

**Where Archival and Fine Art Conservation Meet:
Applying Iron Gall Ink Antioxidant and Deacidification
Treatments to Corrosive Copper Watercolours**

Abstract:

Iron gall ink inherently accelerates both acid hydrolysis and oxidation of cellulose. Stabilization of ink-on-paper artifacts must therefore address both deacidification and application of antioxidants (chelating agents, radical scavengers or peroxide decomposers). Calcium phytate (CaP), a chelating agent for iron(II) ions, is coupled with calcium bicarbonate (CaB) deacidification in an effective treatment for corrosive iron gall inks; however, this treatment must be applied aqueously and does not address the corrosion caused by other transition metal ions present in the inks. A new treatment, involving peroxide decomposer tetra-butyl ammonium bromide (TBAB) coupled with deacidification, is emerging in the literature. TBAB is advantageous as it is not metal specific, and can be applied non-aqueously.

The effects of antioxidants have been well studied for use in archival conservation, but their use in fine art conservation has not been fully investigated. This research examined the effects of antioxidant treatments on metal gall inks and associated media found in fine art on paper. Ideally the fine art media could be safe during treatment, and perhaps even stabilized by the antioxidants. Two common copper-containing "problem" pigments (verdigris and azurite) were studied in a watercolour medium alongside samples of two laboratory prepared inks (pure iron gall ink and a mixed iron-copper gall ink). Accelerated aging allowed monitoring of the treatments over time. Results showed that all treatments produced initial colour changes in all four media. Under the studied aging conditions, verdigris stability was not greatly increased, but neither was it decreased relative to the untreated control. Generally, however, treatment enhanced the stability of the two inks and the azurite watercolours.

Introduction: Project Impetus and Scope

This paper is based on research conducted in my final year of studies in the Masters' of Art Conservation Program at Queen's University in Kingston, Ontario, Canada. The project began with a problem encountered during a summer internship at Library and Archives Canada: how does one treat corrosive iron gall ink inscriptions on the backs of watercolour paintings? Over the last ten to fifteen years, a great deal of research has been performed investigating the stabilization of iron gall ink with combined antioxidant and deacidification treatments. The calcium phytate (CaP) treatment has emerged at the forefront of these investigations.¹ Its effects have been well studied with regards to both the ink and its paper substrate for archival documents, but not as to the effects on other surrounding media found in fine art. The question of whether such treatments can be safely used for watercolours warrants further consideration.

In addition, there was the desire to investigate an exciting emerging treatment, tetra butyl ammonium bromide (TBAB). This antioxidant has the potential to affect positive change in corrosion caused not only by iron ions, but also by other transition metal catalysts, in particular copper induced corrosion. Copper corrosion actually links iron gall ink and watercolours quite closely. Copper ions are found in iron gall inks either as impurities in iron salts or in copper salts called for as individual ingredients in many historic recipes. Similarly in watercolours, several well known pigments, such as malachite, azurite and verdigris are copper-containing minerals. The least stable of these pigments, verdigris, exhibits well documented corrosion characteristics very similar to those of iron gall ink. The parallel nature of verdigris and ink degradation led to the idea that perhaps corrosive copper watercolours would not only be "safe" in iron gall ink treatments, but also stabilized by these same interventions.

Embarking on a project that takes archival treatments and applies them to fine art objects means that it is necessary to consider the differences in methodology. In archival conservation the ultimate goal is long-term stabilization in order to retain the information. In fine art conservation the artist's intent and the aesthetics of the object must play a much more vital role. Slight colour changes that may be acceptable in archival conservation become unthinkable in fine art conservation. So called "more invasive" bench treatments may be set aside in favour of more ideal storage and other preventative measures. In cases such as media corrosion, however,

¹ Neevel, J. G. 2002. (Im)possibilities of the Phytate Treatment of Ink Corrosion. In *Contributions to Conservation: Research in Conservation at the Netherlands Institute for Cultural Heritage (ICN)*. Eds. J. Mosk and N. Tennet. London: James & James Science Publishers. p. 84.

the necessity for stabilization is paramount to all objects lest they disintegrate beyond repair. The manuscript page below (see figure 1) suffers from both verdigris and ink corrosion. Such an artifact would benefit greatly if a successful antioxidant and deacidification treatment could be formulated for both inks and watercolours.



Figure 1: Recto and verso of a Haggadah manuscript page from Library and Archives Canada, showing both verdigris and ink corrosion (Acc # LOWY MS A229).

After establishing the basis for the research, the project aims were simply stated in the form of three questions:

- Can mixed media drawings that include both inks and watercolours be safely treated by iron gall ink treatments (that is without unacceptable change to the media)?
- Are corrosive copper watercolour pigments and iron gall inks stabilized by the same treatments?
- Ultimately, are TBAB and CaP treatments effective in fine arts settings?

The theoretical scope of the project is quite large, encompassing the application of several different antioxidant treatments to both inks and watercolours. The actual avenues of investigation were narrowed to two main paths:

- Testing the iron gall ink treatments on two copper watercolours (azurite and verdigris) to assess the potential for successful treatment – both aesthetically and in terms of stability.
- Further testing of the new emerging TBAB treatment on two laboratory prepared inks (one containing only iron, the other containing both iron and copper). TBAB treatment will be compared to the established CaP treatment. The testing of these inks will also serve as a comparison for the magnitude of colour change observed in the inks relative to the colour change seen in watercolours to help establish acceptable levels of change.

This paper will focus on the results from the first objective, touching only lightly upon the second objective. Despite this emphasis on the watercolours rather than the inks, the chemistry and composition of both media types will be discussed below. In trying to develop treatment

methodologies, it is important to understand the commonalities between the degradation of inks and the watercolours.

Materials: Properties, Composition and Chemistry

Watercolours

Watercolour paints consist of four main ingredients.^{2,3} A binder, usually gum arabic, also serves to increase the luster of the media. Next, the pigment imparts colour. Almost every known artist pigment (organic or inorganic, natural or synthetic) has been employed in watercolour paints. The right pigment to binder ratio (usually close to 1:1) is imperative for the correct working properties of the watercolours. Too much binder makes the paint glassy and likely to crack. On the other hand, too little binder leaves the pigments friable and vulnerable to flaking or abrasion. A third minor ingredient is a humectant, such as honey, sugar or glycerin. The humectant is a hydrophilic substance that allows the watercolour paints to be remoistened and reworked. The final common ingredient is ox gall, a natural wetting agent that breaks up particle agglomerates and helps the paint flow across the paper.

The two pigments chosen for this study are inorganic copper-containing pigments (see figure 2). Both verdigris, a green pigment, and azurite, a blue pigment, have been known since

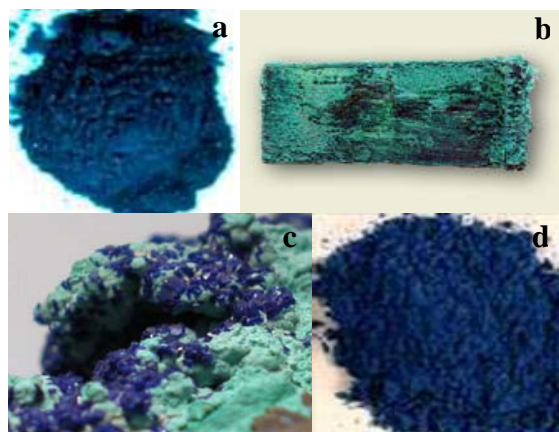


Figure 2: a powdered verdigris, b verdigris as a copper corrosion product, c azurite (blue) and malachite (green) minerals, d powdered azurite

medieval times, and have been employed in both manuscripts and paintings. The first pigment, verdigris, is a basic acetate of copper. This substance is a corrosion product of copper, and can be made by exposing metallic copper to vinegar (acetic acid) in the presence of oxygen.⁴ The pigment has been historically prepared in a number of ways, and takes numerous slightly different chemical forms with x, y and z forming various

² Cohn, M. B. 1977. *Wash and Gouache: A Study of the Development of the Materials of Watercolor*. Harvard University: The Centre for Conservation and Technical Studies, Fogg Art Museum and the Foundation of the American Institute for Conservation. p. 33.

³ Stephenson, J. 1984. Watercolour. *The Artist*. 99(4): 15.

⁴ Bhowmik, S.K. 1970. A Note on the Use and Deterioration of Verdigris in Indian Watercolour Painting. *Studies in Conservation* 12: p. 154.

ratios: $[\text{Cu}(\text{CH}_3\text{COO})_2]_x \cdot [\text{Cu}(\text{OH})_2]_y \cdot z\text{H}_2\text{O}$.⁵ Verdigris was historically one of the first green pigments and, despite being quite unstable, had very wide application.⁶ This green is known to cause paper degradation in a manner similar to iron gall ink. Initially, the pigmentation seems to migrate to the verso of the support, staining it green. Next, the paper becomes brown. This browning begins locally at the pigmented areas, but spreads as a halo. The green of the pigment decreases as the browning spreads, disappearing entirely after a time. The paper finally becomes so brittle that it fragments and perforates.⁷

The second pigment, azurite, is a natural mineral pigment. A blue basic copper carbonate, it is mined side by side with malachite (a green basic copper carbonate).⁸ Indeed, azurite exists in a reversible equilibrium with malachite. Unstable under atmospheric conditions, azurite slowly converts to malachite over time:⁹



Transition metal catalysis occurs in solution with moisture provided from the air. As azurite is much less soluble than verdigris, it is therefore less destructive as a catalyst. Not completely stable, copper carbonates are susceptible to acid attack and decompose upon heating.

Metal Gall Inks

Iron gall inks are made with three main ingredients.¹⁰ The first is a tannin source. Tannins are traditionally taken from the gall nut from an oak tree. Chemically, these tannins are a glucose structure with m-digallic acid groups rather than hydroxyl groups. In the ink formation reaction, the low pH levels result in hydrolysis of the tannins to produce the gallic acid that reacts to form the ink colourant. Modern ink recipes can simply start from purified tannic or gallic acids, rather than oak gall extracts. Next a metal source is needed. Typically iron(II) sulfate, called green vitriol, was used. This salt generally contains other metal impurities, such as copper or

⁵ Kuhn, H. 1993. Verdigris and Copper Resinate. In *Artists Pigments: A Handbook of Their History and Characteristics*. vol. 2, ed. A. Roy. New York: National Gallery of Art, Washington. Oxford U. Press. p. 133.

⁶ Gettens, R. J. and G. L. Stout. 1942. *Painting Materials: A Short Encyclopaedia*. New York, NY: Dover Publications. p. 169.

⁷ Mairinger, F, G. Banik, H. Stachelberger, A. Vendl and J. Ponahlo. 1980. The Destruction of Paper by Green Copper Pigments Demonstrated by a Sample of Chinese Wallpaper. In *Preprint of the Contributions to the Vienna Congress: Conservation within Historic Buildings*. 7-13 September 1980. eds. N. S. Brommelle, Garry Thompson, and Perry Smith. London, UK: ICOM. p. 181.

⁸ Hagadorn, A. 2004. An Investigation into the Use of Blue Copper Pigments in European Early Printed Books. *The Book and Paper Group Annual*. 23: 42.

⁹ Banik, G. 1989. Discoloration of Green Copper Pigments in Manuscripts and Works of Graphic Art. *Restaurator*. 10: 69.

¹⁰ Krekel, C. 1999. Chemistry of Historical Iron all Inks: Understanding the Chemistry of Writing Inks Used to Prepare Historical Documents. *International Journal of Forensic Document Examiners* 5. p. 55.

manganese. In addition, many recipes call for copper(I) sulfate, or blue vitriol.¹¹ Finally, gum arabic from the acacia tree acts as a binder for insoluble particles. The gum also modifies the viscosity of the ink to produce optimal flow for writing or drawing.

To understand what it is about iron gall ink that is corrosive, it is necessary to understand how the ink colourant is formed. It is also important to note that not all iron gall inks are unstable. The right ratio of iron to tannin (3.6:1) produces a balanced ink.¹²

The formation of the ink colourant is a two step chemical process.¹³ In the first step, iron(II) sulfate reacts with gallic acid to produce a colourless, soluble iron(II) gallate complex. Secondly, oxidation (reaction with atmospheric oxygen) forms an iron(III) gallate complex. This final compound is insoluble and coloured (initially a blue-black colour). This chemistry is illustrated in the reaction scheme in figure 3 below.

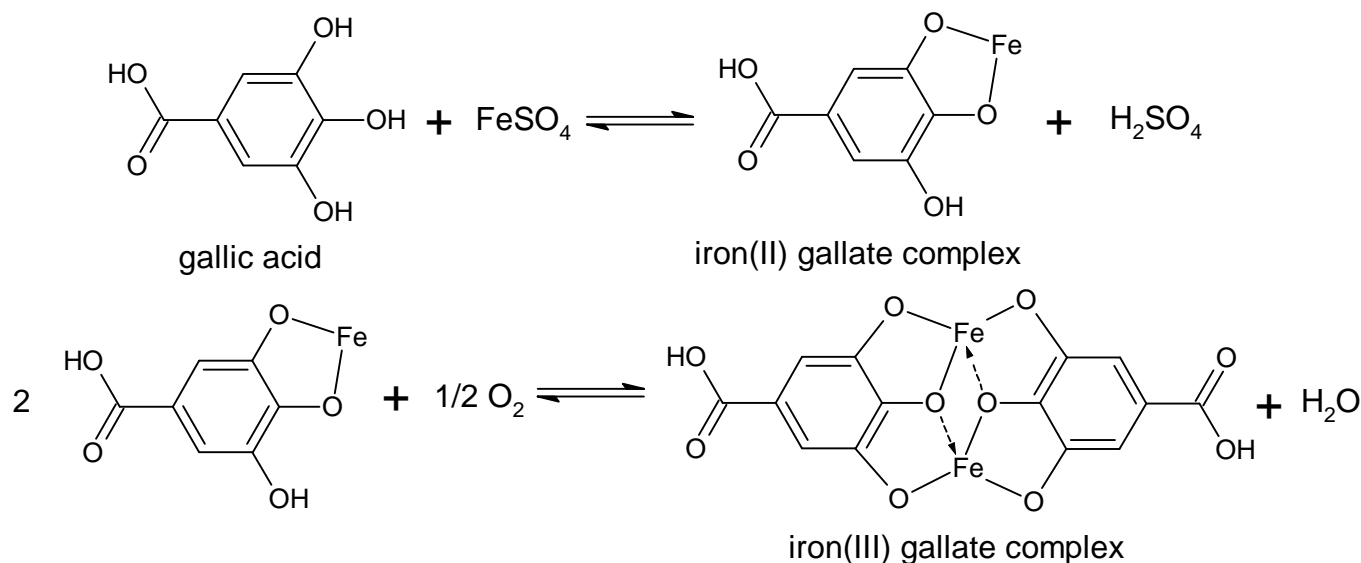


Figure 3: Reaction scheme for the formation of the black iron(III) complex from the colourless iron(II) complex.

Ink degradation occurs by two main mechanisms, the first of which is acid catalyzed hydrolysis. Here, sulfuric acid (a bi-product in the first step of the ink colourant formation reaction), as well as other acids such as wine or vinegar found in ink recipes, break down not only the cellulose (resulting in a decreased degree of polymerization by breaking the glycosidic bond) but also the ink colourants themselves. As the ink breaks down, phenolic degradation

¹¹ Recipe by Ribeaucourt (1792): 2 oz. galls, 1 oz. ferrous sulphate, 0.25 oz. copper sulphate, 1 oz. gum, 1 oz. logwood, 24 oz. water. Retrieved from Fig. 2 in Banik, 1997, p. 21.

¹² Banik, G. 1997. Decay Caused by Iron-gall Ink. *Iron-gall Ink Corrosion: Proceeding European Workshop on Iron-gall Ink Corrosion*. June 16-17, 1997. Amsterdam: Netherlands Institute for Cultural Heritage. p. 22.

¹³ Krekel, 1999, p. 56.

products (see figure 4) result in the brown colour associated with iron gall ink.¹⁴ These brown coloured molecules are slightly soluble, and may cause halting during aqueous treatment.

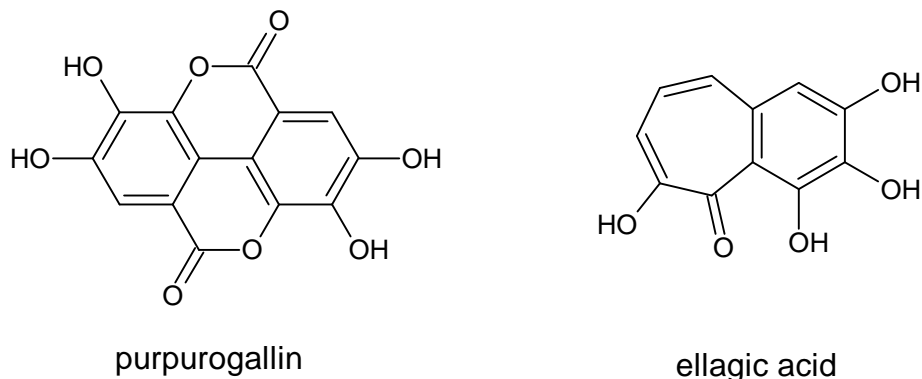


Figure 4: Chemical structures of oxidative iron gall ink degradation products.

The second form of degradation comes from oxidation reactions. Soluble iron(II) ions catalyze two separate processes, shown in figure 5.¹⁵ Focusing on the R groups in the reaction scheme, one can see the breakdown of cellulose to produce the bolded organic radicals and peroxides. The formation of these highly reactive species results in a decreased degree of cellulose polymerization. In the second reaction (the so-called Fenton reaction) the key molecule is the bolded hydroxyl radical. The hydroxyl radical is a highly reactive species; it has the ability to extract a hydrogen atom off of almost any molecule, while propagating the chain reaction of radical production.

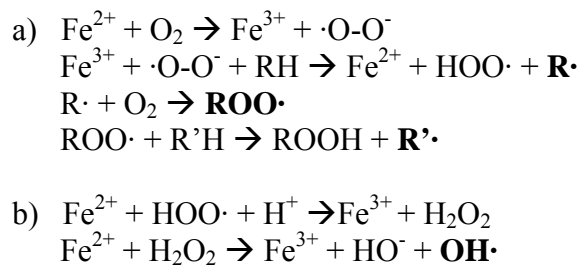


Figure 5: The oxidative degradation of cellulose catalyzed by iron(II): **a)** the direct production of organic radicals and their subsequent oxidation, **b)** the Fenton reaction, or the production of hydrogen peroxide and its decomposition to a hydroxyl radical and a hydroxide ion

¹⁴ Krekel, 1999, pp. 54-55.

¹⁵ Neevel, Johan G. 1995. Phytate: A Potential Conservation Agent for the Treatment of Ink Corrosion Caused by Iron Gall Inks. *Restaurator* 16: pp. 145-146.

Looking at figure 5 it is important to realize that any metal with multiple oxidation states can also act as catalysts in these reactions. Copper, chromium, manganese and other transition metals are therefore also detrimental catalysts. In particular, copper has a higher catalytic activity than iron, especially under alkaline conditions.¹⁶

Preservation Methodology

Conservation of iron gall ink has developed over the last 100 years into a three pronged approach.¹⁷ Antioxidant treatments are used to either deactivate transition metal catalysts or to interrupt the catalytic cycle by destroying peroxides or capturing radicals. Deacidification is employed to neutralize sulfuric acid, as well as other organic acids. Finally, physical reinforcement, generally with Japanese tissue, is often required to strengthen the now brittle paper substrate.

Another consideration in forming a preservation methodology is the issue of aqueous versus non-aqueous treatments.¹⁸ Aqueous treatments offer all of the benefits found in washing paper from removal of degradation products to reformation of cellulose hydrogen bonds. The swelling of paper fibers, however, is a double-edged sword. While swelling encourages penetration of antioxidant and deacidification agents into the paper fibers, it also introduces dimensional stress. The degraded areas of the ink line are more hydrophobic than the surrounding paper, leading to differential wetting and added stress. Aqueous treatments also pose problems for soluble media, and objects like books where aqueous treatment is all but impossible without rebinding. Non-aqueous treatments offer none of the benefits of washing, but pose little risk of dimensional stress or bleeding of media. Additionally, media colour change is likely to be smaller with non-aqueous treatments.

Antioxidants

Two classes of antioxidants can combat the destructive effects of the reactions shown in figure 5.¹⁹ Preventative antioxidants remove or incapacitate the transition metal catalysts. For instance,

¹⁶ Kolar, J. 2004. InkCor – Stabilisation of Iron Gall Ink Containing Paper. *ICOM – CC Graphic Documentation Meeting*. Ljubljana: ICOM. p. 21

¹⁷ Schäfer, I. 2004. Iron Gall Ink Corroded Autographs of the 18th and 19th Centuries: Conservation of Material Characteristics Versus Conservation Treatments. *Proceedings of the International Conference on Durability of Paper and Writing*. November 16-19. Ljubljana, Slovenia: MIP. p. 50.

¹⁸ Reissland, B. 1999. Ink Corrosion Aqueous and Non-Aqueous Treatment of Paper Objects – State of the Art. *Restaurator* 20: 167-180.

¹⁹ Malšič, J., J. Kolar, M. Struč and S. Polanc. 2005. The Use of Halides for Stabilisation of Iron Gall Ink Containing Paper – The Pronounced Effect of Cation. *e-Preservation Science* 2: p. 14.

phytate is a preventative antioxidant for iron ions. On the other hand, chain-breaking antioxidants are not metal specific. Rather than targeting the metal catalysts, they act as peroxide decomposers or radical scavengers removing the propagating species from the catalysis reactions. TBAB is an example of a peroxide decomposer, while lignin can act as a radical scavenger.

Phytate (myo-inositol hexakisphosphate) treatment is perhaps the most well researched antioxidant treatment. Salts of phytic acid coordinate with iron(II), blocking the coordination of peroxide, and preventing the propagation of the Fenton reaction.²⁰ Phytate treatments have been established as an effective method for archival conservation. Studies state that, when coupled with deacidification, phytate treatment theoretically doubles the lifetime of iron-containing paper.²¹ However, this treatment is only really effective aqueously, as it relies heavily on washing the iron-phytate complex out of the paper. Additionally, it only coordinates iron(II) ions. This leaves other transition metal catalysts unaffected and still causing damage.

Tetrabutyl ammonium bromide (TBAB) acts as a chain breaking antioxidant.^{22,23,24} It is the halide, experimentally shown as more effective when coupled with a large cation, that causes peroxide decomposition.²⁵ TBAB is advantageous in that it is not metal specific, while also being effective when applied non-aqueously.²⁶ However it is still a very new treatment, and does not have a proven track record.

Deacidification

The deacidification treatment used with iron gall ink is calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$ or CaB) as it maintains a relatively neutral pH throughout treatment. Too high a pH leads to other alkaline mechanisms of ink degradation. The pH tolerance of the pigments must also be considered. Deacidification is therefore done for the benefit of the cellulose, at the possible detriment of the colouring matter.

²⁰ Neevel, 2002, p. 76.

²¹ Kolar, J, M. Strlič, M. Budnar, J. Malešič, V. S. Šelih, and J. Simčič. 2003. Stabilisation of Corrosive Iron Gall Inks. *Acta Chim. Slov* 50: 756.

²² Malšič, J., J. Kolar, M. Struč and S. Polanc. 2005. The Use of Halides for Stabilisation of Iron Gall Ink Containing Paper – The Pronounced Effect of Cation. *e-Preservation Science* 2: 13-18.

²³ Kolar *et al.*, 2003, pp. 763-770.

²⁴ Kolar, J, J. Malešič, and M. Strlič. 2005. Antioxidants for Stabilization of Iron Gall Ink Corrosion. *ICOM Committee for Conservation Preprints*. 14th Triennial Meeting, The Hague: 12-16 September, 2005. London: James & James. pp. 186-192.

²⁵ Malšič *et al.*, 2005, p. 15.

²⁶ Kolar, *et al.*, 2003, p. 767.

Experimental: Sample Preparation, Treatment and Analysis

Sample Preparation

Laboratory samples (see figure 6) were prepared of two ink formulations and two watercolour paints of different pigmentation. The inks were corrosive formulations. Ink 1 was an iron gall ink (5.5:1 iron to tannin ratio), while ink 2 was an iron/copper gall ink (5.5:1 metal to tannin ratio, 0.7:1 copper to iron molar ratio). The watercolours were made from two unstable copper pigments, verdigris (basic copper acetate) and azurite (basic copper carbonate). Whatman filter paper no. 1 (86.0g m^{-2} , DP: 2630, RSD 0.74%), a pure un-sized cellulose cotton linter formation, was chosen to ensure that interactions with fillers or additives present in other papers would not skew the results of the study.

Each sample consists of a row of five circles of 2.5cm diameter, spaced apart by 1cm. The paper of the sample is held sandwiched between a 4-ply mat board window (with 1cm wide edges) on the verso and four strips of 1cm wide 4-ply mat board on the recto held in place by mini binder clips. This frame served to keep the samples from cockling while they were created and aged. A Mylar® template of the sample layout was prepared with voids cut out at each of the sample circle positions to ensure the spacing and size was consistent between samples. A constant volume of ink and constant mass of watercolour was transferred to each circle with an Eppendorf pipette and a synthetic paintbrush respectively. The five circles allowed for three locations for colour measurements and two locations for pH measurements.

The samples were aged prior to treatment, to simulate old artifacts, at approximately 75%RH and 55°C in a Despatch LEA 1-69 oven for four and a half days. After treatment the samples were submitted to twelve days of accelerated aging at 65%RH and 80°C to monitor the effects of the treatments over time.

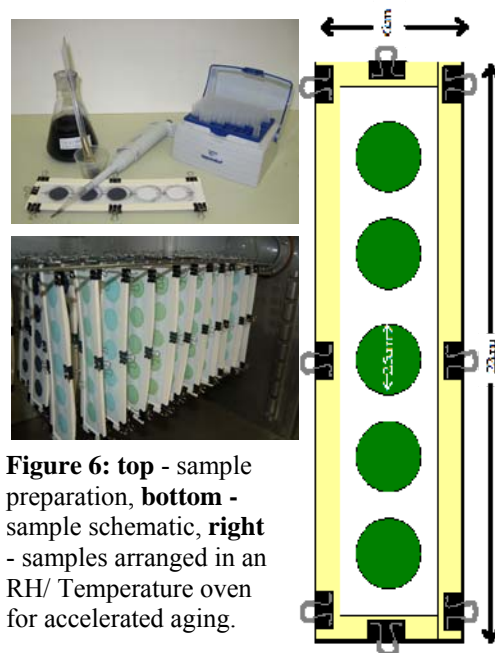


Figure 6: top - sample preparation, bottom - sample schematic, right - samples arranged in an RH/ Temperature oven for accelerated aging.

Antioxidant and Deacidification Treatments

Ten samples of each of the four media types were prepared to allow for several treatment groups, as well as the necessary controls. Note that, unless specified, each sample received both pre-treatment and post-treatment aging. The sample groups are as follows:

- No treatment and no aging
- Pre-treatment aging only (no treatment, no post-treatment aging)
- Pre-treatment and post-treatment aging (no treatment)
- CaP (20 min immersion), CaB (20 min)
- TBAB (20 min), CaB (20 min)
- Water immersion control (40 min)
- TBAB in ethanol (20 min)
- Ethanol immersion control (20 min)
- CaB (20 min)
- Water immersion control (20 min)

CaP was prepared by the following recipe, outlined below for the preparation of 500mL of 1.75mmol/L CaP (equivalent to 0.116% phytic acid):²⁷

- 1.44g 40% phytic acid solution was weighed into a beaker using a pipette
- 0.22g CaCO₃(s) was slowly added, stirring with a glass rod to make a homogeneous paste. Note that CO₂(g) evolved from the paste.
- Approximately 50mL of distilled water was used to dissolve the paste; distilled water was added to make a total volume of 450mL.
- While stirring and monitoring the pH, approximately 4mL ammonia water (1.25%) was added to turn the solution slightly turbid and reach a pH between 5.5 and 6.0.
- Water was added to make the total volume 500mL, ensuring that the pH remained between 5.5 and 6.0.

For the preparation of CaB (Ca(HCO₃)₂), half a litre of a saturated solution at pH 5.88 can be prepared by bubbling CO₂(g) through a mixture of 0.55g CaCO₃ in 500mL distilled water while stirring.²⁸

TBAB was used both aqueously and non-aqueously. The aqueous treatment was a 0.03mol/L solution prepared with distilled water. The non-aqueous treatment was prepared at a concentration of 0.03mol/L in ethanol

²⁷ Neevel, H. and B. Reissland. *Calcium Phytate: Recipe for Preparing an Aqueous Solution for the Chelate Treatment of Ink Corrosion*. Instituut Collectie Nederland (ICN), laboratory handout.

²⁸ Neevel, H. *Calcium Bicarbonate: Recipe for Preparing an Aqueous Solution for the Deacidification Treatment of Ink Corrosion*. Instituut Collectie Nederland (ICN), laboratory handout.

Instrumentation and Analysis

Among other analyses, pH measurements and colourimetry were employed to compare the various treatments. A ROSS Ultra flat surface pH electrode was used for both surface pH and cold extraction measurements. Using the L*a*b* colour space, a Minolta Chroma Meter CR-300 colourimeter was used to record and average three colour readings at each of three locations per sample. These readings were recorded after pre-aging, after treatment and after day one, day three, day six and day twelve of post-treatment aging.

Results and Discussion

Colourimetry

The colourimetry results (see figure 8, page 14) are perhaps easiest to digest and visually comprehend by looking at what happens to the paper support. Qualitatively, this is done by looking at the browning of the support around each media circle. The conclusions drawn from this qualitative analysis are as follows:

- With simple water washing, soluble transition metal ions are spread through the paper.²⁹
- CaB is slightly better, as it hinders acid hydrolysis, but not oxidative degradation.³⁰
- CaP with CaB treatment is effective, but only completely for the pure iron gall ink (ink1). For the watercolours and the mixed metal ink, it is either partially effective (ink 2) or not effective at all (both copper pigments).³¹
- Both non-aqueous and aqueous TBAB treatments are quite effective at preventing discolouration from spreading through the paper with treatment; best results are with non-aqueous treatment. This of course does not equate to stabilization, as illustrated by examining the last sample (the post-treatment aged sample). This sample underwent both pre- and post-treatment aging with little browning of the paper support. These results therefore simply indicate that TBAB treatments are safe to use. TBAB treatments seem to counter the effects of any ions that they spread throughout the paper.³²

²⁹ The spread of ions is seen by the brown colouration that covers the paper after aging. This is compared to the untreated control, where the paper remains white with aging.

³⁰ In the CaB samples, the browning is less intense than in the water immersion controls, as acid hydrolysis is limited by the neutralized pH levels.

³¹ The efficacy of this treatment is judged on the degree of browning in the paper. For ink 1, the paper remains white, indicating that CaP/CaB works. For ink 2, the browning is less than that seen in the washing controls. For azurite and verdigris, the washing controls and the CaP/CaB brown discolourations are at the same level.

³² Both TBAB treatments prevent any brown discolouration from spreading to the paper support.

The total colour change (ΔE^*) is considered perceptible to the human eye if greater than one. An optimal treatment would have an initial colour change less than one, indicating that treatment does not change the appearance of the object. As the object ages, an optimal treatment would also prevent drastic colour change, indicating that oxidation and hydrolytic pathways had been effectively slowed or blocked. For azurite (see figure 9, page 15) it can be seen that the best treatment, in terms of ΔE^* , is $TBAB_{(EtOH)}$. This treatment has very little initial colour change with treatment, as well as an almost flatline rate of colour change over time.

For verdigris (see figure 10, page 15), however, while both TBAB treatments ($TBAB_{(EtOH)}$ and $TBAB/CaB$) cause little initial colour change in treatment, there is drastic colour change on days one through three of aging. It is possible that this dramatic colour change is not due to oxidation by reactions mechanisms that produce peroxides (and hence are unaffected by the presence of TBAB). The colour change could instead be associated with oxidation of the pigment to various copper oxides; the reaction rates of such pathways were likely increased by the high levels of heat used in the accelerated aging regimes.

Watercolour Surface pH

While figure 7 below displays the results for azurite, very similar results were also obtained for verdigris. The surface pH readings show that initially, after treatment, CaB treatments are the most effective at creating an alkaline pH. However, in time, the TBAB treatments seem to be the most effective at maintaining a near neutral pH.

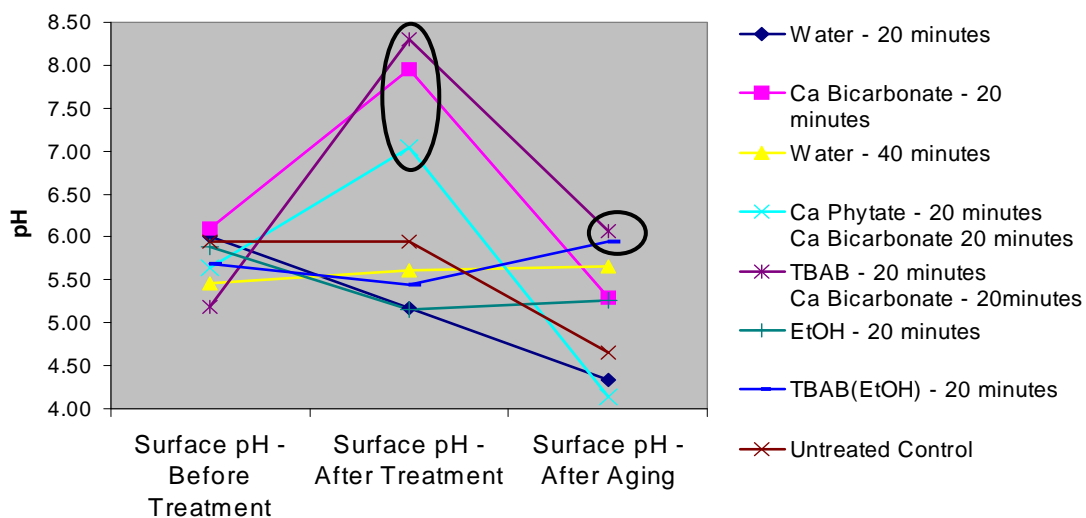
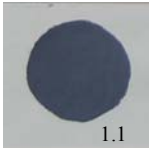
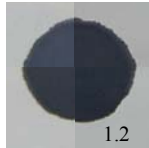
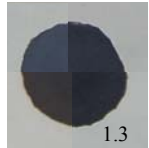
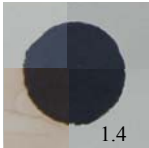
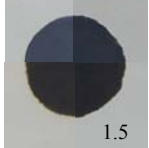
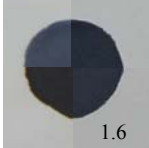
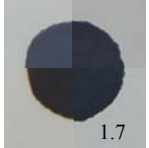
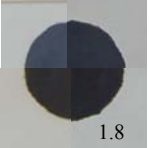
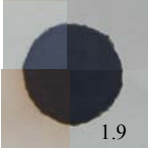
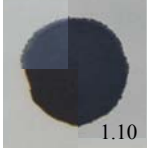
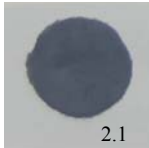
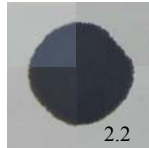
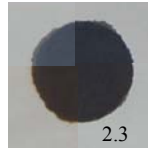
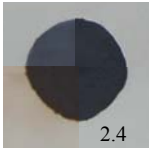
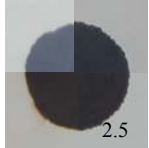
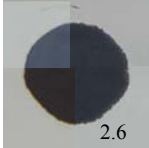
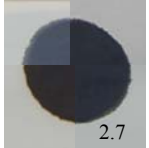
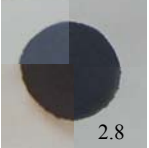
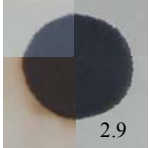
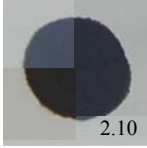
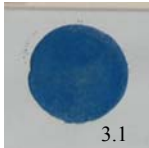
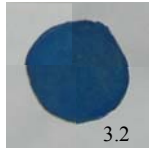
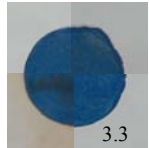
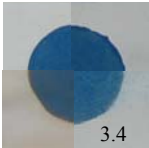
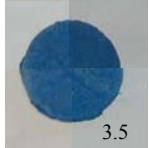
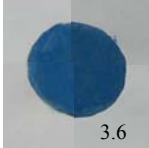
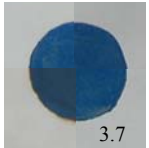
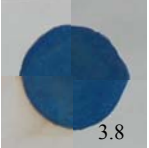
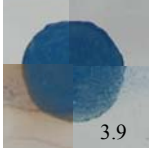
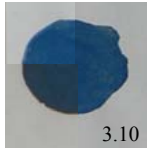
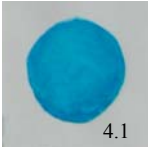
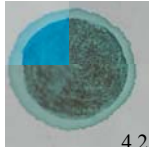
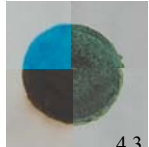
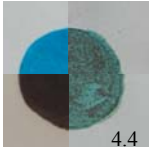
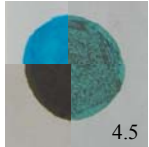
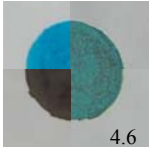
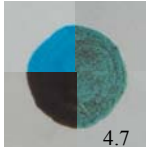
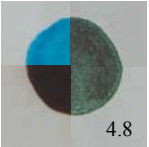
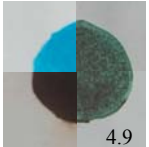
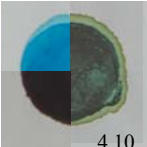


Figure 7: Surface pH readings for azurite recorded before treatment (after pre-treatment aging), after treatment and after twelve days of post-treatment aging.

	Un-aged Control	Pre-aged Control	CaP & CaB	H ₂ O 40 min	TBAB & CaB	TBAB in EtOH	EtOH	CaB	H ₂ O 20 min	Untreated Control
Ink 1 Fe Gall	 1.1	 1.2	 1.3	 1.4	 1.5	 1.6	 1.7	 1.8	 1.9	 1.10
Ink 2 Cu/Fe Gall	 2.1	 2.2	 2.3	 2.4	 2.5	 2.6	 2.7	 2.8	 2.9	 2.10
Azurite	 3.1	 3.2	 3.3	 3.4	 3.5	 3.6	 3.7	 3.8	 3.9	 3.10
Verdigris	 4.1	 4.2	 4.3	 4.4	 4.5	 4.6	 4.7	 4.8	 4.9	 4.10

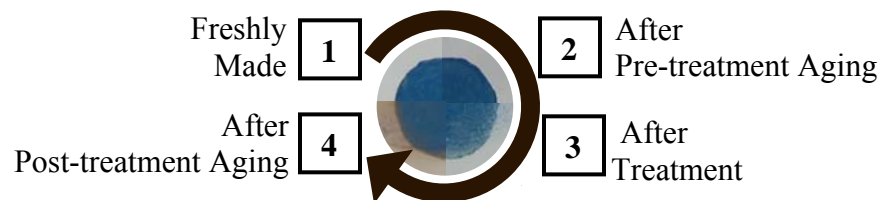


Figure 8: Composite photographs of one spot on each sample compiled from photographs taken when the samples were 1) freshly made, 2) after pre-treatment aging, 3) after treatment and 4) after 12 days of post-treatment aging (see the visual key just above). These photographs qualitatively demonstrate what happens to both the media and to the paper substrate over time.

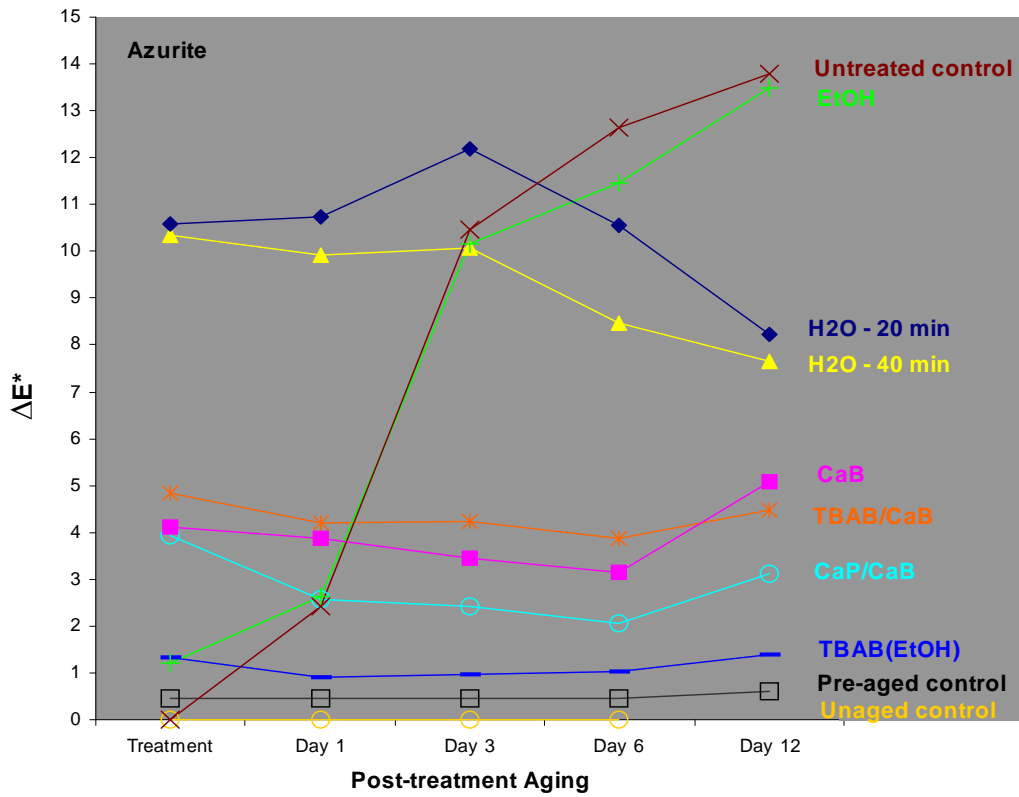


Figure 9: Total colour change (ΔE^*) after treatment and over the course of post-treatment aging for azurite.

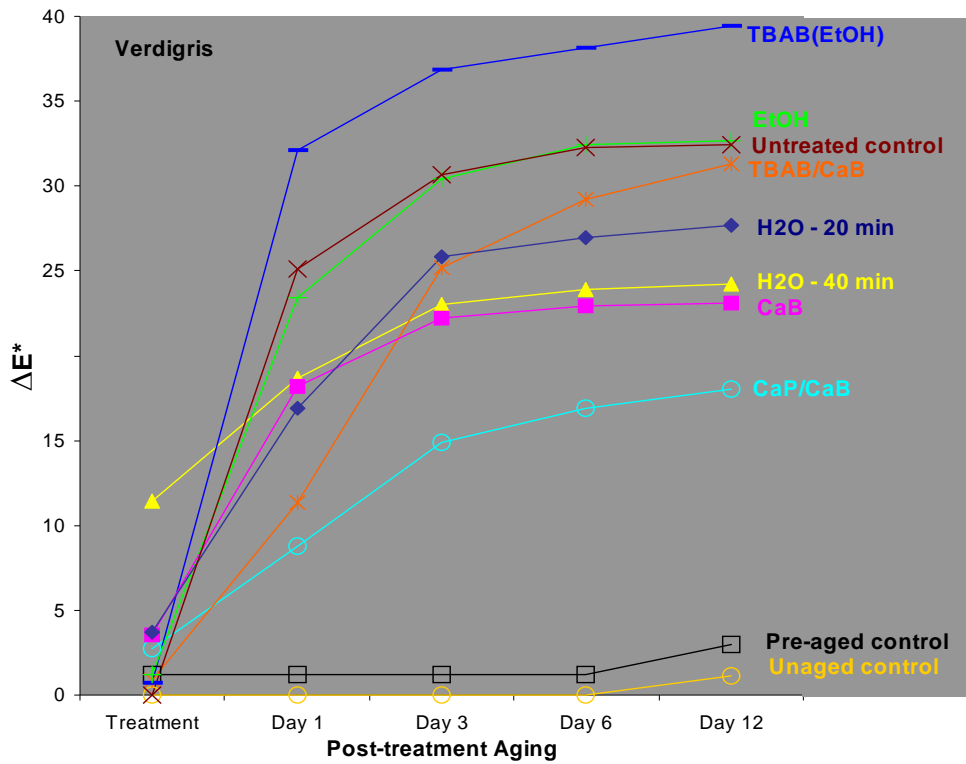


Figure 10: Total colour change (ΔE^*) after treatment and over the course of post-treatment aging for verdigris.

Conclusions

The project began with an outline of three questions. The first of these questions was whether watercolours can be safely treated by iron gall ink antioxidant treatments. To be “safe” a treatment should not alter the media by changing it physically or chemically. While all of the antioxidant and deacidification treatments produced an initial colour change in all of the media, over the course of aging, they each showed drastic improvement over no treatment at all. In proceeding with treatment, the conservator is therefore presented with some choices. After spot testing to ensure that the media is stable, the first choice is aqueous or non-aqueous treatment. With non-aqueous treatment, there is less colour change in the media; however, aqueous treatment is much more beneficial to the paper. The conservator must then decide if this initial colour change is acceptable for fine art conservation. This is a question of short-term change for long-term stability, and must be judged on a case by case basis.

The second question posed by this research was whether corrosive copper watercolours could actually be stabilized by the same antioxidants as iron gall inks. From the surface pH it was shown that initial stability (judged by a neutral pH) was achieved by all CaB treatments. Over time, however, it is the TBAB treatments (with or without deacidification) that show the greatest promise in maintaining neutral pH levels. Colourimetry on the recto of the samples showed that for azurite, while all antioxidant and deacidification treatments produced increased colour stability, TBAB in ethanol was the best treatment. The verso tells a different story. While the colour change on the verso was not quantitatively measured, qualitative analysis clearly shows that the treatment producing the most enhanced stability is TBAB/CaB (see figure 11). TBAB in ethanol produces the second most effective stabilization. For verdigris, results were not as promising. It may be that higher concentrations of antioxidants are required, or simply that thermal aging is not an accurate way to judge the long-term aging properties of verdigris samples.

Finally, the question of the efficacy of TBAB and CaP for fine art was posed. Experimental results demonstrate that for CaP combined with deacidification the pH remains higher than untreated samples. Over time, the media colour change is much less than untreated samples. From the colourimetric results, the aqueous nature of the treatment was confirmed to spread copper corrosion from the watercolour media to the surrounding paper. For TBAB, one can conclude that this treatment is effective in treating azurite. When comparing the verdigris results to the untreated control, it can at least be concluded that TBAB treatments caused no harm.

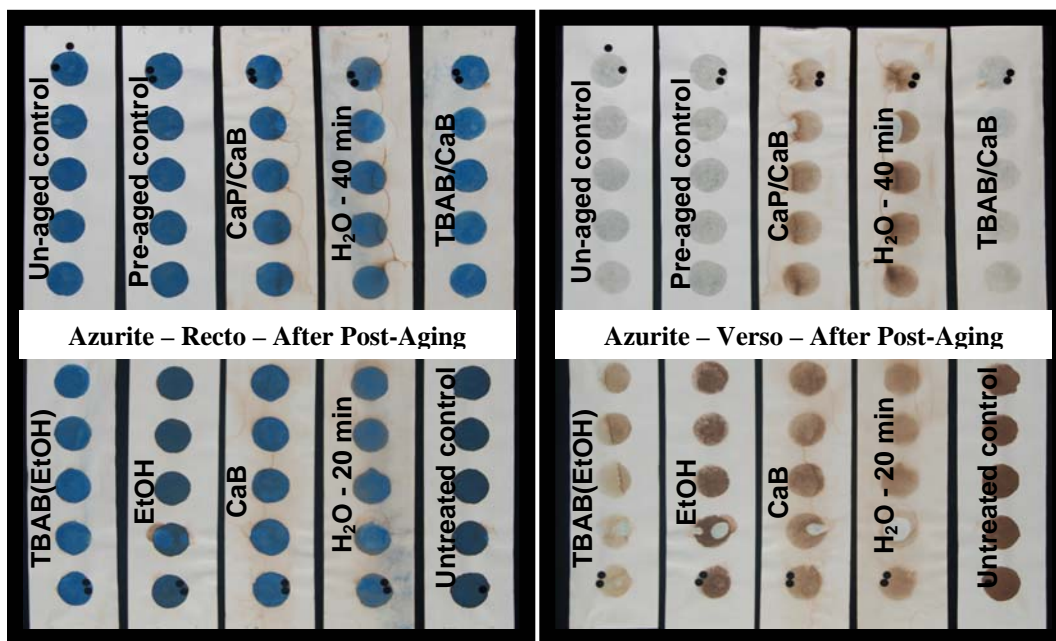


Figure 11: Photographs of each of the azurite samples, first recto then verso, after post-treatment aging. These photographs can be used to visually compare the difference between the unaged, treated and untreated samples.

Further Research

A project such as this tends to lead to many more avenues of investigation. It would be interesting to analyze the immersion baths for removed ions. Does the chelating treatment of phytate remove more ions than simply washing? Additionally, it would be very instructive to monitor the verso of the samples. As seen particularly with the azurite samples the verso gives a good indication of what is happening to the paper, rather than simply monitoring the media itself. Analyzing the paper for colour, pH, degree of polymerization and brittleness would be informative. Additionally, varying the concentration of TBAB in the treatment of the watercolours, while also using more dilute watercolours, would help to determine optimal treatment parameters.

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