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Investigation into Reduction of Foxing Stains in Paper

Supplemental Information for Slideshow Presentation

OVERVIEW:

Foxing is pervasive in works on paper and is difficult to reduce or remove, especially when full aqueous treatment is not a feasible option. Some local or restricted aqueous methods, however, might be useful to better control the process of foxing reduction or removal. Foxing has an organometallic nature: it is part metal and part fungal. The treatment of two foxed chine collé lithographs by Puvis de Chavannes, which were severely disfigured and could not be immersed, prompted this investigation. In a semester-long aqueous cleaning seminar with Richard Wolbers the following bathing procedures were compared in preparation for treating the prints.

Expendable examples of foxed engravings and foxed chine collé prints were used to test reducing agents, chelators, and enzymes that could effectively reduce foxing stains in paper. Previous student work has explored the use of combinations of chelators and enzymes, however this is the first study to incorporate a novel reducing agent that targets the metal component, reducing Fe^{3+} to Fe^{2+} . This reduction renders iron into a more soluble form, enabling the use of common and accessible chelators for its removal. The reducing agent and chelator target the metal component, and the enzyme targets the fungal component. Two novel reducing agents and enzymes were used in various combinations for this study to comparatively test their efficacy. Ascorbic acid and sodium hypophosphite were tested as reducing agents, along with EDTA and DTPA, respectively, as chelators. Two enzymes were employed as well, a commercial lysing enzyme preparation (a combination of enzymes that target the proteins and carbohydrates of a fungal cell wall) and lyticase (an enzyme that targets the 1,3 link on polyglycoside chains, a specific cell wall component for yeast and fungi). Preliminary testing indicated that sodium hypophosphite and lyticase were highly effective in reducing foxing discoloration, and thus became the treatment protocol for the two Puvis prints. Furthermore, the prints were bathed differently - one on the suction table and one on TEK-Wipe, as a variant of blotter washing - to test the efficacy of the solutions in a variety of delivery methods.

Building on the preliminary testing, this study offered a restricted bathing option for the two Puvis de Chavannes prints -- incorporating a new combination of reducing agent, chelator, and enzyme. The prints were treated successfully and safely, significantly reducing the widespread foxing discoloration on both prints while preventing the delamination of the chine layers. The new protocol will provide wider applications for works on paper that cannot withstand aqueous treatment via full immersion bathing by using rigid agarose and gellan gels. It also includes safer, more sustainable reagents than traditional foxing treatments, which have included Dithiothreitol (DTT) as a reducing agent, high pHs, or traditional bleaching agents.

INTRODUCTION:

As incoming second year paper fellows, we each received one of a pair of chine collé lithographs, entitled *Le Ballon* and *Le Pigeon*, from the WUDPAC study collection. The prints are reproduced paintings from the Franco-Prussian War, and much of their beautiful imagery is obscured by pervasive foxing. The original paintings were created in 1870 and 1871 by the famed French painter Pierre Puvis de Chavannes. They were immediately reproduced for distribution as lithographic prints by printmaker Emile Vernier, who also lived and worked in Paris during this time.

A chine collé print has an inherent laminar structure that can be compromised in aqueous treatment and cause delamination or bubbling between the layers. In the chine collé technique, the primary support is commonly a thin Asian paper, *chine* in French. It is pasted on the verso, placed on a thicker secondary support, and simultaneously, the two layers are fused together and the image is printed as they go through the press. Chine collé can be difficult to identify and may be treated improperly, causing bubbling or complete delamination of the chine layer.

Looking at these objects with different illumination sources provides a wealth of information about their condition. Foxing can be organo-metallic in nature, with fungal components and metallic components that cause localized discoloration in the paper support. These discolorations appear as spots, yellow to dark brown in color, and diffuse to concentrated in shape. But what appear to be faint, rust-colored spots in normal light are brighter and more numerous when viewed in longwave UV and in transmitted light. Tide lines are also more easily visible with UV and transmitted light, in the case of *The Pigeon* especially.

Developing a treatment protocol for the two prints that addressed the dual nature of foxing was a challenge that greatly interested WUDPAC faculty member Richard Wolbers, who has worked extensively with aqueous cleaning methods and gels. Both authors participated in Professor Wolbers' aqueous cleaning methods seminar, an elective course in applied conservation science available to second year fellows. Preliminary testing of novel reagents began, building off of previous student research done in these seminars.

PRELIMINARY TESTING:

The first step we took addressed the metallic component. Fe^{3+} ions are notoriously intractable, while Fe^{2+} ions are easier to chelate. Thus, use of a reducing agent to convert Fe^{3+} ions to Fe^{2+} ions would eliminate the need for dilute hydrofluoric acid or strong Fe^{3+} chelators like HBED. Aqueous ferric chloride was applied to an expendable foxed print, and agarose gel plugs containing both reducing agent and chelator were placed on those areas. The gel appeared to be effective, visibly reducing the yellow color of the sample area where the gel was placed. This meant that the Fe^{3+} ions were successfully reduced to Fe^{2+} , chelated, and pulled out of the paper support into the gel plug.

We tested two different reducing agents, ascorbic acid and sodium hypophosphite. We also tested two different enzymes to address the fungal component of foxing. Lysing enzymes attack the chitin in the fungal growth, breaking it down for removal in an aqueous solution. The enzymes used for testing included lyticase and a commercial blend of lysing enzymes.

We tested these various combinations with expendable foxed prints in full immersion baths in three steps. In the first step, the sample was placed into a deionized water bath containing the reducing agent and chelator. Second, the sample was rinsed in a bath of plain deionized water to remove excess reducing agent that would be harmful to the enzyme used in the next step. Third, the object was placed in a deionized water bath containing the enzyme. This preliminary testing showed that sodium hypophosphite with DTPA proved to be more successful in stain reduction than ascorbic acid with EDTA. Lyticase was more successful than the lysing enzyme blend. Sodium hypophosphite has a higher reduction potential than ascorbic acid, and the lyticase enzyme is cheaper, purer, and is not as sensitive to heat as the lysing enzyme blend. They also visibly appeared to reduce the foxing stains the most out of the reagents we tested. This combination formed the foundation of our treatment protocol for the Balloon and Pigeon prints.

In general, the treatment protocol we developed begins with a pre-rinse step to remove easily water-soluble degradation products, followed by the steps tailored to reducing the foxing discoloration. These include the reducing agent and chelator solution, followed by an intermediate rinse step. The enzyme solution comes next, with a final rinse step to remove residues. This general treatment plan can be used for full immersion treatments or controlled applications of moisture.

METHODOLOGY:

Agarose and other gel treatments

In the midst of our research in the fall semester, we were fortunate enough to attend the Gels in Conservation Conference, held in London in October. Papers delivered at the conference included research on a wide variety of gels and their application in the cultural heritage sphere, and were influential in formulating our treatment protocol. Gel treatments are currently in vogue in conservation, with good reason, although they may not be necessary in all applications. However, our two prints were excellent candidates for a gel treatment because we needed to restrict the amount of water brought to them during aqueous cleaning.

Many forms of gels are commonly used in art conservation, with polysaccharide gels such as agarose, gellan, and methyl cellulose most often used in paper conservation. Each gel has specific rheological properties that can act as a reservoir for solutions, restricting the flow of moisture into the paper support, while also acting as a poultice to draw water soluble components out of the support. Some papers, such as the Balloon and Pigeon prints, readily absorb water, so controlling the flow of moisture is paramount. Rigid polysaccharide gel sheets also provide the benefit of physical restriction of the two chine collé paper layers during treatment, as the weight of the gel sheet may help prevent separation caused by the differential expansion of the two layers when subjected to moisture.

Agarose was necessary for this particular because it is a neutral gel - it carries no electrostatic charge. Gellan is a polyanionic molecule and would interact unfavorably with any ionic and enzymatic solutions added to it. Agarose does not have this issue and can carry solutions with aqueous chemistry like our reducing/chelating and enzyme solutions. Agarose provides the additional benefit of strong capillary action, which is determined by its concentration.

Testing different delivery methods

Given that we were able to treat pendant objects, we decided to test the same treatment protocol using different delivery methods. The Pigeon print was bathed on a suction table, and the Balloon print was bathed on TEK-Wipe using the same aqueous solutions in agarose gel sheets. (TEK-Wipe is a highly absorbent, nonwoven fabric that is a blend of polyester and cellulose. Blotter could be used instead of TEK-Wipe, but TEK-Wipe was chosen due to its reusability. It can be washed and used again, proving more sustainable than blotter.) This treatment protocol was the same for both objects, with only minor differences in the delivery methods. In the suction table method, all rinse solutions were sprayed on the object while it was under suction, and each gel sheet was applied to the object for a total of twenty minutes. In the TEK-Wipe method, the TEK-Wipe was saturated with the rinse solutions and each gel sheet was applied to the object for a total of thirty minutes. TEK-Wipe is a highly absorbent, nonwoven fabric that is a blend of polyester and cellulose. These treatment protocols were tested on expendable foxed chine collé prints to ensure they were safe and effective. During testing, we determined the gel dwell times for each technique.

EXPERIMENTAL:

Materials preparation

The bathing portion of each treatment required the same aqueous solutions:

1. One phosphate buffer and reducing/chelating solution to be turned into a 3% agarose gel
2. One phosphate buffer and enzyme solution to be turned into a 3% agarose gel
3. A pre-rinse citrate solution for the first and intermediate rinse steps
4. A calcinated, alkaline solution for the final rinse step

These materials must be prepared immediately prior to treatment due to their limited shelf life, otherwise they will oxidize with exposure to the air. First, we created a buffered solution of sodium phosphate and citric acid, to be used for the two gels. DTPA and sodium hypophosphite were added to half of the buffered solution for the reducing and chelating gel, and the lyticase enzyme was added to the other half of the buffered solution for the enzymatic gel. 3% weight by volume of agarose was added to each of the solutions. Dry agarose powder is insoluble in water at room temperature and must be heated to solubilize it. Each gel solution was cooked, then poured out into a Mylar tray, forming a gel sheet large enough to cover the prints. A plastic squeegee was a useful tool to help evenly spread the gel and ensure a consistent thickness of approximately 0.25". The agarose gel sets as it cools, forming a rigid sheet. While large sheets can be difficult to handle if they are too thin or too thick, we discovered that rolling the gel up like a rug made it easier to handle.

Citrate rinse solution recipe:

Use deionized water. Add enough sodium citrate salt (or citric acid and sodium hydroxide) to reach a conductivity of the solution that within one order of magnitude as the conductivity of the object being bathed. Readings can be taken from the surface of the object with an agarose plug and a conductivity meter. Adjust the solution to pH 6 with citric acid.

Gel solutions recipes:

Phosphate Buffer Solution	Reducing/Chelating Gel	Enzyme Gel
Per 300 ml deionized water:	Per 150 ml of phosphate buffer:	Per 150 ml of phosphate buffer:
1.5g sodium phosphate	Add 1.5g DTPA	Add 1.5g lyticase enzyme
Adjust pH to 7.5 with citric acid	Add 2g sodium hypophosphite	Add 3% w/v of agarose powder
Divide solution in half	Adjust pH to 7.5 with sodium hydroxide	
	Add 3% w/v of agarose powder	

Treatment of the Pigeon print via suction table

Treatment of the Pigeon print began with surface cleaning. After humidifying the object overall in a Gore-Tex package, it was pre-rinsed with a buffered solution of sodium citrate and citric acid at a pH of 6, with a conductivity close to that of the print. Conductivity and pH readings were taken from the surface of both prints with agarose plugs and digital meters. The rinse solution was sprayed with a Dia sprayer while the object was under suction, helping to pull water soluble degradation products down into the blotter beneath it. After changing the blotter and applying a *gampi* barrier layer to the object, the first gel sheet was applied, which contained the reducing and chelating agents. The gel sheet had a total dwell time of twenty minutes, after which the gel and *gampi* were removed and a new blotter was placed on the suction table. The object was rinsed again with the same buffered citrate solution as in the pre-rinse step. The blotter was changed again after rinsing, in preparation for the next gel application.

The enzyme gel was applied to the object (with *gampi* barrier layer) and the same treatment steps were followed as for the reducing and chelating gel. Again the gel had a total of twenty minutes dwell time, after which the gel was removed and the blotter changed. The object was rinsed with a final calcinated water solution of filtered water adjusted to pH 8 with calcium hydroxide. After aqueous treatment was complete, the object was dried in a drying stack of polyester interleaving, blotter, and felts.

Treatment of the Balloon print via TEK-Wipe

The TEK-Wipe method proceeded similarly to the suction table method. The bathing chamber was prepared by saturating the TEK-Wipe with the pre-rinse citrate solution. The squeegee proved useful again to ensure even saturation and planarity of the TEK-Wipe. After humidification in a Gore-Tex package, the print was placed onto the saturated TEK-Wipe, and sprayed lightly overall with the same citrate rinse solution to ensure even wetting.

To prepare for the first gel application, a new layer of TEK-Wipe was put down and saturated in the rinse solution. The object was covered with a *gampi* barrier layer and the reducing and chelating gel. Air bubbles were pressed out to ensure overall contact, and the gel was left on for a total of thirty minutes of dwell time. The print was rinsed after removing the first gel by changing the TEK-Wipe again, spraying the print overall with the rinse solution using a Dia sprayer, and then letting the print bathe for twenty minutes. A new *gampi* layer was laid down and the enzyme gel was applied in the same way as for the reducing/chelating gel. Treatment was finished with a final rinse solution of calcinated water, adjusted to pH 8 with calcium hydroxide. After the final rinse, the print was dried in a drying stack like the Pigeon.

RESULTS:

Visual observations

Overall, this treatment proved successful in reducing overall and local discoloration and did not delaminate the chine layer from the secondary support. Examination in UV light indicates a more drastic reduction of foxing spots in the Balloon print, although there is visible reduction of the Pigeon print's foxing as well. The treatment was more successful in reducing the discoloration caused by the pale, diffuse form of foxing, but severe foxing spots show a dramatic improvement after treatment as well.

After treatment, the Pigeon print is visibly brighter overall and appears slightly less yellow. More diffuse areas of foxing appear to be reduced more significantly than more concentrated areas of foxing, especially in the upper right corner. The overall brightening and stain reduction is easily visible on the verso. Examination in UV light also shows overall brightening and the slight reduction of foxing spots, although it is evident that foxing is still widespread, if not visible in normal illumination. There is a rectangle of brighter autofluorescence visible on the verso, addressed in the Discussion section.

The Balloon print also brightened overall and appears slightly less yellow after treatment. This object had a paler, more diffuse form of foxing than the Pigeon, and thus exhibits a more drastic stain reduction, easily visible on the verso. Under UV light, the foxing appears to be reduced but is still present in some areas. On the verso, it is evident that the foxing spots that remain are less sharply defined.

Quantifying the results

The extent of foxing reduction and overall brightening is recognizable in visible examination, but quantifying these changes with colorimeter readings provides excellent proof that these treatments were successful. A Minolta CR-221 colorimeter was used to take measurements of representative areas of each support, foxing on each support, and the minimum and maximum densities of the printed image. The secondary supports of both prints appeared significantly brighter, with a ΔL^* value of over 2 for each. The human eye can detect a change in L^* value greater than 1, which explains why the overall brightening is so apparent. Furthermore, the b^* value decreased remarkably for both, indicating a reduction of the supports' yellow hue. Tracking the ΔL^* and Δb^* values of foxing spots also indicates the efficacy of the treatments. The foxing spots measured on the Balloon print had a much greater degree of brightening and reduction in yellowing than the Pigeon print. This may be because of differences in the type of foxing found on the two prints, and their response to the treatment protocol and delivery method.

	The Pigeon			The Balloon		
	ΔL^*	Δa^*	Δb^*	ΔL^*	Δa^*	Δb^*
Primary support	+1.79	-0.30	-2.60	+1.92	-1.19	-2.10
Secondary support	+2.03	-0.33	-3.23	+2.09	-0.58	-2.3
Primary support foxing	+3.06	-0.76	-4.09	+5.76	-1.62	-3.84
Secondary support foxing	+1.03	-0.16	-0.91	+4.94	-1.57	-4.63
Dmax	+0.75	+0.11	-0.88	-1.77	+0.23	-0.12
Dmin	+1.82	-0.23	-2.07	+1.41	-0.35	-1.52

DISCUSSION:

There is a great deal to discuss in regard to the success of these specific treatments, as well as their wider applications. A comparison of the two delivery methods yields some interesting factors to consider, which will guide the conservator in choosing between them.

The most apparent difference between these methods is the equipment necessary. The suction table is a common feature in paper labs, however it does require an investment in a large, expensive piece of equipment. Labs without this specialized equipment can get good results with smaller, more easily available supplies such as absorbent material, like TEK-Wipe or blotter. The conservator must also consider the amount of time each treatment requires. The suction table has a quicker total treatment time, whereas the TEK-Wipe treatment is much longer. Each treatment has a different level of intensity, where the suction table requires full attention and active participation throughout the entire treatment. The TEK-Wipe treatment, however, proceeds more slowly, so the conservator has more time to monitor treatment or make changes.

While the agarose gel sheets control moisture in both treatments, the gel used in the suction table method acts as a reservoir to slowly dispense the aqueous solutions while under suction. The gel used in the TEK-Wipe method functions as a poultice as it dries, actively drawing up water soluble components into the agarose matrix. The amount of pressure exerted upon the object also differs between the two techniques. The pull from the suction adds to the weight of the gel sheet in the suction table method, while the object in the TEK-Wipe method has only the weight of the gel upon it. The needs of the object will dictate what treatment method to pursue. The suction table offers greater physical restraint and control of moisture, but does exert more pressure on the object. Thus, the TEK-Wipe method may be more suitable for delicate objects or those that are not relatively planar.

The degree of rinsing possible varies greatly between the two delivery methods. The suction table allows for more rinse solution to be sprayed overall in multiple passes, while the amount of solution necessary to saturate the TEK-Wipe is a limiting factor. Similarly, the uniformity of rinse solution application also varies. The suction table relies on a sprayed application of the rinse solutions, which has the potential for unevenness due to human error. The TEK-Wipe method provides more even wetting because the absorbent layer is saturated overall with the rinse solution before the object is placed upon it. This could be a reason why the Pigeon print was brighter than the Balloon print after treatment. More solubilized products were moving out of the Pigeon print on the suction table. It could also appear brighter because it is cooler, due to the reduction of yellow hue reflected in the Δb^* value. An examination of their versos in ultraviolet light displays another result of rinsing. The Pigeon print, on the right, has a rectangle of brighter autofluorescence, which may be the adhesive migrating through the secondary support matrix. Although the chine layer did not separate from the secondary support, some of the adhesive may have moved in the rinsing steps due to the pull of the suction. This degree of adhesive movement is not seen on the verso of the Balloon print.

Finally, one topic that is of particular interest to us is sustainability, both environmental and economic. The suction table requires electricity, whereas the TEK-Wipe method does not. TEK-Wipe can be washed and reused, and may be a more sustainable choice than blotter, which cannot be reused after it is saturated with degradation products. Although we used blotter in the suction table protocol, TEK-Wipe can be used

instead. Similarly, we strove to create a gel treatment protocol that used relatively inexpensive materials which were applied only when necessary, and do not have adverse environmental effects.

Future research

Our general treatment protocol for the step-wise reduction of foxing stains can be applied to a variety of delivery methods based on the needs of the object in question. These include full immersion baths, or more controlled applications of moisture, like gels or blotter washing. Further testing can be done with enzymes that have a higher activity level than lyticase. This may further reduce discoloration from foxing than what we found in our experiments. Similarly, repeated steps or multiple applications of the reducing/chelating and enzymatic solutions may provide better results. One could also undertake other paths of research and analysis such as residue studies and artificial aging experiments.

CONCLUSION:

The treatment we have just described is an innovative one, which provides a method for successful overall aqueous treatment of foxed chine collé prints, including the use of a new reducing agent, enzyme, and gel delivery method. But it is our hope that this is only a first step towards an increase in research led by conservators and students like us. Having multiple delivery methods to choose from allows labs with varying resources to execute a successful treatment with the same basic chemistry, and allows for easy customization for each object that needs treating. This treatment illustrates that the conservator has many options that each have their own advantages. It all depends on the resources at hand and the needs of the object.

ADDENDUM: Case studies at other institutions

Since the presentation of this research at ANAGPIC 2018, Madison Brockman treated a foxed chine collé during her summer internship at the Legion of Honor, one half of the Fine Arts Museums of San Francisco (FAMSF). The treatment protocol was based upon the protocol presented in this paper, with some modifications due to supply availability. The object was an early 19th century chine collé print, with pronounced foxing throughout the primary and secondary supports. The foxing was predominantly the pale, diffuse form seen in the Pigeon and Balloon prints, which seemed to make it an excellent candidate for this treatment, as it had good results in reducing this specific discoloration. The chine collé was also in excellent condition physically, so conservator Victoria Binder and Madison decided to hybridize the two delivery methods to accommodate the controlled TEK-Wipe bathing and rinsing on the suction table to ensure clearance of the solutions. As with the Balloon and Pigeon prints, treatment of this object was successful in reducing the foxing discoloration, brightening the object overall, and in maintaining the bond between the primary and secondary supports.

Treatment Steps and Modifications

The treatment of the FAMSF object proceeded similarly to that of the Balloon and Pigeon prints:

1. Surface cleaning.
2. Humidification in a Gore-Tex package.
3. A pre-rinse step with citrate rinse solution, pH 6. The rinse solution was used to saturate a sheet of TEK-Wipe or bathe the object for 30 minutes. The object was then transferred to the suction table and the citrate rinse solution was briefly sprayed onto the object while it was under low suction to ensure clearance.
4. The reducing/chelating gel, pH 7.5, applied in the TEK-Wipe bathing method.
5. An intermediate rinse step with citrate rinse solution, as in step 3 (TEK-Wipe then spray application under suction).
6. The enzyme gel, pH 7.5, applied in the TEK-Wipe method.
7. A final rinse step with calcinated water, pH 8 with calcium hydroxide, applied as in step 3 (TEK-Wipe then spray application under suction).
8. Drying/flattening between cotton towels, then in a blotter stack.

Some reagents were modified due to their availability:

1. In ordering chemical supplies for this treatment, we unfortunately found that sodium hypophosphite is difficult to attain due to its status as a DEA List 1 chemical under 21 CFR 1310.02. It can more easily be attained by larger labs and university research institutions (like UD/Winterthur) that have established connections to chemical companies they order from. When ordering, one must register with the DEA and indicate what the chemical will be used for. This process would have been successful eventually, but due to the time consuming bureaucracy involved, obtaining the sodium hypophosphite during the last month of an eight-week internship was not feasible. Similarly, private practices or small labs with no administrative staff to handle the chemical ordering may have difficulty in obtaining the sodium hypophosphite. Ascorbic acid is readily available and was used instead, in the same quantity and for the same purpose as a reducing agent. Note that ascorbic acid residues will turn brown when oxidized, similar to an apple, but it is a highly water soluble molecule and can easily be cleared from the paper support with thorough rinsing to avoid an undesirable color shift of the support.
2. Tribasic ammonium citrate salt was already available in the FAMSF paper lab from a previous citrate bathing seminar led by Antoinette Dwan, so it was used in place of making the citrate solution “from scratch” with citric acid and a base (ammonium hydroxide or sodium hydroxide, for example). Citrate salts are generally more costly than making the solutions from scratch, so if cost is a factor in decision-making, then these may not be the best options.

Further research

This treatment will be tested on several other objects in the coming year, adding to our collective understanding of how the chemical reagents synergize with each other in different delivery methods. Victoria Binder at FAMSF is in the process of treating another discolored print with citrate bathing solutions, also introduced by Madison during her summer internship there. Pending curatorial and conservation permission, Madison hopes to treat one or two foxed prints with a full immersion protocol with the reagents presented in this study during her third year internship at the Los Angeles County Museum of Art.