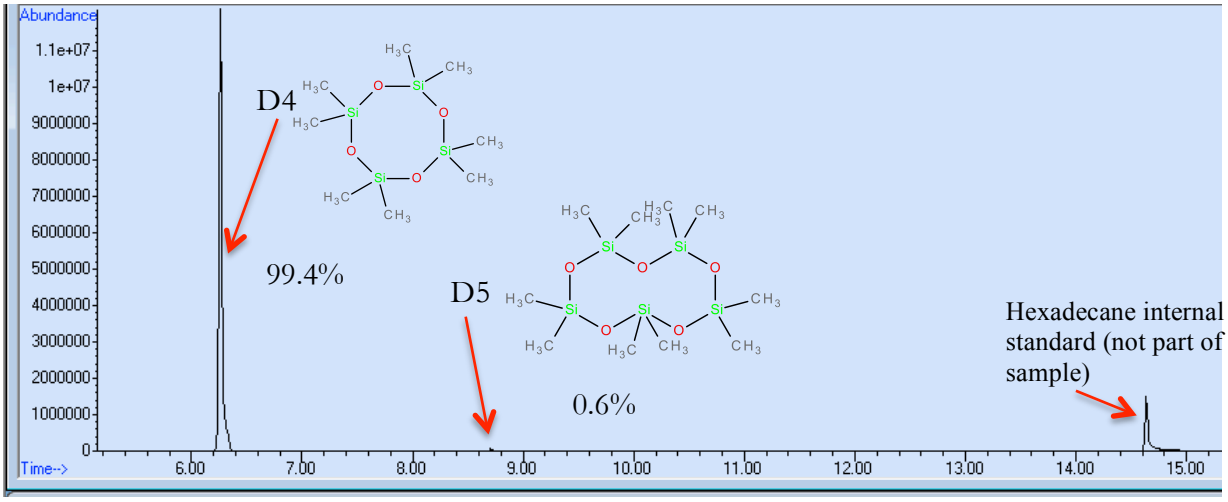


Fig. 25. Total ion chromatogram of D4 solvent sample.

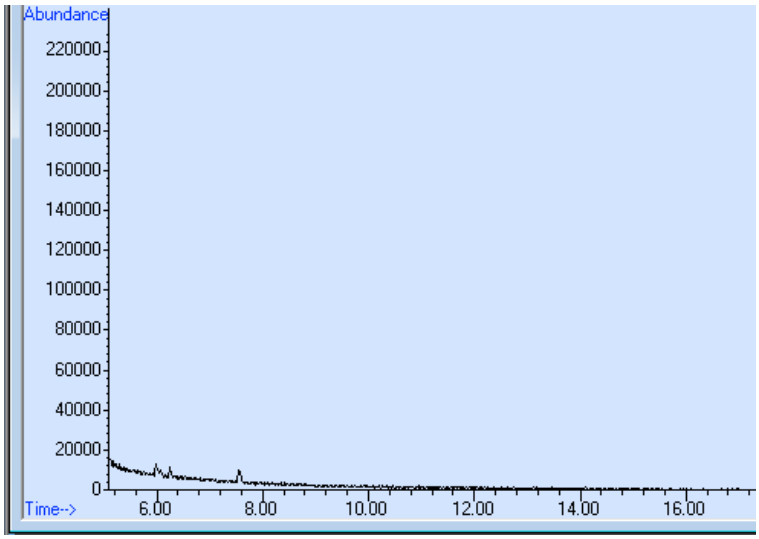


Fig. 26. Total ion chromatogram of cyanotype paper sample after saturation with D4 and 1-hour exposure in ambient air conditions.

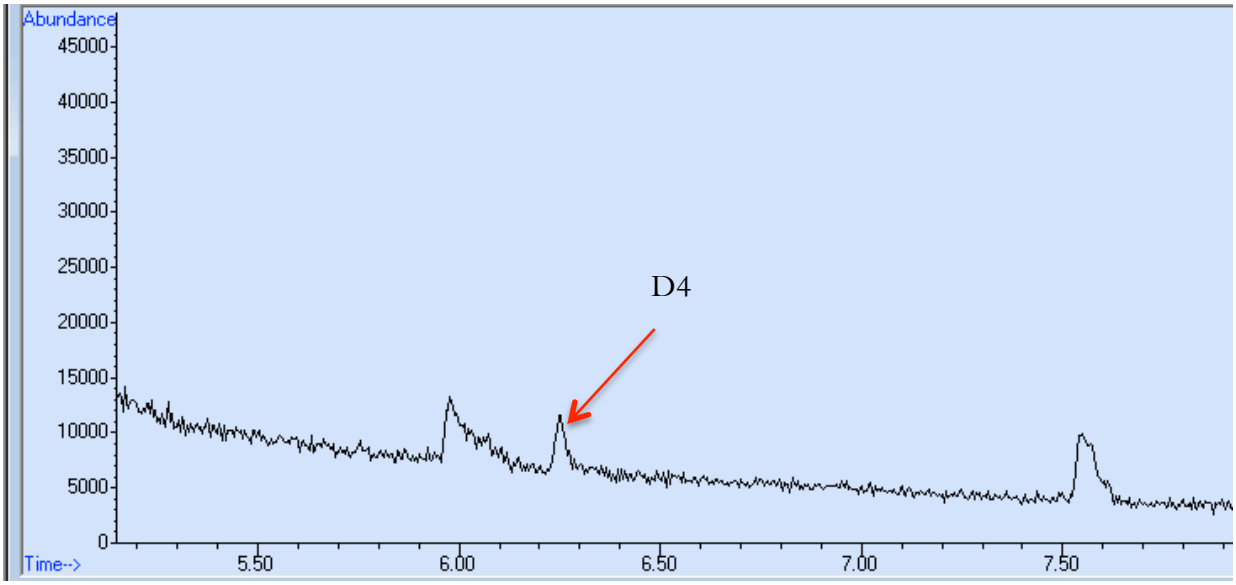


Fig. 27. Expanded view of total ion chromatogram of cyanotype paper sample after saturation with D4 and 1-hour exposure in ambient air conditions. The D4 peak is highlighted

3.4.2 Gravimetric Analysis

The results of the gravimetric trials showed that it took approximately 2.0 hours for 0.2104 grams of D4 solvent to visibly volatilize and record a reading of 0.0010 grams in a cyanotype paper sample. For the fiber-base, gelatin silver paper sample, it took approximately 2.5 hours for 0.1650 grams of D4 solvent to visibly volatilize and record a reading of 0.0000 grams was recorded. Figures 28 and 29 record these findings and the time intervals.

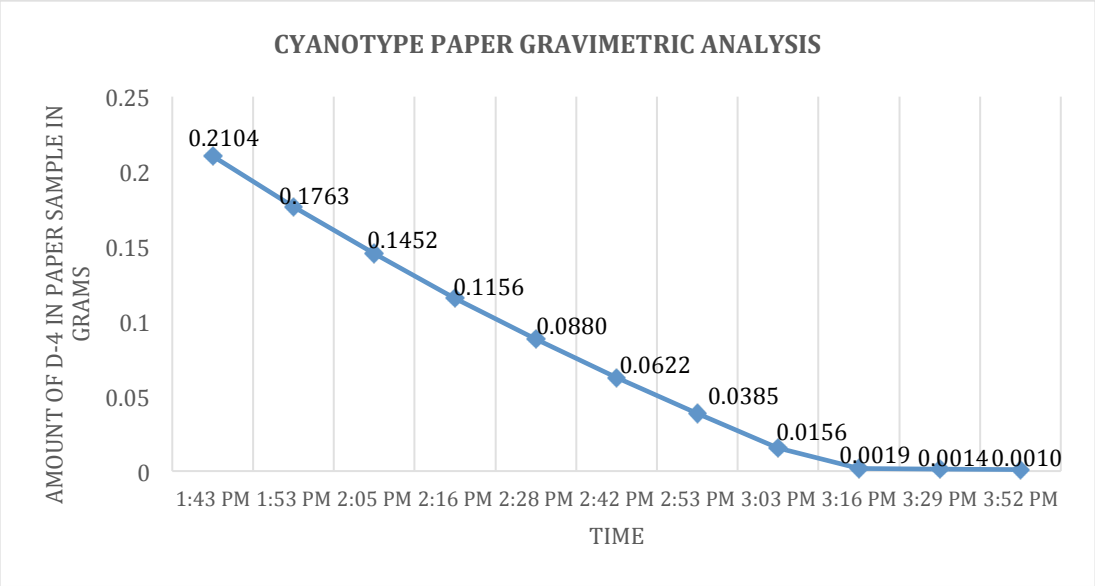


Fig. 28. Cyanotype gravimetric trials during a 2.0-hour period

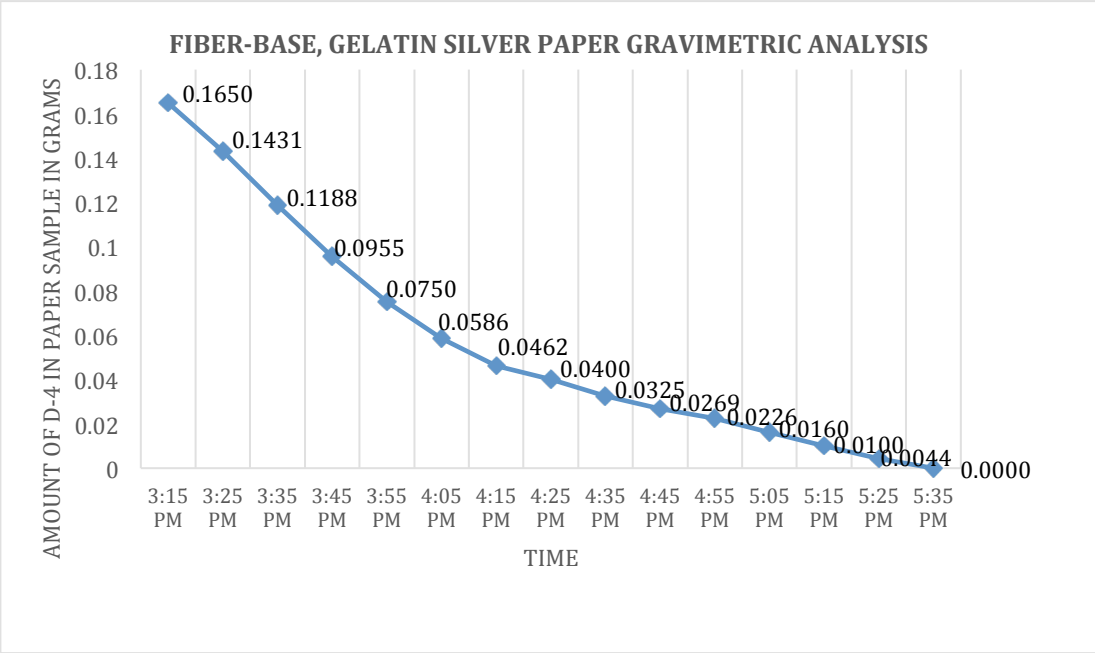


Fig. 29. Fiber-base, gelatin silver gravimetric trials during a 2.5-hour period

3.5 DISCUSSION

The results show that the D4 solvent used in this experiment is relatively pure, with the polymer octamethylcyclotetrasiloxane making up the bulk (99.4%) of the solvent.

For the cyanotype paper, the results confirm that the solvent does volatilize from the paper support. Although, further trials are warranted, this is a promising result. In the fiber-base, gelatin silver paper since a trace amount of solvent is found following the 24-hour period, this could mean that once the solvent reaches such a low level it shows a slight binding to the paper sample. Though, its reduction to less than half of the initial amount applied, indicates that the solvent may completely volatilize from the paper support, but it requires more time to do so.

The gravimetric trials show us a visible plot of the volatilization of the solvent from the respective papers. It should be understood when comparing the gravimetric analysis and GC/MS findings, that after the 2.5 hour mark, the solvent is present in these papers, although it appears to have visibly volatilized from the samples.

3.6 CASE STUDY ONE: TREATMENT OF AN INK-STAINED CYANOTYPE PHOTOGRAPHIC PRINT

3.6.1 Selection of a Stained Print

For the first case study, two cyanotypes were selected for experimental treatment. Both prints belonged to the author and were deemed appropriate as representative samples of the cyanotype process. Since these photographs were not stained initially, the author used a water-soluble felt tipped marker to create ink stains that would respond to treatment by capillary washing or local reduction with an aqueous-based rigid gel. Artificial ageing was not done on the prints.

3.6.2 Conventional Treatment Approach: Capillary Washing

In the first part of this experimental treatment, capillary washing, which is considered a conventional treatment approach for stain reduction in cyanotypes, was used on one of the ink-stained prints. Blotter was used as the capillary support.

The cyanotype, supported on a piece of webbed polyester, was lightly misted with deionized water[10] in order to encourage relaxation and even wetting during treatment. The cyanotype print and webbed polyester support were then placed on a piece of blotter dampened with deionized water. The cyanotype print was bathed using this method for a total of 30 minutes, changing the position of the print on the blotter in ten-minute intervals. The print was allowed to dry between blotters and under weight for one week.

3.6.3 Innovative Treatment Approach: Local Stain Reduction with Rigid Agarose Gel Using D4 Solvent as a Masking Agent

In the second part of this experimental treatment case study, D4 was used as a temporary masking agent to facilitate local stain reduction using an aqueous-based rigid gel. The rationale was to use D4 as a masking agent to minimize the appearance of visible tidelines that could result from local treatment using an aqueous-based gel. Based on its immiscibility with water, it was thought that the D4 would prevent or minimize this phenomenon from occurring.

The ink-stained print was placed into a small tray on a piece of polyester webbing and the D4 solvent was then applied to the sample using a pipette. The amount of D4 solvent applied was enough to visibly saturate the sample. The tray was propped so the excess solvent would form a well at the bottom of the tray. One-eighth inch (1/8" or 3.1 mm) thick pieces of 5% agarose gel were applied to the ink stains on the object. Then a piece of 3-mil Melinex® was placed over the cyanotype and gel block in order to encourage contact of the gel block with the object. The gel remained on the object for 30 minutes before the D4 was visibly beginning to volatilize from the surface, as the object looked less saturated with solvent. Also, the gel itself looked to have been "exhausted" as it began to turn blue from the ink. Another application of D4 was applied to the cyanotype print and a new gel block was placed on the stain. The treatment was allowed to continue for another 30 minutes. Figures 30, 31, 32, and 33 show the stained print before and after treatment.

[10] The pH of the deionized water used in the experiments in this section was measured at 6.5 with a HORIBA Twin pH Waterproof Compact pH Meter B-212 calibrated with Fisher Scientific SB107-500 Buffer Solution to pH 7.00.

3.6.4 Results of Both Treatment Approaches

The capillary washing treatment reduced the stain significantly, but some of the staining material did remain in the support. The innovative treatment showed moderate success. The gel pulled noticeable amounts of the staining material from the support and D4 prevented the formation of visible tidelines, but sinking of the staining media occurred in the support (fig. 33).

3.6.5 Discussion of Both Treatment Approaches

The capillary washing technique worked as anticipated. Since the staining material was water soluble, this treatment approach is intuitive for use with this type of stain. The moderate success of the innovative treatment yields some promise that D4 might be suitable as a temporary masking material for these types of treatments. However, the sinking of the staining media due to the application of the gel poses a concern. This area requires further investigation in order to determine its suitability for local work. Perhaps capillary washing of the stained sample prior to application of the D4 solvent and gel[11] would be an approach to optimizing this treatment.

[11] Using an approach similar to the previous study on foxing reduction, but still utilizing D4 to mask the surface during subsequent local work.

Fig. 30. Ink stained cyanotype before treatment with D4 as masking agent (recto).

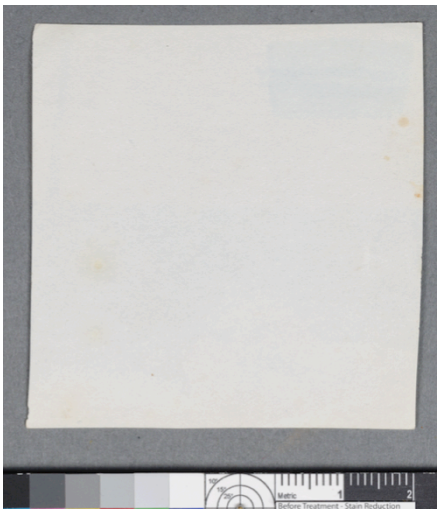


Fig. 31. Ink stained cyanotype before treatment with D4 as masking agent (verso).

Fig. 32. Ink stained cyanotype after treatment with agarose gel and D4 as a masking agent (recto).

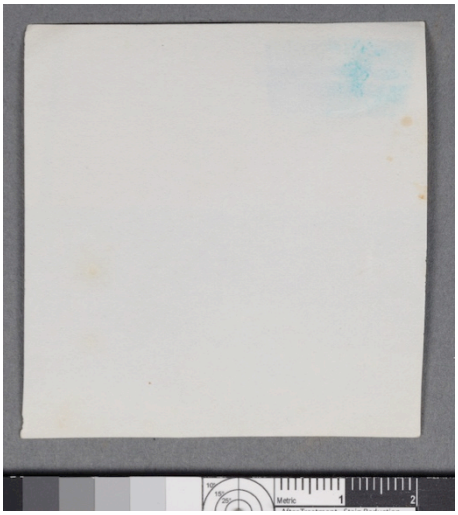


Fig. 33. Ink stained cyanotype after treatment with agarose gel and D4 as masking agent (verso). Note sinking of ink into support.

3.7 CASE STUDY TWO: TREATMENT OF A SOOT-SOILED FIBER-BASE, GELATIN SILVER PHOTOGRAPHIC PRINT

3.7.1 Selection of a Soot-soiled Print

For the case study, two fiber-base, gelatin silver photographs with similar surface sheen (slight gloss) were selected for experimental treatment. As with the cyanotype prints, the fiber-base, gelatin silver prints also belonged to the author and were deemed appropriate for experimental study. As in the above case study, a comparison of conventional and experimental treatments were employed. The photographs, though bearing some surface grime were not in a fire, but had soot applied to their surface by coming contact with candle soot, this was done by the author. The prints were not artificially aged.

3.7.2 Comparison of Conventional Treatment Approaches for Reduction of Sooty Surface Soil Reduction Using D4 Solvent and a D4-Based Microemulsion

For the comparison treatments, the photograph was masked in different areas using Melinex® strips so cleaning could be done in a gridded fashion. The author used traditional dry surface cleaning techniques (vulcanized rubber-based chemical soot sponges, and cosmetic sponges), as well as an accepted aqueous technique (Kodak Photo-Flo 200, as a dilute solution of 1 drop Photo-Flo:100 mL deionized water), and two innovative techniques (100% D4 solvent and a microemulsion of 10:20:70: deionized water, D4, and the surfactant L-3[12]).

The dry methods were done by dragging the sponge across the surface, as one would in a treatment. The solutions were applied using hand-rolled swabs that were rolled across the surface to prevent streaking of the sooty material. The verso of the print was surface cleaned using a combination of dry techniques: the cosmetic sponge and chemical soot sponge.

[12] This 10:20:70 microemulsion consists of 10 parts deionized water, 20 parts D4 solvent, and 70 parts L-3 (laureth-3) surfactant. The engineering of this microemusion is similar to that used in stone and paintings conservation as described in section 3.2.2 and in theory it works by the same mechanism of lifting the grime from the surface by swelling and pulling the grime into the matrix of the microemulsion. The surface was not masked with D4 and the microemulsion was swab applied. D4 was not used to mask the surface because it was felt that the D4 would "clean" the surface rather than work as a masking agent.

Fig. 34. Soot soiled fiber-base gelatin photograph before overall treatment with D4 solvent.

Fig. 35. Soot soiled fiber-base, gelatin silver photograph after overall treatment with D4 solvent.

3.7.3 Overall Treatment of a Soot-Soiled Print Using D4 Solvent

Since one goal of this experiment was to see if D4 could be a viable approach for cleaning a soot soiled fiber-base, gelatin silver photograph, it was utilized in a full treatment of a sooty print. The photograph used for this treatment had a small tear and cracks in its emulsion, some of the cracks were consolidated with a dilute solution of warm gelatin (primarily areas where the concern of flaking/loss of emulsion was highest) with the knowledge that any soot present in the cracks would be consolidated as well. The verso of the print was surface cleaned using a combination of cosmetic sponge and vulcanized rubber-based chemical soot sponge wedges. The recto was cleaned using 100% D4 solvent only, applied using a hand-rolled swab, as done in the above cleaning test. Figures 34 and 35 show the recto of the soot-soiled print before and after treatment.

3.7.4 Results of Both Treatment Approaches

The results and observations for the comparison approach are as follows:

- **Cosmetic sponges:** reduced soot soil
- **Vulcanized rubber-based chemical soot sponge**: reduced soot soil very well
- **D4 Solvent (100% concentration):** reduced soot well, did have a "saturated" appearance when applied and darkened crack along lower right corner, no swelling of binder layer noticed.
- **Kodak Photo-Flo 200:** reduced soot, but caused some of the grime to become embedded into the binder layer, minimal swelling of binder layer noticed.
- **10:20:70 (H2O:D4:L3) microemulsion:** reduced soot and very minimal swelling of binder layer noticed[13].

The results and observations for the overall treatment approach are as follows:
For overall treatment of a photograph, the D4 solvent worked well at reducing the appearance of (and removing traces of) the sooty soiling material on the photographic emulsion. Since the solvent has such a low surface tension, it readily saturated the photographic print, including the

[13] There are potential clearance concerns; in paintings conservation treatments, microemulsions with similar composition are cleared with mineral spirits (Ford 2013). However, mineral spirits were not used to clear the area.

areas where there were cracks in the emulsion. In these areas the soot appears to have become embedded along the crack. However, it is uncertain if this is a result of the solvent and no attempts were made to clean the edges of the cracks with a dry surface cleaning technique. The soot on the verso of the print was reduced to an extent with the combination of chemical soot sponge and cosmetic sponge wedges.

3.7.5 Discussion of Both Treatment Approaches

The dry surface cleaning techniques worked as expected and no alteration of the surface was noticed[14]. The aqueous, pure solvent, and microemulsion techniques proved to be effective in reducing the appearance of soot soil. The aqueous and microemulsion techniques resulted in minimal swelling of the gelatin binder layer, as was anticipated due to the presence of water in both solutions. The pure solvent cleaning with D4 did not result in swelling of the binder, and poses viability as a treatment option for reduction this type of surface soil. Areas of concern that warrant further investigation are, saturation of cracks in the emulsion and subsequent darkening and that py-GC/MS results found trace residues of the solvent in similar supports after 24-hours.

3.8 CONCLUSIONS AND FUTURE RESEARCH

As with any innovative technique, further testing is needed, however, the combined results are encouraging and yield areas for further research. Since D4 volatilized from the cyanotype paper supports, and these supports are typically composed of cotton rag, it is likely the solvent will volatilize from non-photographic supports bearing the same composition. Additionally, its success in reducing sooty surface soil on fiber-base, gelatin silver photographs with a slight gloss indicate that it might be a viable option for use on these types of materials. Since the solvent remains in this type of support after 24 hours, further testing is currently underway to determine if and when the solvent volatilizes to an undetectable level in these supports.

[14] No alteration noticed with and without the aid of magnification

Nonetheless, for these and other types of photographic materials, several avenues for the continuation of research have been identified and include but are not limited to:

- Modification of gel thickness and/or percentage, as well as length of treatment to optimize use as a local treatment method on cyanotypes.
- Determining long-term effects of D4 solvent on cyanotypes and fiber-base, gelatin silver photographs through artificial ageing trials.
- Determining the impact of D4 on photographic image material through use of the Photographic Activity Test (P.A.T.).
- Testing the solvent on fiber-base and resin-coated, gelatin silver photographs with different surface characteristics.
- Exploring the use of D4 solvent on other sensitive photographic materials, such as inkjet and digitally output materials, which have treatment challenges that differ *significantly* from analog materials.

4. CONCLUSION

The authors see great promise in adapting innovative aqueous and non-aqueous techniques to suit the needs of paper and photograph conservators. However, as with any treatment, tailoring these techniques to meet the specific needs of an object is critical. While further avenues of investigation have been identified, additional work on these experimental treatments described in this paper is required to refine them and collect additional data to aid our understanding of these preliminary findings. Nevertheless, the results from these initial trials indicate that the techniques described here may find application in the conservation of works on paper and photographic materials.

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SOURCE OF MATERIALS

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