

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

ABSTRACT

Iron-gall ink accelerates both acid hydrolysis and oxidation of cellulose. Stabilization of ink-on-paper artifacts must therefore use both deacidification and antioxidant treatments (chelating agents, radical scavengers, or peroxide decomposers). Calcium phytate (CaP), a chelating agent for iron (II), and calcium bicarbonate (CaB) is 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 in the inks. New antioxidant treatments, including peroxide decomposer tetra-butyl ammonium bromide (TBAB), are emerging in the literature. TBAB is advantageous, as it is not metal specific and can be applied non-aqueously.

Antioxidants have been studied primarily for use in archival conservation; 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 fine art media would be unaffected during treatment or perhaps even stabilized by the antioxidants. Two common copper-containing pigments (verdigris and azurite) were studied in a watercolor 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 color 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 watercolors.

INTRODUCTION: PROJECT IMPETUS AND SCOPE

This paper is based on research conducted in the final year of studies in the Master's of Art Conservation Program

Presented at the Book and Paper Group session, AIC 37th Annual Meeting, May 20–23, 2009, Los Angeles, California.

at Queen's University in Kingston, Ontario, Canada, completed in 2007. 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 watercolor 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 (Neevel 2002). 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 watercolors 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 watercolors 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 watercolors, 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 watercolors 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 color changes that may be acceptable



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

in archival conservation become unthinkable in fine art conservation. So called “more invasive” bench treatments may be set aside in favor of more ideal storage and other preventive measures. In cases such as media corrosion, however, the necessity for stabilization is paramount to all objects lest they disintegrate beyond repair. The manuscript page in 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 watercolors.

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 watercolors be safely treated by iron-gall ink treatments (that is, without unacceptable change to the media)?
- Are corrosive copper watercolor 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 watercolors. The actual avenues of investigation were narrowed to two main paths:

1. Testing the iron-gall ink treatments on two copper watercolors (azurite and verdigris) to assess the potential for successful treatment—both aesthetically and in terms of stability.
2. 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 would be compared to the established CaP treatment. The

testing of these inks would also serve as a comparison for the magnitude of color change observed in the inks relative to the color change seen in watercolors 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 the emphasis on the watercolors 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 watercolors.

MATERIALS: PROPERTIES, COMPOSITION, AND CHEMISTRY

Watercolors

Watercolor paints consist of four main ingredients (Cohn 1977; Stephenson 1984). A binder, usually gum arabic, also serves to increase the luster of the media. Next, the pigment imparts color. Almost every known artist pigment (organic or inorganic, natural or synthetic) has been employed in watercolor paints. The right pigment-to-binder ratio (usually close to 1:1) is imperative for the correct working properties of the watercolors. 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 watercolor 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.

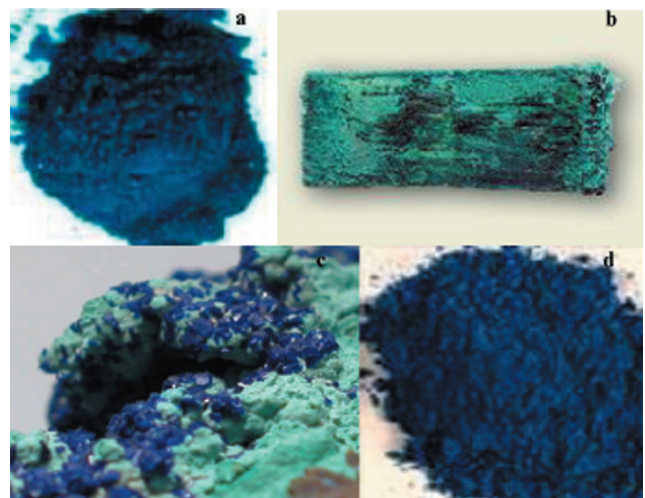


Fig. 2. a) powdered verdigris, b) verdigris as a copper corrosion product, c) azurite (blue) and malachite (green) minerals, and d) powdered azurite

The two pigments chosen for this study are inorganic, copper-containing pigments (fig. 2). Both verdigris, a green pigment, and azurite, a blue pigment, have been known since 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 (Bhowmik 1970). 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 ratios: $[\text{Cu}(\text{CH}_3\text{COO})_2]_x \cdot [\text{Cu}(\text{OH})_2]_y \cdot z\text{H}_2\text{O}$ (Kuhn 1993). Verdigris was historically one of the first green pigments and, despite being quite unstable, had very wide application (Gettens and Stout 1942). 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 (Mairinger et al. 1980).

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) (Hagadorn 2004). Indeed, azurite exists in a reversible equilibrium with malachite. Unstable under atmospheric conditions, azurite slowly converts to malachite over time (Banik 1989): $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (malachite) + $\text{CO}_2(g) \leftrightarrow 2\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ (azurite) + $\text{H}_2\text{O}(l)$. 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 (Krekel 1999). 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 colorant. 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 manganese. In addition, many recipes call for copper(I) sulfate, or blue vitriol.¹ 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 colorant 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 (Banik 1997).

The formation of the ink colorant is a two-step chemical process (Krekel 1999). In the first step, iron (II) sulfate reacts with gallic acid to produce a colorless, soluble iron (II) gallate complex. Secondly, oxidation (reaction with atmospheric oxygen) forms an iron (III) gallate complex. This final compound is insoluble and colored (initially a blue-black color). This chemistry is illustrated in the reaction scheme in figure 3.

Ink degradation occurs by two main mechanisms, the first of which is acid-catalyzed hydrolysis. Here, sulfuric acid (a byproduct in the first step of the ink colorant 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 colorants themselves. As the ink breaks down, phenolic degradation products (fig. 4) result in the brown color associated with iron-gall ink (Krekel 1999). These brown-colored molecules are slightly soluble, and may cause haloing during aqueous treatment.

The second form of degradation comes from oxidation reactions. Soluble iron (II) ions catalyze two separate processes, shown in figure 5 (Neevel 1995). Focusing on the R groups in the reaction scheme, one can see the breakdown of

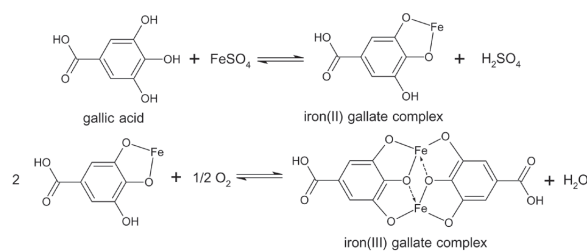


Fig. 3. Reaction scheme for the formation of the black iron (III) complex from the colorless iron (II) complex

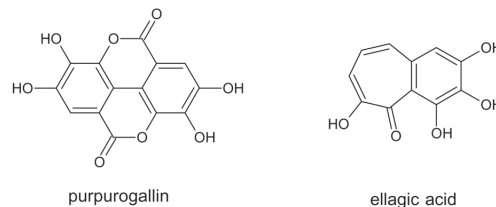


Fig. 4. Chemical structures of oxidative iron-gall ink degradation products

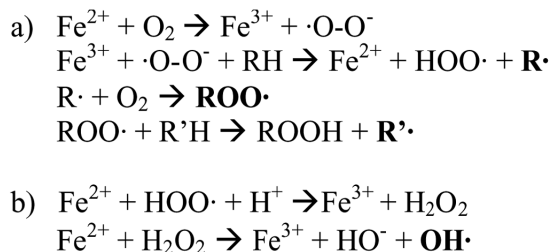


Fig. 5. The oxidative degradation of cellulose catalyzed by iron (II): a) the direct production of organic radicals and their subsequent oxidation, b) the Fenton reaction, or the production of hydrogen peroxide and its decomposition to a hydroxyl radical and a hydroxide ion

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.

Looking at figure 5 it is important to realize that any metal with multiple oxidation states can also act as a catalyst 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. At a pH of 8.0, copper is twenty times more effective a catalyst than iron, while at a pH of 9.0 its catalytic activity has increased to two hundred times that of iron (Kolar 2004).

Preservation Methodology

Conservation of iron-gall ink has developed over the last one hundred years into a three-pronged approach (Schäfer 2004). 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 (Reissland 1999). 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 color 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 (Malšič et al. 2005). Preventive antioxidants remove or incapacitate the transition metal catalysts and tend to be metal-specific. For instance, phytate is a preventative antioxidant for iron ions. Chain-breaking antioxidants, on the other hand, 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 (Neevel 2002). 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 (Kolar et al. 2003). 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 effectively coordinates iron (II) ions by blocking all coordination sites. Other transition metal catalysts are left active and are still able to cause damage.

Tetrabutyl ammonium bromide (TBAB) acts as a chain-breaking antioxidant (Kolar et al. 2005). It is the halide, experimentally shown as more effective when coupled with a large cation, that causes peroxide decomposition (Malšič et al. 2005). TBAB is advantageous in that it is not metal specific, while also being effective when applied non-aqueously (Kolar et al. 2003). However it is still a very new treatment and does not have a proven track record.

Deacidification

The deacidification treatment most commonly 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 coloring matter.

EXPERIMENTAL:

SAMPLE PREPARATION, TREATMENT AND ANALYSIS

Sample Preparation

Laboratory samples (fig. 6) were prepared of two ink formulations and two watercolor 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 watercolors 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, unsized, 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 2.5 centimeter diameter, spaced apart by 1 centimeter. The paper of the sample is held sandwiched between a 4-ply mat board window (with 1 centimeter-wide edges) on the verso and four strips of 1-centimeter-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 watercolor was transferred to each circle with an Eppendorf pipette and a synthetic paintbrush, respectively. The five circles allowed for three locations for color 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.

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 minute immersion), CaB (20 minutes)
- TBAB (20 minutes), CaB (20 minutes)
- Water immersion control (40 minutes)
- TBAB in ethanol (20 minutes)
- Ethanol immersion control (20 minutes)
- CaB (20 minutes)
- Water immersion control (20 minutes)

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) (Neevel and Reissland n.d.):

- 1.44g 40% phytic acid solution was weighed into a beaker using a pipette.
- 0.22g $CaCO_3(s)$ was slowly added, stirring with a glass rod to make a homogeneous paste. Note that $CO_2(g)$ evolved from the paste.
- Approximately 50 mL of distilled water was used to dissolve the paste; distilled water was added to make a total volume of 450 mL.
- While stirring and monitoring the pH, approximately 4 mL of 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 500 mL, ensuring that the pH remained between 5.5 and 6.0.

For the preparation of CaB ($Ca(HCO_3)_2$), half a liter of a saturated solution at pH 5.88 can be prepared by bubbling $CO_2(g)$ through a mixture of 0.55 g $CaCO_3$ in 500 mL distilled water while stirring (Neevel n.d.).

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 0.03 mol/L in ethanol.

Instrumentation and Analysis

Among other analyses, pH measurements and colorimetry were employed to compare the various treatments. A ROSS Ultra flat surface pH electrode was used for both

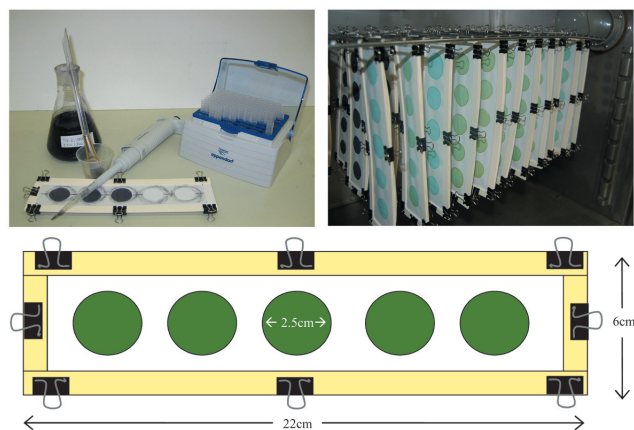


Fig. 6. Sample preparation (top left); samples arranged in an RH/temperature oven for accelerated aging (top right); sample schematic (bottom)

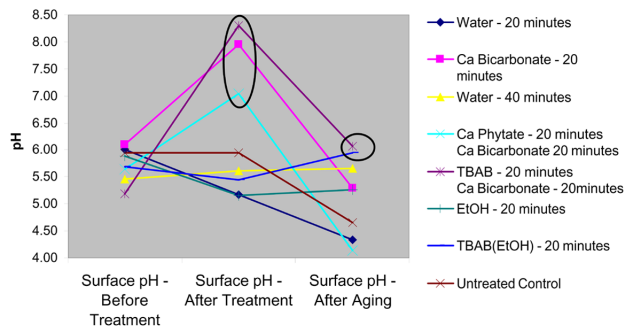


Fig. 7. Surface pH readings for azurite recorded before treatment (after pre-treatment aging), after treatment, and after twelve days of post-treatment aging

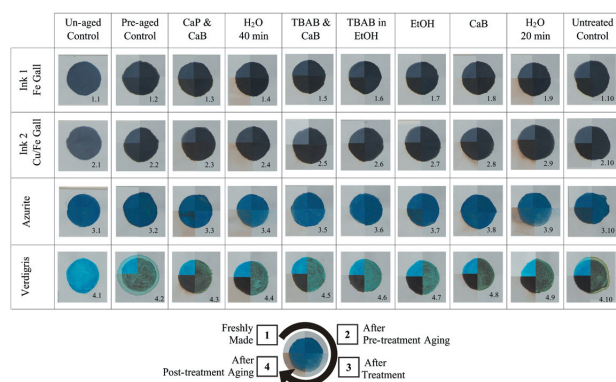


Fig. 8. Composite photographs of one spot on each sample compiled from photographs taken when the samples were: 1) freshly made, 2) after pre-treatment aging, 3) after treatment, and 4) after twelve days of post-treatment aging (see the visual key just above). These photographs qualitatively demonstrate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

surface pH and cold extraction measurements. Using the $L^*a^*b^*$ color space, a Minolta Chroma Meter CR-300 colorimeter was used to record and average three color 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

Colorimetry

The colorimetry results (fig. 8) 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:

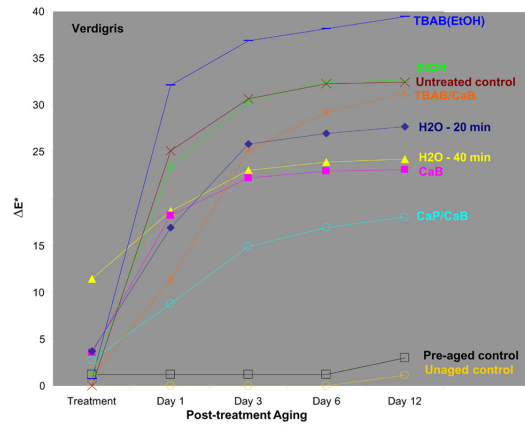
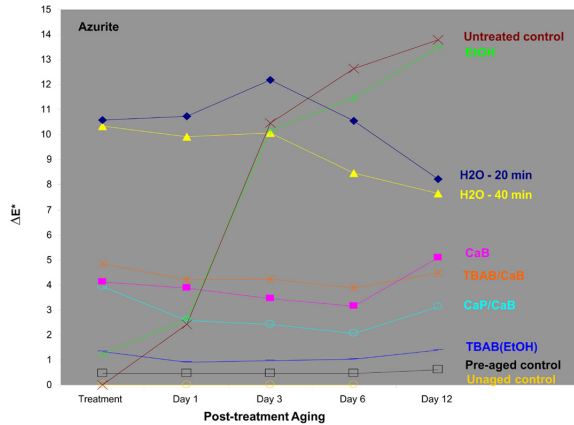
- With simple water washing, soluble transition metal ions are spread through the paper.²
- CaB is slightly better, as it hinders acid hydrolysis, but not oxidative degradation.³
- CaP with CaB treatment is effective, but only completely for the pure iron-gall ink (ink 1). For the watercolors and the mixed metal ink, it is either partially effective (ink 2) or not effective at all (both copper pigments).⁴
- Both non-aqueous and aqueous TBAB treatments are quite effective at preventing discoloration 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.⁵

The total color change (ΔE^*) is considered perceptible to the human eye if greater than one. An optimal treatment would have an initial color 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 color change, indicating that oxidation and hydrolytic pathways had been effectively slowed or blocked. For azurite (fig. 9) it can be seen that the best treatment, in terms of ΔE^* , is TBAB_(EtOH). This treatment has very little initial color change with treatment, as well as an almost flatline rate of color change over time.

For verdigris (fig. 10), however, while both TBAB treatments (TBAB_(EtOH) and TBAB/CaB) cause little initial color change in treatment, there is drastic color change on days one through three of aging. It is possible that this dramatic color change is not due to oxidation by reactions mechanisms that produce peroxides (and hence are unaffected by the presence of TBAB). The color 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.

Watercolor Surface pH

While figure 7 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. This may raise questions about the sufficiency of the buffer deposited by calcium bicarbonate treatments.



LEFT TO RIGHT

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

Fig. 10. Total color 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 watercolors 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 color 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 color change in the media; however, aqueous treatment is much more beneficial to the paper. The conservator must then decide if this initial color 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 watercolors 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. Colorimetry on the recto of the samples showed that for azurite, while all antioxidant and deacidification treatments produced increased color stability, TBAB in ethanol was the best treatment. The verso tells a different story. While the color change on the verso was not quantitatively measured, qualitative analysis clearly shows that the treatment producing the most enhanced stability is TBAB/CaB (fig. 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.

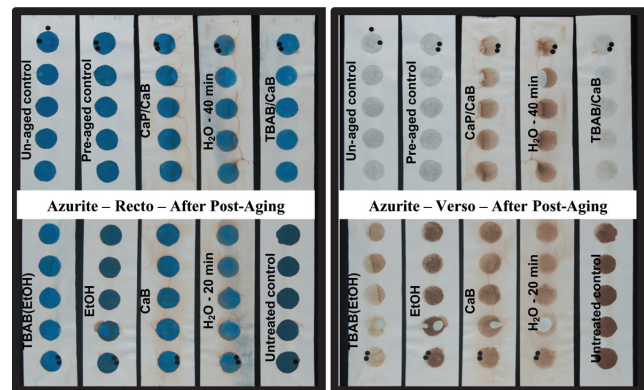


Fig. 11. Photographs of each of the azurite samples, first recto then verso, after post-treatment aging. These photographs can be used to visually compare the difference between the unaged, treated, and untreated samples

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 color change is much less than untreated samples. From the colorimetric results, the aqueous nature of the treatment was confirmed to spread copper corrosion from the watercolor 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.

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 color, pH, degree of polymerization, and brittleness would be informative. Additionally, varying the concentration of TBAB in the treatment of the watercolors, while also using more dilute watercolors, would help to determine optimal treatment parameters.

ACKNOWLEDGEMENTS

Many people provided invaluable input throughout the course of this research project. Thanks to Season Tse (Canadian Conservation Institute) and Maria Trojan-Bedynski (Library and Archives Canada) for aid in formulating and executing the project. Additional thanks to various key players from Queen's University for providing materials and assistance: Alison Murray, Bernard Ziolkiewicz, Barbara Klempan, John O'Neill, and Mark Reitsma. Finally, I thank my fellow MAC students for their support and solidarity during my years of study.

NOTES

1. 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 figure 2 in Banik, 1997, p. 21.
2. The spread of ions is seen by the brown coloration that covers the paper after aging. This is compared to the untreated control, where the paper remains white with aging.
3. 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.
4. 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 discolorations are at the same level.
5. Both TBAB treatments prevent any brown discoloration from spreading to the paper support.

REFERENCES

- Banik, G. 1989. Discoloration of green copper pigments in manuscripts and works of graphic art. *Restaurator* 10: 61–73.
- . 1997. Decay caused by iron-gall ink. In *Iron-gall ink corrosion: Proceedings of the European workshop on iron-gall ink corrosion, June 16–17, 1997*, 21–26. Amsterdam: Netherlands Institute for Cultural Heritage.
- Bhowmik, S.K. 1970. A note on the use and deterioration of verdigris in Indian watercolour painting. *Studies in Conservation* 12: 154–156.
- 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.
- Gettens, R. J., and G. L. Stout. 1942. *Painting materials: A short encyclopaedia*. New York, NY: Dover Publications.
- Hagadorn, A. 2004. An investigation into the use of blue copper pigments in European early printed books. *Book and Paper Group Annual* 23: 41–55.
- Kolar, J. 2004. InkCor: Stabilisation of iron gall ink containing paper. In *ICOM—CC Graphic Documentation Meeting*, 21–22. Ljubljana: ICOM.
- Kolar, J., J. Malešič, and M. Strlič. 2005. Antioxidants for stabilization of iron gall ink corrosion. In *ICOM Committee for Conservation Preprints, 14th Triennial Meeting, The Hague: 12–16 September, 2005*, 186–192. London: James & James.
- Kolar, J., M. Strlič, M. Budnar, J. Malešič, V. S. Šelih, and J. Simčič. 2003. Stabilisation of corrosive iron gall inks. *Acta Chimica Slovenica* 50: 763–770.
- Krekel, C. 1999. Chemistry of historical iron gall inks: Understanding the chemistry of writing inks used to prepare historical documents. *International Journal of Forensic Document Examiners* 5: 54–58.
- Kuhn, H. 1993. Verdigris and copper resinate. In *Artists pigments: A handbook of their history and characteristics*, vol. 2, ed. A. Roy, 131–158. New York: National Gallery of Art, Washington. Oxford University Press.
- 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 wall-paper. In *Conservation Within Historic Buildings: Preprints of the Contributions to the Vienna Congress. September 7–13, 1980*, 180–185. Vienna, Austria: International Institute for Conservation.
- Malšič, J., J. Kolar, M. Strlič, 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.
- Neevel, H. n.d. *Calcium bicarbonate: Recipe for preparing an aqueous solution for the deacidification treatment of ink corrosion*. Instituut Collectie Nederland (ICN), laboratory handout.
- Neevel, H, and B. Reissland. n.d. *Calcium phytate: Recipe for preparing an aqueous solution for the chelate treatment of ink corrosion*. Instituut Collectie Nederland (ICN), laboratory handout.
- Neevel, J. G. 1995. Phytate: A potential conservation agent for the treatment of ink corrosion caused by iron-gall inks. *Restaurator* 16: 143–160.
- . 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. Japp A. Mosk and Norman H. Tennet, 74–86. London: James & James Science Publishers.

- Reissland, B. 1999. Ink corrosion aqueous and non-aqueous treatment of paper objects: State of the art. *Restaurator* 20: 167–180.
- Schäfer, I. 2004. Iron gall ink corroded autographs of the 18th and 19th centuries: Conservation of material characteristics versus conservation treatments. In *Proceedings of the International Conference on Durability of Paper and Writing, November 16–19*, 50–51. Ljubljana, Slovenia: MIP.
- Stephenson, J. 1984. Watercolour. *The Artist* 99(4): 14–15.

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