IRON DEGRADATION IN TEXTILES: APPLYING A PAPER CONSERVATION TREATMENT TO TEXTILES

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ABSTRACT–The combination of iron(II) sulfate and tannic acid has been used as a colorant for millennia. Together they form the main components of iron gall ink, which can have detrimental effects on paper substrates. Iron and tannic acid are also used together in textile dyes, resulting in textile substrates that show similar damage. This damage is believed to be caused by two mechanisms: oxidative degradation and acid hydrolysis. In 1995, paper conservator Johan Neevel proposed a multistep treatment using phytate and bicarbonate baths to neutralize both mechanisms. In the decades that followed, paper conservators have rigorously tested the procedure for efficacy as well as short-term and long-term effects. It has proven to be a reliable treatment option with minimal side effects. This study constitutes the initial steps in testing the treatment for expanded use on textiles. A variety of historical samples from study collections testing positive for free iron(II) ions were treated with different variations of phytate and bicarbonate baths used by the paper conservation community following the protocol set out by the Instituut Collectie Nederland. The samples were artificially aged and analyzed along with a control. Changes in the samples were evaluated empirically and the results assessed.

DEGRADACIÓN FÉRRICA EN TEXTILES: APLICACIÓN DE UN TRATAMIENTO DE RESTAURACIÓN DE PAPEL A TEXTILES

RESUMEN — La combinación de sulfato de hierro (II) y ácido tánico ha sido usada como colorante desde hace miles de años. Juntos forman los principales componentes de la tinta ferrogálica, la que puede tener efectos perjudiciales en sustratos de papel. El hierro y el ácido tánico también se usan en combinación como tintes textiles, causando daños similares en sustratos textiles. Se cree que este deterioro es causado por dos mecanismos: degradación oxidativa e hidrólisis ácida. En 1995, el conservador de papel Johan Neevel propuso un tratamiento de varias etapas usando baños de fitato y bicarbonato para neutralizar ambos mecanismos. En las décadas siguientes, los conservadores de papel han sido rigurosos en evaluar la eficacia del procedimiento, así como los efectos a corto y largo plazo, demostrando ser una opción confiable de tratamiento con efectos colaterales mínimos. Este estudio comprende los pasos iniciales de las pruebas para la expansión del tratamiento sobre textiles. Una variedad de ejemplos históricos de colecciones de estudio que dieron positivo a la presencia de iones libres de hierro (II) fueron tratados con diferentes variaciones de baños de fitato y bicarbonato usados por la comunidad de conservadores de papel, siguiendo el protocolo dispuesto por el *Instituut Collectie Nederland*. Las muestras fueron envejecidas artificialmente, junto a un control. Los cambios en las muestras fueron evaluados empíricamente y los resultados fueron determinados.

1. INTRODUCTION

Iron-tannate dyes are a ubiquitous textile colorant chemically similar to iron gall ink. They commonly produce shades of black, brown, or gray. Textile conservators routinely encounter them in 19th century printed fabrics, embroidery yarns, and ethnographic textiles. Unfortunately, the dye's chemical similarity to iron gall ink extends to how they degrade the substrates on which they exist. Given the compositional similarity between paper and cellulosic textiles, it was suspected that a treatment involving phytate and bicarbonate developed for iron gall ink-inscribed paper could be applied to iron-tannate dyed textiles. While preliminary experiments involving this treatment's use on solid-colored textiles were undertaken in the previous decades, questions about its applicability to a wider range of textiles remained (Wilson 2013; Sato, Okubayashi, and Sato 2011; Daniels 1999). Because of the fashion-oriented nature of the Museum at the Fashion Institute of Technology (Museum at FIT) in New York, most textiles within the collection showing iron degradation also include dyes other than iron-tannate in both woven and printed patterns and in composite designs, such as embroidery. Further examples can be found on noncellulosic textiles, such as silk. It was our hope that this promising treatment could be used on these textiles as well.

2. IRON GALL INK

Into the 20th century, iron gall ink was one of the most popular inks in use for many different mediums. This can largely be attributed to its indelibility: it will neither rub nor wash away (Neevel 2001). It is also comparatively easy to prepare using two main ingredients, iron and tannic acid. The iron was added in the form of a salt, namely iron(II) sulfate, historically known as "iron vitriol" (Neevel 2001). The tannic acid was most commonly sourced from gallnuts, which are rich in a specific type of tannic acid known as gallotannic acid. Gallotannic acid is hydrolyzed to gallic acid during the ink manufacturing process. Confusion can arise because, in the past, the terms "tannic acid" and "gallotannic acid" were frequently used interchangeably.

The ease with which the ink can be mixed belies the complicated interaction between the iron and gallic acid. The iron(II) ions first react with gallic acid to form iron(II) gallate, which is colorless and soluble in water. The iron(II) ions then oxidize via atmospheric oxygen to iron(III) ions, changing the colorless iron(II) gallate into the colored and insoluble iron(III) pyrogallate complex (Botti 2005).

In order to bind all of the iron to gallic acid, the ratio between the two ingredients should be 1:1. However, historical recipes show that iron(II) sulfate was routinely added in an excess of 50% or more. This excess has proved to be extremely problematic.

3. IRON-TANNATE DYES

Iron and tannic acid are also used together in textile dyes and are referred to as iron-tannate dyes. Whereas iron gall ink producers favored gallotannic acid sourced from gallnuts, textile dyers used a larger range of tannic acids from a variety of plant materials. Fabrics dyed with iron and tannic acid alone are shades of black, brown, or gray, but many tannin-containing dyestuffs—such as marigold, cutch, and logwood—contribute additional colors, meaning that a large variety of muddy-colored textiles can have an iron-tannate element (Liles 1990).

3.1 IRON-TANNATE DYES IN MUSEUM COLLECTIONS

Iron-tannate dyes are ubiquitous throughout global cultures and have been found in Maori garments, African Kuba cloths and Adinkras, Islamic carpets, North American skin bags, and Japanese dolls (Wilson 2013). For this reason, they are quite prevalent in museum collections. At the Museum at FIT, potential iron-tannate–dyed textiles usually take the form of American and European printed fabrics, black weighted silks, and fine embroidery.

3.2 IRON-TANNATE DYED TEXTILE DEGRADATION

Unfortunately, many iron-tannate–dyed textiles show signs of degradation that cannot be attributed to their age alone. In order to understand why, we decided to return to the research involving iron gall ink. As mentioned before, when the two main ingredients used in iron gall ink—iron(II) sulfate and gallic acid—are used in a 1:1 ratio, the iron(II) ions bind with the gallic acid to form a relatively stable iron(III) gallate complex. When iron(II) sulfate is added in excess, the surplus iron(II) ions and sulfur lead to both oxidative degradation and acid hydrolysis, respectively (Botti. Mantovani, and Ruggiero 2005). These mechanisms manifest themselves through a loss in mechanical strength, which can appear as missing threads or areas of fabric that have fallen out (fig. 1).

3.2.1 Metal-Catalyzed Oxidation

The oxidative degradation caused by unbound iron(II) ions can occur in two ways: through direct production of organic radicals and their subsequent oxidation, and through the Fenton reaction (fig. 2). Both

Fig. 1. Printed cotton dress, showing loss of the iron-tannate–printed elements (Courtesy of the Putnam Historical Society, #29 31-A).

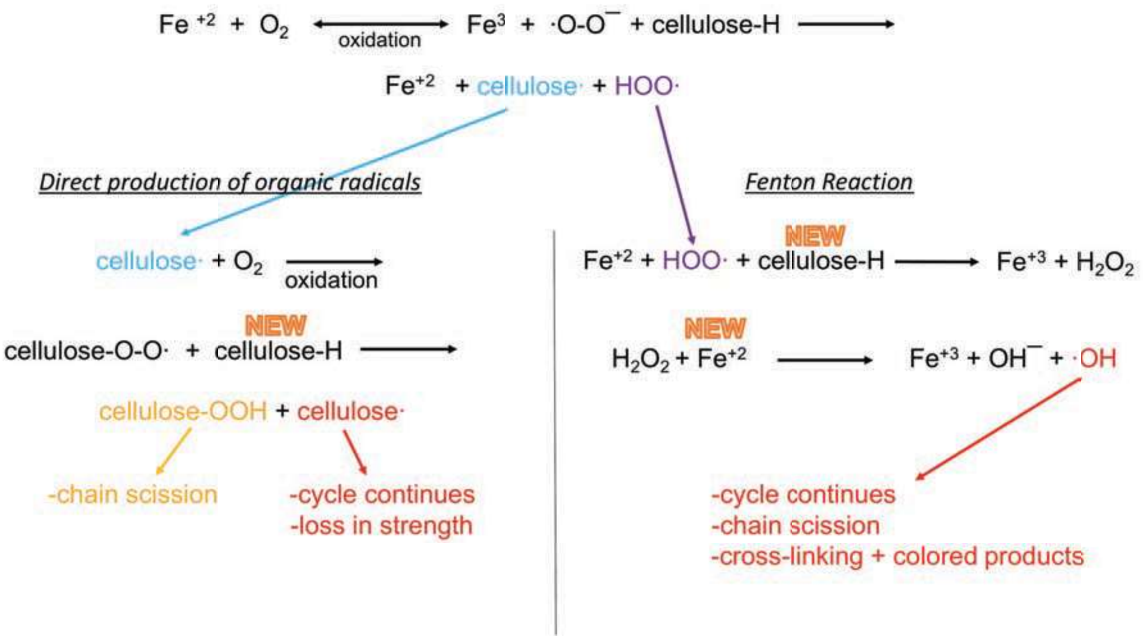


Fig. 2. Schematic of the metal-catalyzed oxidation of cellulose, through both direct production of organic radicals and their subsequent oxidation, and through the Fenton reaction.

paths of degradation start in the same way: iron(II) is oxidized by atmospheric oxygen, forming iron(III) and a superoxide radical. When iron(III) and the superoxide radical react with cellulose, the iron(III) is returned to iron(II), meaning that there is an endless supply of iron(II) ions to keep this reaction going indefinitely. Meanwhile, the superoxide radical absconds a hydrogen from the cellulose, turning itself into a perhydroxyl radical and the cellulose into a cellulose radical, both of which cause a loss of mechanical strength (fig. 3).

At this point, two different paths can be taken. With direct production of organic radicals and their subsequent oxidation, the cellulose radicals oxidize in air to form a cellulose peroxy radical. This cellulose peroxy radical then reacts with a new cellulose molecule to form cellulose hydroperoxide and another cellulose radical. Cellulose hydroperoxide results in chain-scission when it reacts with iron(II) and the cellulose radicals, in addition to continuing the cycle of degradation, are another source of a loss in mechanical strength.

In the Fenton reaction, the perhydroxyl radical can react with iron(II) and a different cellulose molecule, forming iron(III) and hydrogen peroxide. The hydrogen peroxide then reacts with a new iron(II) ion, producing more iron(III) as well as a hydroxide ion and a hydroxyl radical. The hydroxyl radical is very reactive, readily oxidizing cellulose to form organic radicals. This leads not only to chain scission, but also cross-linking of cellulose molecules and the formation of colored products (see fig. 3) (Neevel and Mensch 1999).

3.2.2 Acid-Catalyzed Hydrolysis

Acid hydrolysis is caused by the sulfuric acid by-product formed when the iron ions in iron(II) sulfate bind with the tannic acid. Acid hydrolysis, like metal-catalyzed oxidation, will result in chain scission of the cellulose molecules and a loss of mechanical strength.

Iron-tannate–dyed textiles can show varying degrees of degradation depending on the quality and ratio of ingredients used and the environment in which they are stored. However, the chemical processes described earlier will still be in action.

Fig. 3. Examples of loss of mechanical strength (blue circle) and cross-linking (purple circle) caused by iron-tannate dyes (MFIT P87.20.13A).

4. A PAPER CONSERVATION TECHNIQUE

In 1995, paper conservator Johan Neevel proposed a multistep treatment using phytate and bicarbonate baths to neutralize both metal-catalyzed oxidation and acid-catalyzed hydrolysis in iron gall ink–containing papers.

4.1 PHYTIC ACID

Although both iron(II) and sulfuric acid are water soluble, iron(III) is not. Therefore, any excess iron in that forms will remain after a water rinse. As discussed before, iron(III) is constantly being reduced back to iron(II) and vice versa, meaning that iron(II) ions will quickly reappear.

Phytic acid is found in plant-based materials, such as seeds, nuts, and pollen. It is an antioxidant that prolongs the viability of these materials by blocking the iron-catalyzed oxidation of unsaturated lipids.

The phytic acid binds to both iron(II) and iron(III) ions, forming water-soluble iron phytate complexes and inhibiting the iron-catalyzed oxidation, specifically by inhibiting the production of hydroxyl radicals by blocking the coordination site for hydrogen peroxide on the iron(II) ion. In addition, phytate also encourages iron(II) to become and stay iron(III) by lowering the redox potential. Furthermore, because the iron ions are firmly bound to the phytate, even if not all iron phytate complexes are washed away, free iron ions will not reappear.

4.2 BICARBONATE

While the phytate addresses the iron-catalyzed oxidative degradation, it does not address acid hydrolysis. For this reason, it is necessary to follow the phytate bath with a bicarbonate bath to create an alkaline reserve within the substrate. In the decades of testing done by the paper conservation community, neither treatment done individually has proved nearly as effective as the two done in conjunction with each other.

5. EXPERIMENTAL GOALS

In 2012, Helen Wilson tested the phytate/bicarbonate treatment on model iron-tannate–dyed textiles and found that the procedure successfully remediated the degradation process (Wilson, 2013). Therefore, the following experiment was designed to answer further questions about the phytate/bicarbonate treatment's use on textiles, including its effects on historical textiles, on textiles containing non-iron-tannate dyes, and on materials other than cellulosic textiles, particularly those commonly present in costumes. Furthermore, while a range of phytate bath variations have been used in paper conservation, these variations had yet to be tested on textiles. Of particular interest was the use of tap water in lieu of purified water and the addition of ethanol into the bath, which will be expounded on in section 7.1.

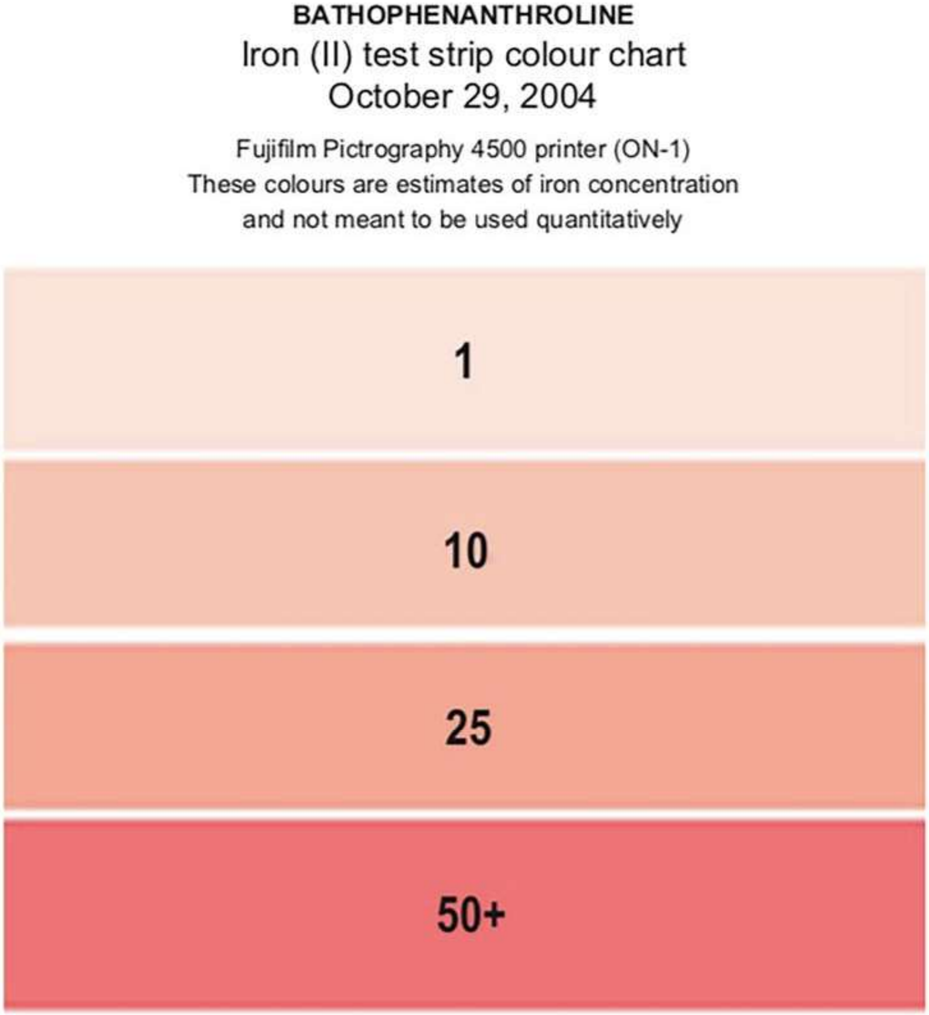
6. IDENTIFYING EXPERIMENTAL SAMPLES VIA BATHOPHENANTHROLINE

Seven printed cellulosic textile fragments dating from the 18th and 19th centuries from the study collection of FIT's Fashion and Textile Studies program were identified as containing free iron(II) ions using bathophenanthroline indicator paper, developed by Neevel and Reissland of the Netherlands' Institute for Cultural Heritage [1].

The chemical compound bathophenanthroline (4,7-diphenyl-1,10-phenanthroline) has a high sensitivity for iron(II) ions, a low sensitivity for other metal ions, and very low water solubility. In the pH range of 2 to 9, the indicator reacts with iron(II) ions to form a magenta-colored iron complex. Because of its low water solubility, bathophenanthroline-impregnated paper is essentially a nonbleeding test that can be used directly on artifacts (Neevel and Reissland 2005).

6.1 BATHOPHENANTHROLINE PROCEDURE

The bathophenanthroline test strips are used by first wetting the strip with deionized water. Excess water is blotted and the test strip placed on the area to be tested. It is then covered with Mylar and pressed down for 30 seconds. If there is free iron present in the textile, the paper will turn magenta during drying. The intensity of magenta color is proportional to ferrous iron content. Vuori and Tse (2005) developed a semiquantitative color chart that estimates the amount of iron(II) present from 1 up to 50 parts per million (ppm), with no visible difference in intensity of color above 50 ppm (fig. 4). However, because the amount of water used and pressure exerted can change with every test, the estimated amount of iron(II) ions cannot be considered definitive.



BATHOPHENANTHROLINE
Iron (II) test strip colour chart
October 29, 2004

Fujifilm Pictrography 4500 printer (ON-1)
These colours are estimates of iron concentration
and not meant to be used quantitatively

Fig. 4. Semiquantitative color chart for bathophenanthroline, developed by Vuori and Tse (Courtesy of the Canadian Conservation Institute).

7. EXPERIMENTAL SETUP

Ten samples (7.5 cm × 10 cm) were cut from each of the 7 textile fragments selected for the experiment (fig. 5). Of these 10, 1 sample was left untreated as a control, 1 received a distilled water rinse only, and 4 pairs were treated in 1 of the 4 bath variations. After treatment, one sample from each pair was dried at ambient room conditions and one sample was dried on the suction table. In both cases, the samples were sandwiched between muslin.

Preparation of solutions and treatment procedures followed the protocols developed by Neevel et al., which are outlined on https://irongallink.org, hosted by the Cultural Heritage Agency of The Netherlands. Although a variety of phytate and bicarbonate salts have been used in paper conservation, calcium phytate and calcium bicarbonate were selected in accordance with these protocols. The calcium bicarbonate was prepared a day in advance and the calcium phytate solution was prepared immediately before use, as outlined in figure 6. Based on experimental studies in paper conservation, the pH of the calcium phytate solution was adjusted to between 5.8 and 6.0 to optimize its efficiency (Kolar et al. 2007).

7.1 EXPERIMENTAL BATH VARIATIONS

Based on a survey of paper conservation literature, four phytate bath variations were prepared.

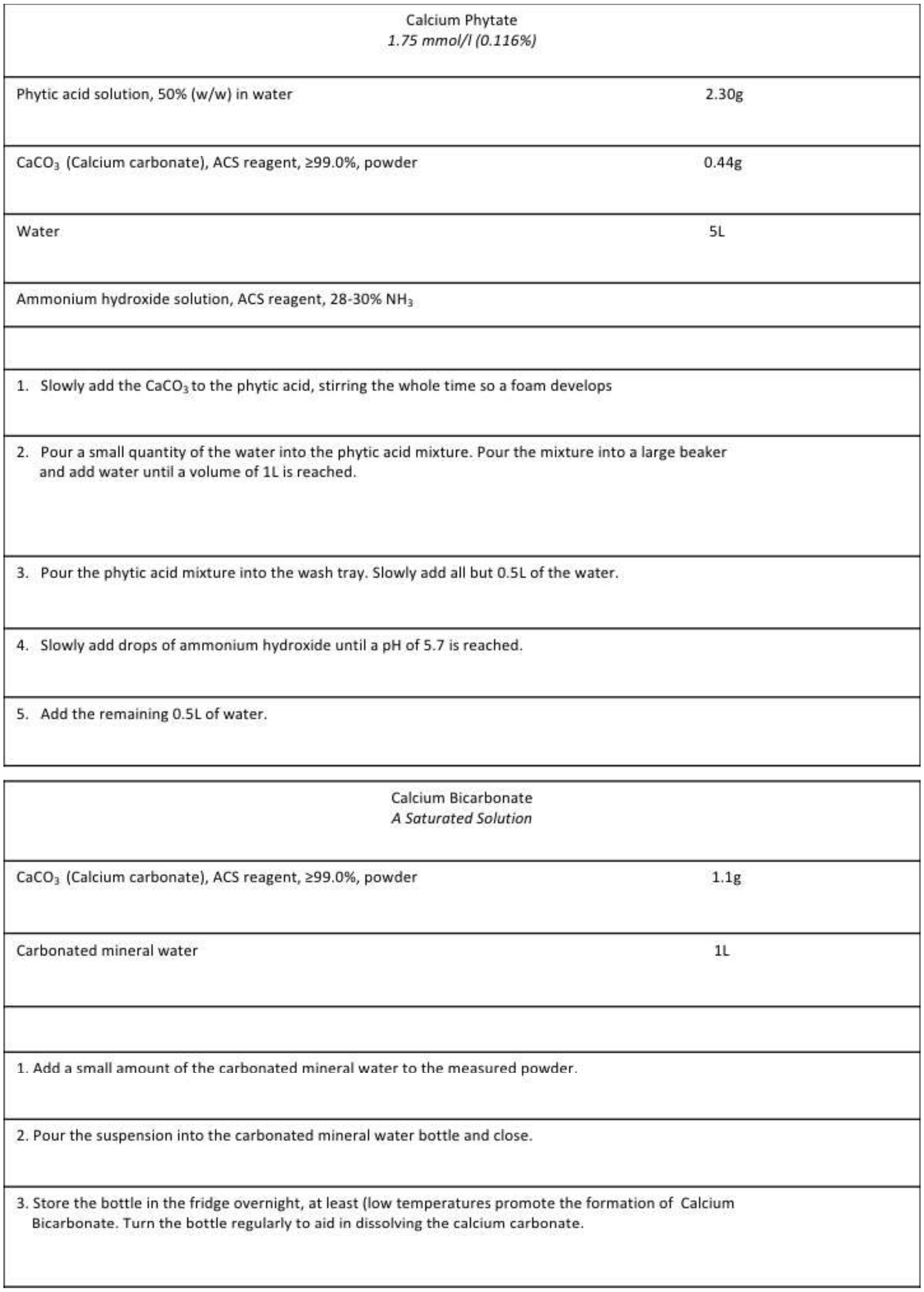
7.1.1 Tap Water

In the treatment of iron gall ink corrosion on paper, the use of tap water is recommended because the salts present in the water reduce the risk of ink bleeding and removal of desirable alkaline components in the paper (Albro et al. 2008). It is also readily accessible.

7.1.2 Deionized Water

In both paper and textiles, deionized water is the most effective in removing detrimental components, such as transition metal ions and sulfuric acid.

Fig. 5. Historical samples used in initial experiment.



Calcium Phytate *1.75 mmol/l (0.116%)*	
Phytic acid solution, 50% (w/w) in water	2.30g
$CaCO_3$ (Calcium carbonate), ACS reagent, ≥99.0%, powder	0.44g
Water	5L
Ammonium hydroxide solution, ACS reagent, 28-30% NH_3	
1. Slowly add the $CaCO_3$ to the phytic acid, stirring the whole time so a foam develops	
2. Pour a small quantity of the water into the phytic acid mixture. Pour the mixture into a large beaker and add water until a volume of 1L is reached.	
3. Pour the phytic acid mixture into the wash tray. Slowly add all but 0.5L of the water.	
4. Slowly add drops of ammonium hydroxide until a pH of 5.7 is reached.	
5. Add the remaining 0.5L of water.	

Calcium Bicarbonate *A Saturated Solution*	
$CaCO_3$ (Calcium carbonate), ACS reagent, ≥99.0%, powder	1.1g
Carbonated mineral water	1L
1. Add a small amount of the carbonated mineral water to the measured powder.	
2. Pour the suspension into the carbonated mineral water bottle and close.	
3. Store the bottle in the fridge overnight, at least (low temperatures promote the formation of Calcium Bicarbonate. Turn the bottle regularly to aid in dissolving the calcium carbonate.	

Fig. 6. Calcium phytate and calcium bicarbonate recipes.

7.1.3 Prespraying With Ethanol

In the treatment of iron gall ink corrosion on paper, ethanol is used to help wet out paper. Severely degraded areas in the substrate are hydrophobic while adjacent areas are usually hydrophilic. Because ethanol has a much lower surface tension than water and restricts expansion, it causes far less stress on substrates as it is absorbed (Albro et al. 2008). Prespraying was followed by submersion in the calcium phytate bath prepared with deionized water.

7.1.4 3:1 Deionized Water: Ethanol

Ethanol-modified baths are used both to aid in wetting out the substrate and in the treatment of water-soluble components that are insoluble in ethanol (Albro et al. 2008).

7.2 EXPERIMENTAL PROCEDURE

Two samples of each of the seven textile fragments were placed in each of the four bath variations. The baths were covered with Mylar to limit reaction with atmospheric oxygen, and the samples were left for 20 minutes. Upon removal, the samples were blotted of excess solution and placed in the prepared calcium bicarbonate solution. The baths were again covered with Mylar and left for 20 minutes. After removal, they were again blotted of excess solution. One sample from each bath variation was dried in ambient conditions and the other on the suction table.

8. ARTIFICIAL AGING

A strip (4 × 7.5 cm) of each test sample and control were artificially aged for 19 days at 80°C and 60%RH. Without access to an environmental chamber that can control relative humidity, the samples were instead aged within a sealed enclosure containing a small amount of water. Pretesting with 10%RH to 100%RH indicator cards indicated that, at 80°C, a relative humidity of 60% could be reached in a sealed 50-mL test tube containing a 0.25-g sample by adding 0.03 mL of tap water to the bottom of the test tube.[2] Each sample was suspended from a slit in the test tube stopper by a cotton thread stitched through the top of the sample. The stoppers were wrapped with Teflon tape and held down with blue board and Velcro to minimize the possibility of the stoppers popping out during aging (fig. 7). The samples were aged for a total of 19 days, testing the surface pH and iron(II) ion presence after 5, 12, and 19 days. The water in each test tube was reset during testing.

Fig. 7. Artificial aging setup.

9. RESULTS

The efficacy of the treatments were evaluated through free iron(II) ion presence, pH value, comparative observation of treated and untreated sample fibers under stereoscopic microscope, and tactile comparison. The results are discussed next and seen in Table 1.

9.1 BATHOPHENANTHROLINE RESULTS

9.1.1 Distilled Water Rinse

The bathophenanthroline test paper indicated that, immediately after treatment, samples rinsed in distilled water tested negative for iron(II) ions. However, after aging, these samples tested positive for free iron(II) ions, with increasing color intensity after each week of aging.

9.1.2 Ethanol-Modified Phytate Baths/Suction Table Dried

Immediately after treatment, some of the samples treated with the ethanol-modified baths and/or dried on the suction table tested positive for free iron(II) ions in the Canadian Conservation Institute (CCI)-estimated 1 to 25 ppm range. However, these samples had originally tested in the CCI-estimated 50+ ppm range, showing that the treatment was successful in removing most, if not all, free iron(II) ions. Furthermore, the intensity of the results did not increase after aging.

9.1.3 Water Phytate Baths

Most promising, the bathophenanthroline test strips indicated that all of the samples treated with tap or deionized water bath variations that were subsequently dried at ambient room conditions tested negative for free iron(II) ions after both treatment and aging.

9.2 SURFACE PH RESULTS

The surface pH of all of the samples was tested before treatment, after treatment, and after aging. Prior to treatment and aging, the surface pH of the seven textiles ranged between 4 and 6. After treatment, the pH rose to between 5.5 and 7.0. After 19 days of aging, the samples treated with a distilled water rinse alone had a surface pH ranging between 3 and 5, while all of the treated samples ranged between 4 and 6.

It was found that drying the samples on the suction table resulted in a lower pH than drying at ambient room conditions. This suggests that the suction action pulls the alkaline buffer out of the textile substrate.

9.3 PHYSICAL EFFECTS

No variation of the phytate/bicarbonate treatment adversely affected the appearance of the dyes present in the samples beyond that commensurate with an aqueous treatment removing colored acidic degradation products.

There was very little appreciable change in the hand of the textiles after treatment in each of the bath variations. However, the samples of the most acidic textiles with the highest concentration of free iron(II) ions did become more supple. While each of the treated samples discolored slightly and became slightly less flexible with aging, the samples treated with only a distilled water rinse were far more brittle and discolored, and several developed areas of loss where the iron-tannate dye was present (fig. 8).

Table 1. Quantitative Results of the Different Types of Phytate Baths

Bath Type	Free Iron(II) Ions Before Aging	Free Iron(II) Ions After Aging	Surface pH After Treatment	Surface pH After Aging
Distilled water rinse (control)	No indication	7 positive indications: 1 ppm, 10 ppm, 25 ppm, 25 ppm, 25 ppm, 50+ ppm, 50+ ppm	Range: 4–6 Average: 4.64	Range: 3–5 Average: 3.86
Prepared with distilled water; air dried	No indication	No indication	Range: 6–7 Average: 6.57	Range: 4.0–5.5 Average: 4.86
Prepared with distilled water; suction dried	No indication	2 positive indications: 1 ppm, 1 ppm	Range: 6–7 Average: 6.29	Range: 4.5–6.0 Average: 5.07
Prepared with tap water; air dried	No indication	No indication	Range: 6–7 Average: 6.64	Range: 4.5–5.5 Average: 4.86
Prepared with tap water; suction dried	3 positive indications: 1 ppm, 1 ppm, 1 ppm	4 positive indications: 1 ppm, 1 ppm, 1 ppm, 1 ppm	Range: 5.5–7.0 Average: 6.36	Range: 4.0–5.5 Average: 4.64
Presprayed with ethanol; air dried	2 positive indications: 1 ppm, 10 ppm	2 positive indications: 1 ppm, 10 ppm	Range: 5.5-7.0 Average: 6.43	Range: 4–6 Average: 5.07
Presprayed with ethanol; suction dried	1 positive indication: 1 ppm	2 positive indications: 1 ppm, 10 ppm	Range: 6–7 Average: 6.5	Range: 4.5–5.0 Average: 4.93
Prepared with 3:1 distilled water: ethanol; air dried	2 positive indications: 1 ppm, 10 ppm	3 positive indications: 1 ppm, 10 ppm	Range: 6–7 Average: 6.79	Range: 5–6 Average: 5.14
Prepared with 3:1 distilled water: ethanol; suction dried	2 positive indications: 1 ppm, 1 ppm	2 positive indications: 1 ppm, 1 ppm	Range: 6–7 Average: 6.72	Range: 5–6 Average: 5.14

Although paper conservators have occasionally noted salt deposits forming on the surface of the ink and paper after treatment (Albro et al. 2008), no such deposits were visible on any of the samples when viewed under a stereomicroscope. No other change to the fibers was noted (fig. 9).

Fig. 8. Treated versus untreated samples, after aging.

Fig. 9. Sample textile, untreated control (left) and treated in a phytate bath with deionized water (right), under 100× magnification.

10. PRACTICAL APPLICATIONS

Following the initial experiment, the question of whether the treatment could be applied broadly to costumes and, more specifically, to materials other than cellulosic textiles was pursued. To this end, the treatment was tested on a 19th century printed dress and a silk-embroidered sampler, both belonging to the study collection of private individuals.

10.1 TREATMENT OF A PRINTED DRESS

The selected garment was a mid-19th century printed cotton and linen day dress severely altered for theatrical use (fig. 10). The brown dye in the print tested positive for iron(II) ions in the CCI-estimated 50+ ppm range. The nylon lace trim, rayon ties, and large brown tideline stains provided the opportunity to test how the treatment would affect a diverse combination of materials and stains.

Given the size of the dress, the strongly positive bathophenanthroline indication result, and the significant level of discoloration and staining, it was decided to first rinse the dress in three successive tap water baths. It

Fig. 10. Before and after images of the treated 19th century dress.

was reasoned that, in addition to the water-soluble staining, this would remove most of the soluble iron(II) ions, leaving only the water-insoluble iron(III) ions for the phytate to bind. A preparation of 20 L of calcium phytate/deionized water solution and 20 L of calcium bicarbonate solution was used on the dress in the same manner as outlined in section 7. Upon removal from the calcium bicarbonate bath, the dress was placed between lengths of muslin and left to dry in ambient conditions.

Fig. 11. Before and after images of the treated sampler.

After treatment, the surface pH of the dress rose from 5 to 6 and the bathophenanthroline indicator strips tested negative for free iron(II) ions. The associated metal hooks and eyes, nylon lace, rayon ties, and polyester Reemay sling did not react adversely to the treatment, and the hand of the main fabric was significantly improved. The treatment had no visible effect on the color of the other dyes in the print.

10.2 TREATMENT OF SAMPLER WITH IRON-TANNATE–DYED SILK

The sampler dates from the 1830s and consists of multicolored silk thread worked on a linen substrate (fig. 11). The brown thread tested positive for iron(II) ions in the CCI-estimated 50+ ppm range. A preparation of 1 L of calcium phytate/deionized water solution and 1 L of calcium bicarbonate solution was used on the sampler in the same manner as outlined in section 7. Upon removal from the calcium bicarbonate bath, the sampler was placed between muslin and left to dry in ambient conditions.

Following treatment, the surface pH rose from 5.0 to 6.5. However, bathophenanthroline test strips indicated that while there were no iron(II) ions present in some areas that had previously tested positive, in others free iron(II) remained in the CCI-estimated range of 25 to 50 ppm. While we surmise that this was because not enough phytate was present in the 1-L bath to complex all of the free iron(II) and iron(III) ions, it is also possible that the treatment is not fully effective on silk.

11. CONCLUSIONS

This experiment shows that the phytate-bicarbonate treatment is successful in removing iron(II) and binding iron(III) on historical textile. It further shows the treatment was most effective when the textile was prerinsed, the calcium phytate solution was prepared with tap or deionized water, and the textile was air dried. All samples are being preserved for continued monitoring for resurgence of free iron(II) and for salt deposit formation. Future experiments should include treatment effects on tensile strength, flexibility, extensibility, and brittleness, as well as effects to dyes' light sensitivity.

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NOTES

[1] Bathophenanthroline is the only nonbleeding indicator used to detect iron(II). Other commercial indicator papers that test for soluble iron salts all use water-soluble indicators.

[2] Standard humidity cards are best read at 75°F. When using the card at higher or lower temperatures, a temperature correction factor of 2.5%RH must be used for each 10°F from 75°F. At 176°F (80°C), there is therefore a 25%RH error in the indication spot, manifesting itself in a bluer or more violet color at the indication spot rather than a clear transition between blue and pink.

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SOURCES OF MATERIALS

Iron Gall Ink Test Paper
Preservation Equipment Ltd.
Vince's Rd
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Tel: +44(0) 1379 647400
https://www.preservationequipment.com/

Ethanol, 95+%, Pure Anhydrous, Denat. with up to 5% v/v Ether, Ammonium Hydroxide Solution, ACS Reagent, 28% to 30% NH3, Calcium Carbonate, ACS Reagent, ≥99.0%, Powder, Phytic Acid Solution, 50% (w/w) in Water
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