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Treatment Considerations for the Haggadah Prayer Book: Evaluation of Two Antioxidants for Treatment of Copper-Containing Inks and Colorants

ABSTRACT

The Altona Haggadah, ca. 1763, is an illuminated manuscript containing iron-gall ink and numerous drawings with pigments such as atacamite, or basic copper chloride. It was deacidified with Wei T'o in 1987. Additional treatment is necessary to delay further damage to the paper caused by copper-catalyzed oxidation. The water sensitivity of the manuscript required that only non-aqueous treatments be considered. Two antioxidants, tetrabutylammonium bromide (TBAB) and 1-ethyl-3-methylimidazolium bromide (EMIMBr) were chosen for testing. Wei T'o and Bookkeeper were used for deacidification.

Iron-gall ink, iron-copper ink, atacamite, and verdigris were applied on unsized Whatman #1 paper and pre-aged. Six combinations of antioxidant and deacidification treatments were used on pre-aged samples. The treated pigment and ink samples were aged at 80°C and 65% RH. Both aged and unaged samples were evaluated using color measurement, zero-span tensile tests, and pH measurement. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was also carried out by an external laboratory to determine the concentrations of magnesium, iron, and copper in the samples. The tensile strength results showed that deacidification alone benefitted the two sets of acidic ink samples; treatment with the two antioxidants did not provide additional protection. The benefits of antioxidants with deacidification were clearly shown with atacamite samples; the results with verdigris samples were inconclusive.

INTRODUCTION

The treatment of the Altona Haggadah, an illuminated manuscript containing iron-gall ink and numerous drawings with copper-containing pigments, prompted research into non-aqueous treatments to delay further damage to the paper caused by hydrolysis and copper-catalyzed oxidation.

Condition of the Haggadah

"Haggadah" means "telling" in Hebrew. A Haggadah consists of scriptural passages, prayers, hymns, and rabbinic literature meant to be read during the Jewish Passover Seder meal. This 1763 Altona Haggadah is an illuminated manuscript, part of the Jacob M. Lowy Judaica Collection belonging to Library and Archives Canada (fig. 1). The format of the text and illustrations closely follows that of the 1695 Amsterdam Haggadah, one of the earliest printed versions of Haggadot.

This Haggadah was written and illustrated in color in Altona, Germany, a major center of Jewish life and scholarship at the time. It is particularly important since it does not represent high book art but rather gives testimony to the way a middle-class Ashkenazi Jewish family of the 18th century would have celebrated the Passover holiday.

The text block consists of 24 leaves (12 folios) gathered into 6 sections of 2 folios each. The paper is a medium-weight handmade paper with a *fleur-de-lys* watermark visible on the last page. The text is written in iron-gall ink. Green, red, and blue pigments were used in the illustrations. Pigment analysis carried out at the Canadian Conservation Institute (CCI) identified the red pigment as vermilion, the blue pigment as Prussian blue, and the green pigment as atacamite (copper chloride hydroxide) (Helwig and Corbeil 2008).

Prior Treatments

Cracks and losses in the paper caused by corrosion from the ink and green atacamite pigment can be found throughout the manuscript (fig. 2). Prior to 1987, many of these weak areas were repaired with thin Japanese paper, which was pasted directly over the illustrations in some cases. Examination in 1987 revealed that several new areas of the paper had deteriorated and were in need of support, especially in areas of more densely applied ink.

Conservation treatment in 1987 included removing the manuscript from its covers and dismantling the pages.

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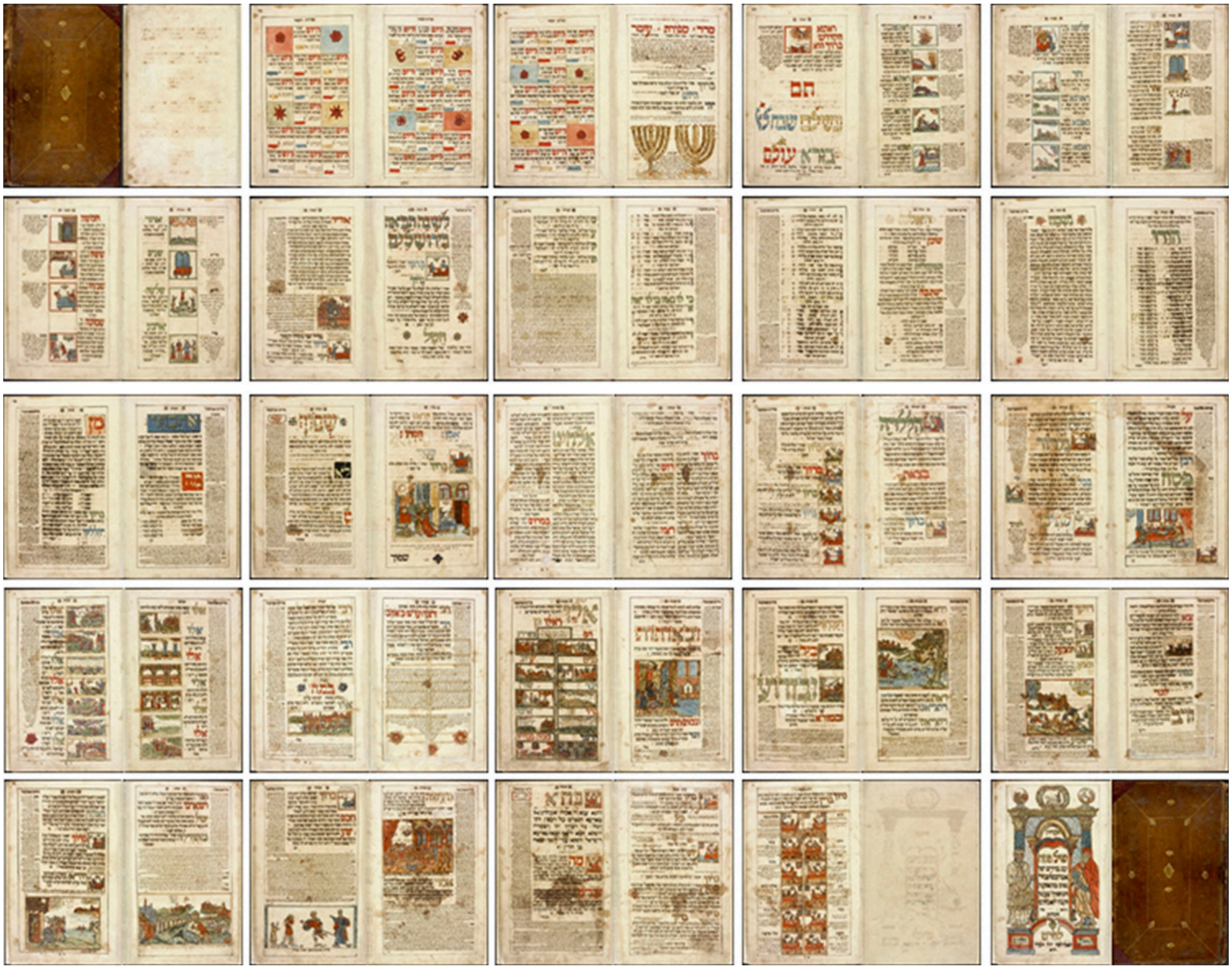

Fig. 1. 1763 Altona Haggadah, Jacob M. Lowy Judaica collection, Library and Archives Canada, accession # LOWY MS A229 (Courtesy of Library and Archives Canada)

Fig. 2. Inks and pigments on the Haggadah (Courtesy of Library and Archives Canada)

Damaged and weak areas of the paper were repaired with thin Japanese paper and carboxymethyl cellulose (CMC) adhesive. Deacidification began using an aqueous solution of magnesium bicarbonate applied with an ultrasonic mister. This was quickly discontinued, as feathering became evident in some of the inked areas. Instead, the pages were deacidified by spraying with Wei T'o #2 solution (methyl/ethyl magnesium carbonates in 1,1 dichloro-1-fluoroethane [HCFC-141B] and methanol).

CURRENT TREATMENT NEEDS

In 2007, reexamination of the Haggadah showed that the deacidification treatment carried out in 1987 was unable to completely protect the paper from continued deterioration caused by the ink and pigments. Many new cracks and losses were found in the inked lines and areas with green atacamite.

Fig. 3. 1987 repair using Japanese tissue (top) and most recent repairs using the gelatin-coated Berlin tissue (bottom) (Courtesy of Library and Archives Canada)

Fig. 4. Before and after images of the digital stain reduction (Courtesy of Library and Archives Canada)

On eight of the pages, ink had penetrated to the verso of the page, making the text difficult or almost impossible to read. On the remaining pages, the burn-through effect was visible, but had not yet obscured the text.

The deteriorated condition of the Haggadah prompted discussions about the need for further treatment to effectively delay damage caused by oxidation catalyzed by copper and iron in the ink and pigment. Due to the water sensitivity of many elements in the manuscript, only non-aqueous methods could be considered for future treatment. In 2007, solvent-based treatments were only in experimental stages and required further research before they could be applied to originals.

Since then, the corroded pages have been mechanically stabilized using gelatin-coated Berlin tissue—one of the lightest tissues presently available (Fig. 3). Research indicates that type-B gelatin with a high or medium Bloom degree has a considerable capacity to protect paper by preventing migration of free ironII ions (Kolbe 2004). The gelatin-coated tissue (0.4% Type-B gelatin, 275 Bloom) was reactivated *in situ*, using a 3:1 ethanol–water solution (Pataki 2009; Titus et al. 2009). Figure 3 shows the difference between repairs done in 1987 and recent repairs.

For the purpose of publication, wine stains obscuring several pages of the Haggadah were also reduced digitally using Adobe Photoshop software (fig. 4).

Following the mechanical stabilization of the manuscript, a joint research project was developed between Library and Archives Canada and CCI to investigate possible solvent-based treatment options for the Haggadah.

ANTIOXIDANTS FOR TREATMENT OF PAPER WITH COPPER-CONTAINING INKS AND PIGMENTS

The two main mechanisms of paper deterioration are hydrolysis, catalyzed by acid (Nevell 1985; Zou et al. 1994), and oxidation, a complex process catalyzed by transition metal ions, among other factors (Strlič et al. 2004; Šelih et al. 2007). The predominant degradation pathway is pH dependent. As the pH of paper increases, the relative importance of acid hydrolysis decreases (Strlič et al. 2004).

Deterioration of paper caused by copper has been studied in detail (Williams et al. 1977; Mairinger et al. 1980; Banik and Ponahlo 1982; Shahani 1986; Banik 1989; Daniels 1987, 2002; Kolar et al. 2003; Henniges et al. 2006a, 2006b). The result is browning and, eventually, weakening of the paper directly in contact with the copper pigment and the paper in close proximity to the pigment. The European Union-funded InkCor project identified a number of antioxidants that can be used in non-aqueous solutions (Kolar et al. 2008). Halides were among the most effective for treatment of both iron- and copper-based inks and pigments (Malešič et al. 2005 and 2006; Kolar et al. 2008).

Two possible antioxidants were selected for further testing: tetrabutylammonium bromide (TBAB) and 1-ethyl-3-methylimidazolium bromide (EMIMBr). Both function as peroxide decomposers (Kolar et al. 2008), and both are soluble in ethanol. EMIMBr is reported to be more effective than TBAB and even more effective than aqueous calcium and magnesium phytates (Kolar et al. 2008). For deacidification, Wei T'o was chosen for testing because the Haggadah was previously treated with Wei T'o. Bookkeeper spray was also chosen, because it is the non-aqueous deacidification agent that is used at Library and Archives Canada.

Whatman #1 paper was selected for preparing the samples because it is a well-characterized paper, has been used in many recent studies, and has properties that resemble those of the paper of the Haggadah. The selection of the pigments, inks, and experimental conditions was based on a review of recent literature (Malešič et al. 2005; Maitland 2007; Kolar et al. 2008). TBAB has been tested on verdigris and azurite on paper (Maitland 2007), and EMIMBr has been tested on iron-tannate-dyed cotton and silk textiles (Wilson et al. 2011).

Two iron-gall inks—with and without copper—were included because the Haggadah text is written in iron-gall ink, and historically many iron-gall inks also contained copper contaminants. Atacamite was included because it was found on the Haggadah, and verdigris was included because it is well known to cause discoloration in paper (Banik 1989) and was included in previous studies (Maitland 2007; Kolar et al. 2008).

This joint project sought to confirm the efficacies of these two halides on paper inscribed with iron-gall inks (with and without copper), verdigris, and atacamite, and to add to existing data.

EXPERIMENTAL METHODS

Preparation of inks and pigments

Iron-gall ink with a 5.5:1 iron–tannin ratio was prepared by dissolving gum arabic (15.7 g) in deionized water (500 ml). Iron sulphate ($FeSO_4.7H_2O$; 21 g) and tannic acid (24.6 g) were then added sequentially. Iron-gall ink with copper was prepared using a 5.5:1 ratio of iron and copper to tannin and a 0.7:1 ratio of copper to iron. Gum arabic (15.7 g) was dissolved in deionized water (500 ml) as before. Iron sulphate ($FeSO_4.7H_2O$; 12.23 g) and copper sulphate ($CuSO_4.5H_2O$; 7.73 g) were then added to the gum arabic solution, followed by tannic acid (24.6 g) (Kolar et al. 2003; Malešič et al. 2005). Both inks were filtered prior to use.

Verdigris (copperII acetate, $Cu(OH)_2{\cdot}(CH_3COO)_2{\cdot}5H_2O$; Kremer 44450; 30 g) and atacamite (copperII chloride hydroxide, $Cu_2Cl(OH)_3$; Kremer 103901 and synthesized at CCI; 27 g) were each weighed out on glass plates. Acetone was then added until each pigment was thoroughly wetted. Next, sufficient water was added to each pigment until smooth slurries were formed. Liquid gum arabic was added (Winsor & Newton; 25 g for verdigris and 22.5 g for atacamite), and each slurry mixture was ground on a glass plate with an etched glass muller until the pigment particles were fine. The mixtures were placed into petri dishes and air dried. Once dried, each pigment was further ground without additional moisture to achieve a fine powder, resulting in 30.5 g of verdigris and 31 g of atacamite, both containing gum arabic.

Application of inks and pigments to paper and pre-aging

A total of 35 samples were prepared for each of the ink, pigment, and paper control groups. Whatman #1 paper was used as substrate for both the ink and pigment samples. To ensure even distribution of the ink, single sheets of Whatman #1 paper, 10 x 20 cm, were immersed in an ink bath for 30 seconds, removed, and hung diagonally to dry. Any excess ink that pooled at the bottom corner was removed by blotting to create a more even sample.

Pigment mixtures were prepared by adding 1.5 g of pigment to 5 ml of water. To ensure an even distribution of the pigment, 2 ml of the pigment solution was airbrushed onto Whatman #1 paper. A Mylar mask was used to provide a consistent sample area of 5 x 19 cm. This resulted in an estimated pigment concentration of approximately 0.0034 g/cm^2. Figure 5 is a representation of the ink and pigment samples.

Pre-aging was carried out in a Votsch climatic chamber, type VC 0020, using a cycle of 55°C at 80% RH for 6 hours followed by 55°C at 35% RH for 18 hours. The inks were aged for 1 day (24 hours), while the pigment and paper control samples were aged for 72 hours. Different aging periods for inks and pigments were chosen based on the results of a preliminary aging test, which indicated that a longer period of aging would cause ink samples to become too brittle for treatment and further heat aging. The Whatman paper controls and the pigment samples, however, could be safely aged for 72 hours. Each group of samples was aged separately to avoid contamination.

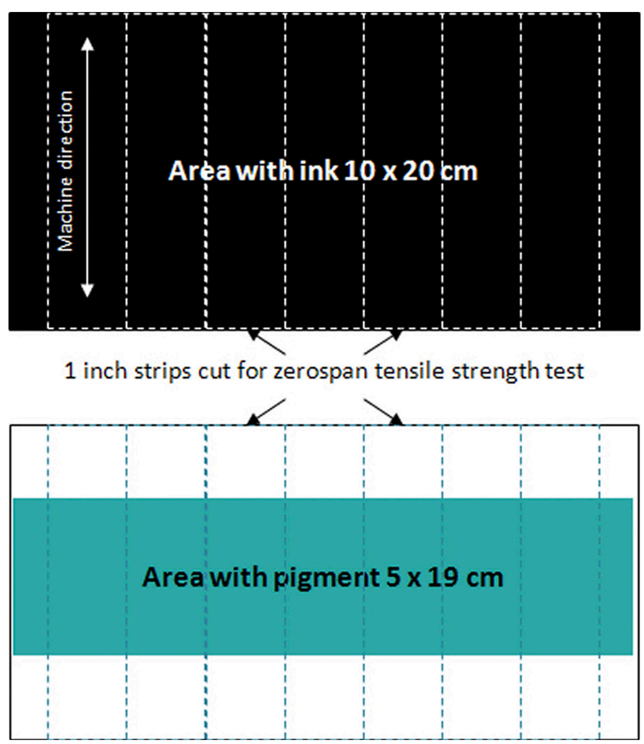

Fig. 5. Diagram of ink and pigment samples

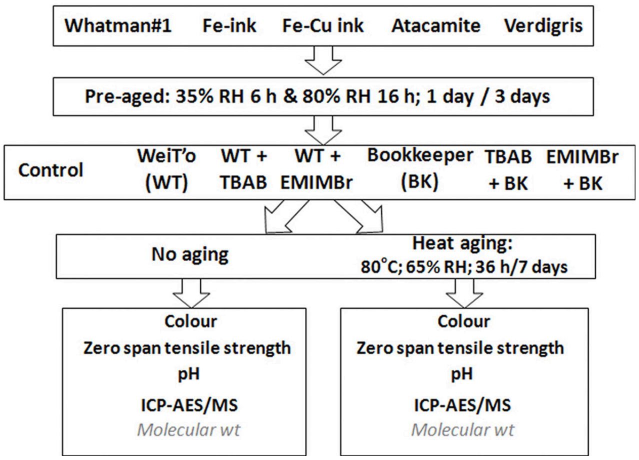

Fig. 6. Sequence of treatment, aging, and analysis

TREATMENT

Figure 6 shows the sequence of pre-aging, treatment, accelerated heat aging, and analyses. Each set of pre-aged samples was divided into seven groups of five sheets each and subjected to six separate treatments: Wei T'o alone (WT); Wei T'o followed by TBAB (WT+TBAB); Wei T'o followed by EMIMBr (WT+EMIMBr); Bookkeeper alone (BK); TBAB followed by Bookkeeper (TBAB+BK); and EMIMBr followed by Bookkeeper (EMIMBr+BK). One group of samples was kept as the untreated control group. The application of Wei T'o to samples prior to treatment with antioxidants was intended to simulate the deacidification of the Haggadah in 1987, prior to possible future treatment with an antioxidant.

Wei T'o solution was applied to samples by brushing through a layer of Reemay. After application of the Wei T'o, samples receiving further treatment were left for seven days before treatment with an antioxidant. TBAB and EMIMBr (0.03 M) solutions were prepared by dissolving the powders in anhydrous ethanol (Kolar et al. 2008). Samples were immersed in antioxidant baths for 20 minutes, with a ratio of five sheets per 200 ml of solution. Treated samples were then air dried. Bookkeeper deacidification solution was applied by spray to selected dried samples.

Accelerated heat aging

Two of the five sheets of each of the treated samples and untreated controls were subjected to heat aging in an ESPEC environmental chamber at 80°C and 65% RH. The inks were aged for only 36 hours; the Whatman controls and the pigment samples were aged for 7 days.

Analysis

Color measurements were taken using a Minolta CR300 Chroma Meter with a D65 illuminant. Pigmented samples were analyzed on the recto (pigment side) and the verso (paper side), and the inked samples and Whatman paper controls were analyzed only on the recto, as they showed no difference in color between the recto and verso. Color measurements were taken after pre-aging and before treatment, after treatment, and after heat aging.

Zero-span tensile strength was measured using a Pulmac tensile tester following the TAPPI standard (TAPPI 1985). The samples were cut into strips 1 in. (2.54 cm) wide along the machine direction, and were conditioned at 23°C and 50% RH for at least three days before testing.

The TAPPI standard (TAPPI 1988) for measuring pH was modified for small samples. Deionized water (8.5 ml) was added to samples (~0.12 g) and extracted for 1 hour. Measurements of the extract were taken using an Orion EA940 Ionanalyzer with an Orion ROSS® Ultra-flat pH combination electrode. The pH of the deionized water was also measured.

A multi-element scan of selected samples was conducted by Caduceon Environmental Laboratories Ottawa (Caduceon 2012) using inductively coupled plasma atomic emission spectroscopy (ICP-AES, EPA method 6010).

RESULTS AND DISCUSSION

Color change after treatment

The change in color and appearance immediately after treatment is an important factor for evaluation. Treatments that cause significant changes in color or appearance will not be used even if they are beneficial to the paper. Figure 7a summarizes the change in color coordinates of the samples after treatment; Figure 7b indicates color change after heat aging.

The Whatman papers were yellowed slightly after Wei T'o treatment. The iron and iron-copper inks darkened and became more yellow with time, even without treatment. All the inks treated with Wei T'o and an antioxidant became darker (decrease in L*) and less blue or more yellow (increase in b*). Visually, the inks appeared more saturated. Some ink samples treated with Bookkeeper had an uneven white deposit of magnesium oxide (MgO) on their surfaces, which accounts for their increased L* values.

After deacidification, both the verdigris and atacamite samples showed very little change in color, with or without antioxidants, both on the pigment and the paper sides. The Bookkeeper-treated samples were slightly lighter on the pigment side, likely from the MgO deposit.

Color change after heat aging

After heat aging, both the Bookkeeper- and Wei T'o-treated Whatman papers became darker (decrease in L*) and more yellow (increase in b*) compared to the untreated controls, and Wei T'o-treated samples were more yellow than Bookkeeper-treated samples. Slight yellowing is commonly

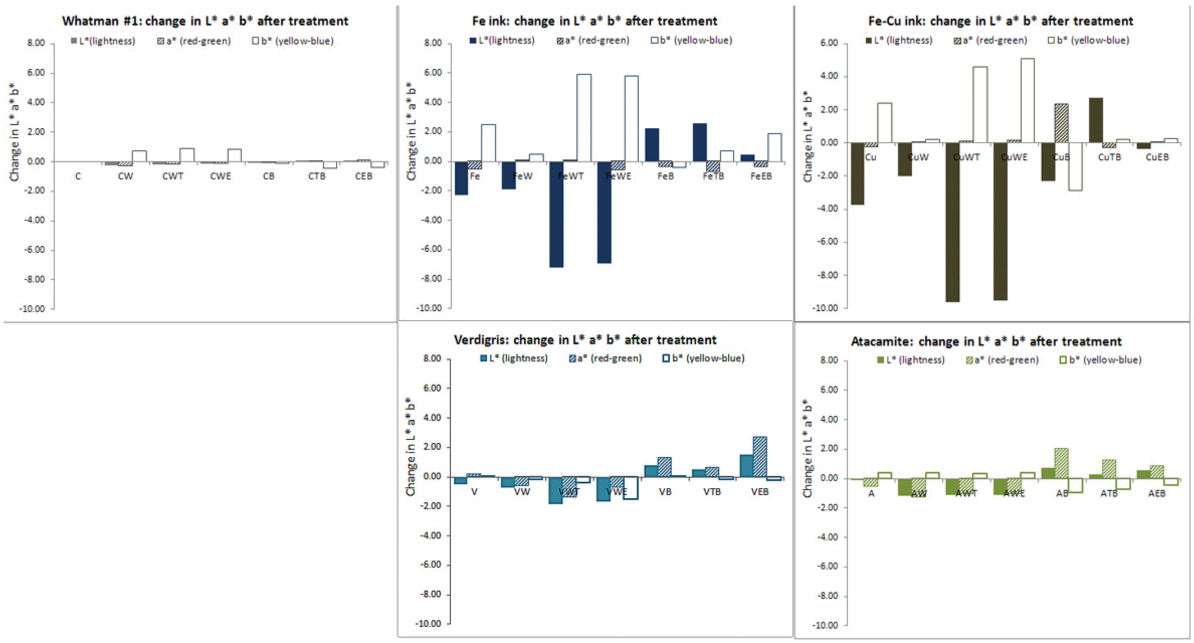

Fig. 7a. Change in L* (lightness), a* (red–green), and b* (yellow–blue) after treatment (C=Whatman #1 control; Fe=iron-gall ink; Cu=iron-gall ink with copper; V=verdigris; A=atacamite; W=Wei T'o; B=Bookkeeper; T=TBAB; E=EMIMBr)

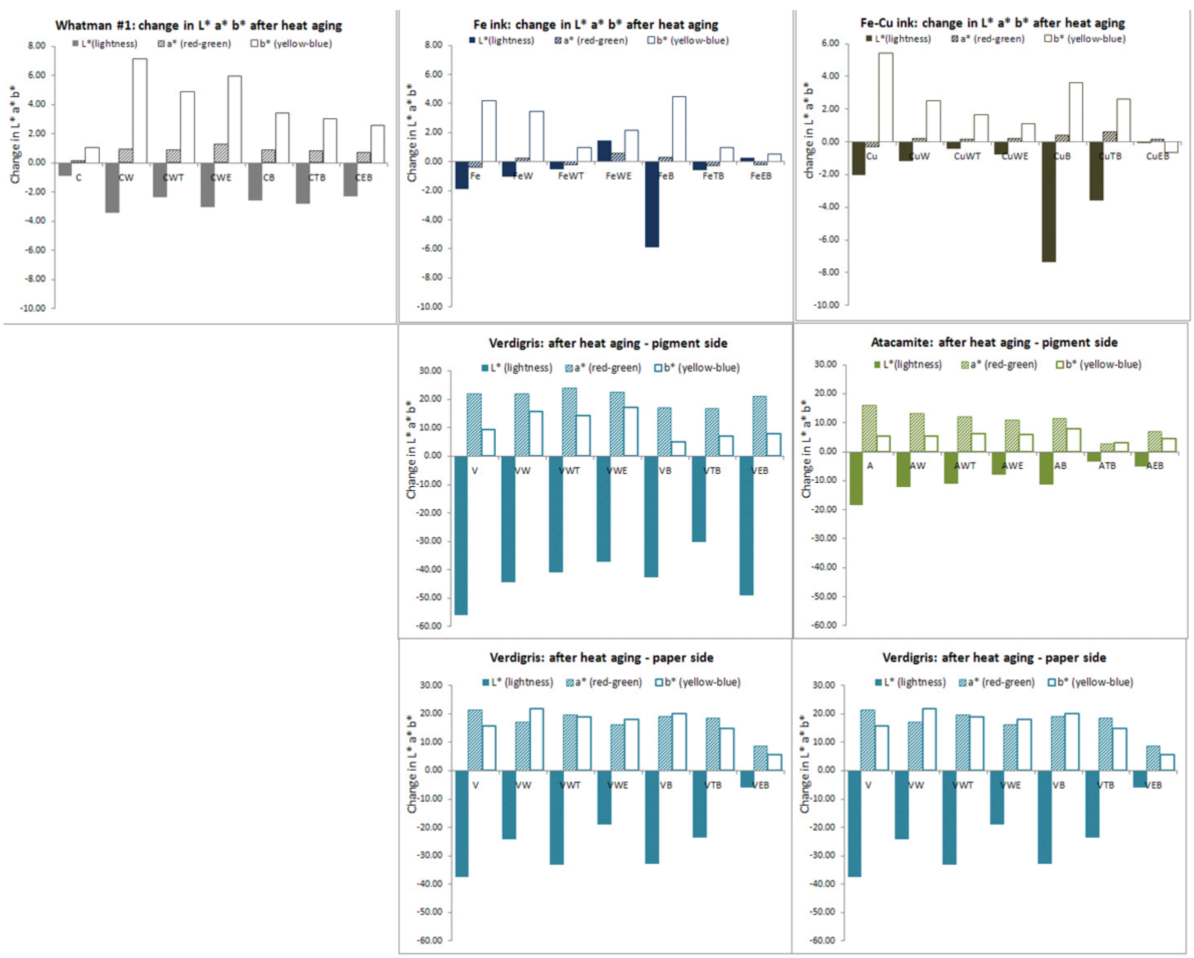

Fig. 7b. Color change in L* (lightness), a* (red–green), and b* (yellow–blue) after heat aging (80°C, 65% RH; inks for 36 hours; Whatman #1 controls and pigments for 7 days)

observed with magnesium-deacidified papers, especially ligneous papers such as newsprint. The benefits of deacidification with magnesium compounds have been demonstrated despite this yellowing (Dupont et al. 2002), and the results of this study confirm them.

After heat aging at 80°C, the ink samples treated with antioxidants showed the least color change. Both untreated control inks became more yellow (increase in b*) and slightly darker (decrease in L*). The samples treated with Bookkeeper but without an antioxidant showed the most darkening and yellowing.

Heat aging caused verdigris to decompose, forming a dark brown copper oxide. Most of the measured color change on the pigment side is a result of this conversion. A heavy white deposit on the pigment side of the Bookkeeper-treated samples became very prominent on the dark brown pigment. Compared to the untreated control, all of the treated samples were less dark. On the paper side, a combination of the dark copper oxide coming through the paper and copper-catalyzed oxidation of the paper resulted in darkening (decrease in L*). The treatment that reduced this darkening most significantly was EMIMBr+BK.

After heat aging, atacamite samples became darker on both the pigment and the paper sides. Darkening on the paper side was mainly caused by copper-catalyzed oxidation. The three treatments that resulted in the least color change were TBAB+BK, EMIMBr+BK and WT+EMIMBr.

pH

Paper stability is largely determined by pH (Zou et al. 1994; Bégin et al. 1998; Strlič et al. 2004). Below pH 7.3, the rate of cellulose deterioration is a function of pH: the lower the pH, the higher the rate (Strlič et al. 2004). Figure 8 shows the pH of all the samples after treatment and after heat aging. Both Wei T'o and Bookkeeper deacidification increased the pH of Whatman #1 paper from 6 to 10. Neither treatment with antioxidants nor heat aging changed the pH.

Without treatment, the two heat-aged sets of ink samples had a pH of approximately 2.5. Both Wei T'o and Bookkeeper treatments, with and without antioxidants, increased the pH of the inks to varying degrees, but the inks remained acidic (below pH 6). This means not all the acids were neutralized.

In general, the iron-gall inks with copper had lower pH than iron-gall inks without copper after treatment. For the iron-gall inks without copper, Wei T'o-treated samples had higher pH than Bookkeeper-treated samples. The Bookkeeper-treated ink samples increased marginally in pH. The WT+EMIMBr combination produced an anomalously high pH, possibly due to an uneven application of Wei T'o. Neither treatment with antioxidants nor heat aging changed the pH.

Both Wei T'o and Bookkeeper treatments increased the pH of the atacamite samples from 6 to 10. Wei T'o-treated samples had higher pH than Bookkeeper-treated samples. Heat aging lowered the pH for all the samples to different degrees. Those treated with antioxidants had higher pH.

Verdigris samples had a pH of 6 prior to treatment. Wei T'o treatment increased the pH to 10; after heat aging, the pH decreased to 8. The Bookkeeper-treated verdigris samples showed an unusual pattern. After treatment, the pH of the pigmented areas remained at 7, while the surrounding paper had a pH of 10. The lower pH in the pigmented areas could result from a reaction between the magnesium oxide in

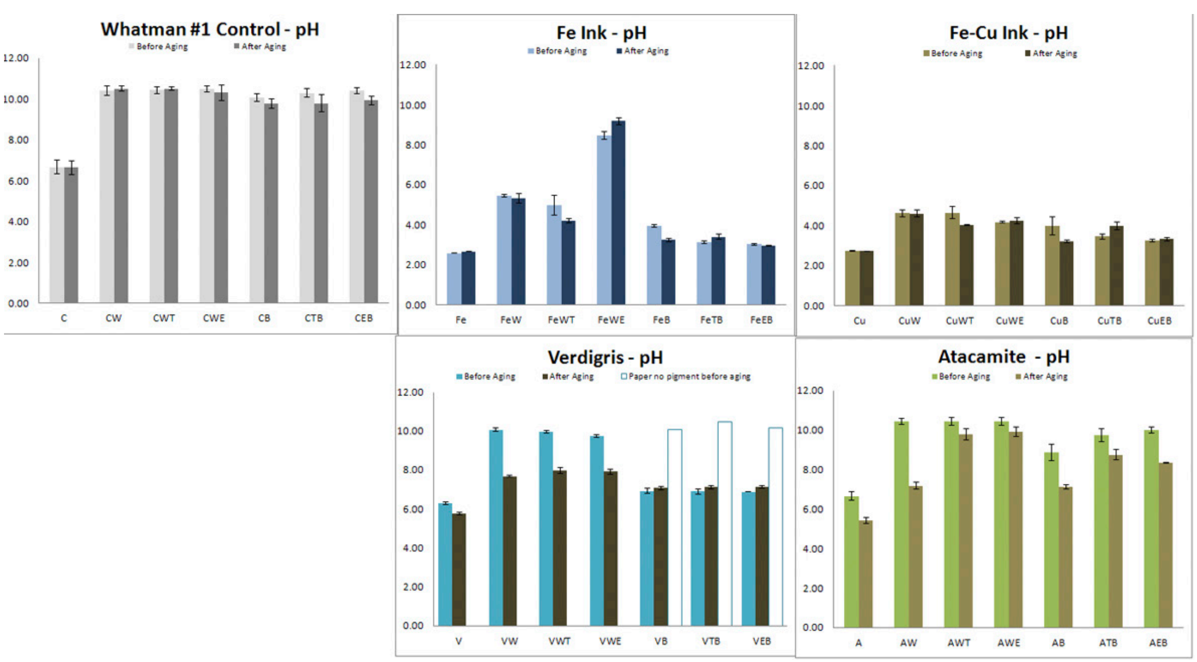

Fig. 8. pH of ink and pigment samples before and after heat aging (80°C, 65% RH; inks for 36 hours; Whatman #1 controls and pigments for 7 days)

Bookkeeper and the copper acetate in verdigris, perhaps forming a buffer. After heat aging, the pH of the pigmented areas did not decrease, as it did in the case of the Wei T'o-treated verdigris, but remained at 7. The addition of antioxidants did not change the pH.

ICP-AES: Concentration of copper, iron, and magnesium in samples

Table 1 summarizes the concentrations of copper, iron, and magnesium ions in the ink and pigment samples. The magnesium content of the samples reflects the deposition of the two deacidification agents: methyl/ethyl magnesium carbonates in Wei T'o and magnesium oxide in Bookkeeper. Magnesium content ranges from 90 to 550 µmol/g of sample. The differences are largest among the iron-gall ink samples. Overall, Wei T'o-treated samples, especially those with antioxidants, have the highest concentrations of magnesium.

As expected, iron concentration is significant only in the two sets of ink samples. The concentration is quite uniform among all the ink samples, with an average of 264 µmol/g for iron-gall ink samples without copper, and 175 µmol/g for iron-gall ink samples with copper.

The copper concentration was the main interest for this study. The average copper content in the samples of iron-gall ink with copper was 120 µmol/g with a copper:iron ratio of 0.68, confirming the molar ratio of the original ink preparation. For the pigment samples, though the application was not unusually heavy, the copper content of the samples was much higher than in the copper-containing inks. For verdigris it was 1270 µmol/g, and for atacamite, 2060 µmol/g. While these concentrations are higher than those found in other studies (Kolar et al. 2008), they are representative of a single application of a pigment solution to paper, like the colorants found in the Haggadah.

	No treatment	WeiT'o	WeiT'o + TBAB	WeiT'o + EMIMBr	Book-keeper (BK)	TBAB + BK	EMIMBr + BK
Whatman#1							
Mg umol/g	0.82	281	547	531	324	210	356
Fe umol/g	0.13	0.11	0.14	0.16	0.36	0.30	0.30
Cu umol/g	0.11	0.28	0.08	0.11	0.13	0.47	0.19
Iron gall ink							
Mg umol/g	5.35	551	328	90	291	181	118
Fe umol/g	283	206	269	244	297	272	276
Cu umol/g	0.25	0.13	0.19	0.19	0.16	0.27	0.22
Iron Copper ink							
Mg umol/g	4.94	420	317	356	220	312	156
Fe umol/g	171	201	172	150	177	171	179
Cu umol/g	120	124	120	105	126	118	124
Atacamite							
Mg umol/g	5.35	206	292	275	168	167	150
Fe umol/g	0.36	0.52	0.36	0.38	0.52	0.50	0.43
Cu umol/g	2110	2457	1780	2000	2236	1953	1890
Verdigris							
Mg umol/g	6.17	234	412	347	247	377	128
Fe umol/g	0.52	0.04	0.04	0.04	0.23	0.30	0.16
Cu umol/g	1277	1276	1387	1080	1669	1124	1069

Table 1. ICP-AES Results: Concentration of copper, iron, and magnesium in samples

Zero-span tensile strength

Zero-span tensile strength is a sensitive test for measuring paper fiber strength. There is a good correlation between zero-span tensile strength and the molecular weight of paper (Jerosch et al. 2002). While molecular weight analysis is very sensitive to changes, especially with undegraded paper, zero-span tensile strength tests are sensitive even for degraded papers (Caulfield and Gunderson 1988). The zero-span tensile strength results are expressed as percent retention after heat aging: a ratio of the strength after aging to that before aging (fig. 9). The lower the percentage of retention, the weaker the paper after aging. These results were used to determine the effectiveness of treatments in protecting paper.

Whatman paper without inks or pigments is a stable paper. Its zero-span tensile strength did not change after seven days of heat aging. Deacidification and antioxidant treatments did not affect fiber strength, even though the paper became slightly darker and more yellow after heat aging.

For the two acidic inks, both Wei T'o and Bookkeeper deacidification greatly improved the zero-span tensile strength of the paper, even though for some of the Bookkeeper-treated samples, the pH was increased only marginally. Wei T'o-treated samples, with a higher pH, retained more strength than Bookkeeper-treated samples. The addition of antioxidants did not improve strength retention beyond that achieved by deacidification alone. Figure 10 shows the change in percent retention of tensile strength with the corresponding pH. Below pH 6, small increases in pH are correlated with substantial increases in fiber strength retention.

With atacamite samples, deacidification alone improved paper strength marginally. The combination of deacidification and antioxidant treatments resulted in marked improvement in paper strength compared to no treatment or deacidification alone. Bookkeeper with antioxidants gave the best results.

Results from the verdigris samples were not definitive. Treatment with Wei T'o, with or without an antioxidant, did not improve paper strength even though the pH of the samples was very alkaline. Bookkeeper-treated samples showed some improvement in paper strength, especially with EMIMBr.

Summary

Cellulose or paper deterioration follows two main pathways: acid-catalyzed hydrolysis, the predominant reaction below pH 7 (Strlič et al. 2004), and oxidation, a process catalyzed by ions of transition metals such as iron and copper, and predominant at neutral or slightly alkaline pH. For treatment

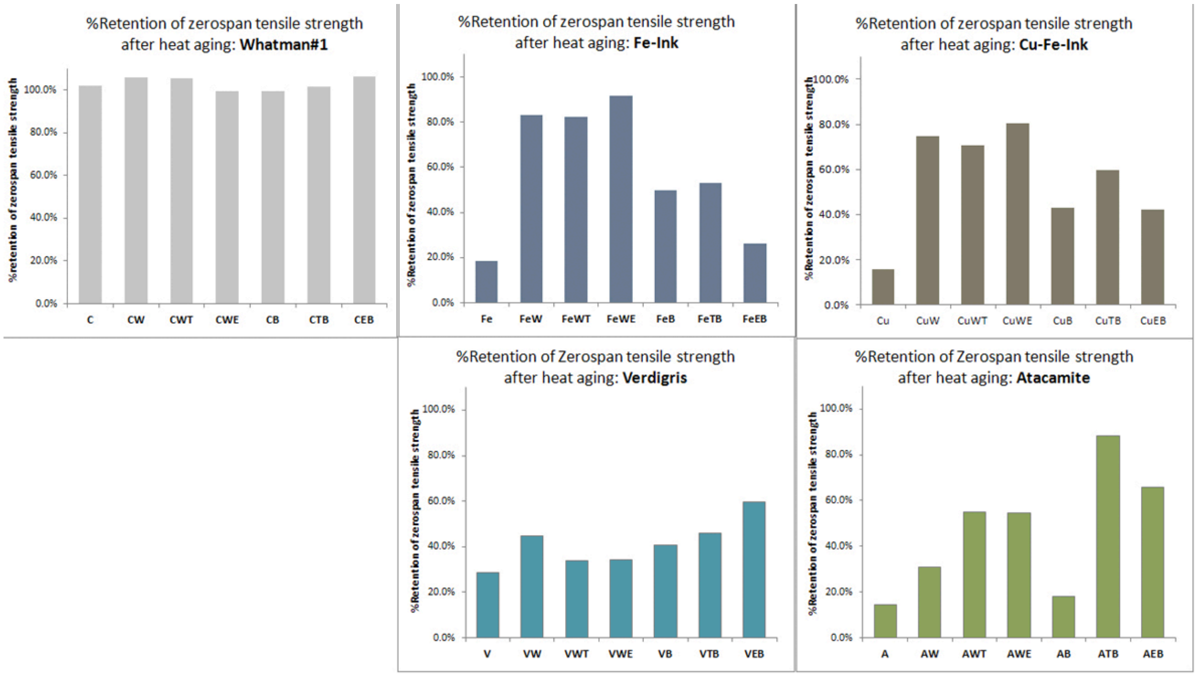

Fig. 9. Percent retention of zero-span tensile strength with and without heat aging (80°C, 65% RH; inks for 36 hours; Whatman #1 controls and pigments for 7 days)

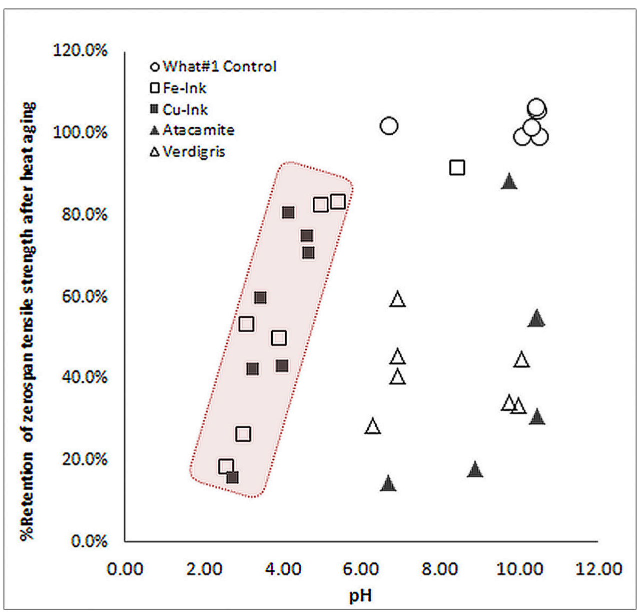

Fig. 10. Correlation of percent retention of zero-span tensile strength (after heat aging) with pH (before aging)

decisions, if the paper is acidic, the priority is to neutralize the acids. Deacidification treatments do not automatically ensure neutralization of all the acids. It is important to verify the pH of the inked lines on the manuscript, not of the surrounding paper alone. If the paper is not acidic, then the priority is to mitigate oxidation by interrupting the effects of transition metal ions.

The acidic ink samples from this study showed that even a small increase in pH will stabilize paper against strength loss. Since the inks remained acidic (below pH 6) after deacidification, deterioration by hydrolysis will continue, albeit at a lower rate. Because of the predominance of hydrolysis, the benefits of antioxidants presumably were not evident in these samples because of their acidic pH. While deacidification increased the stability of the paper, treatment with Wei T'o made the inks appear more saturated, darker, and more yellow. Treatment with Bookkeeper left white deposits and caused the inks to appear slightly darker.

In 2007, the pH of the inked areas on the Haggadah was determined to be 5.0, an increase from 3.6 prior to the 1987 Wei T'o treatment. While the ink is still slightly acidic today, it is believed that the Wei T'o treatment has delayed corrosion. Deacidification was necessary, but it was not sufficient.

With the verdigris samples, very little change in color or appearance was observed after treatment. Heat aging at 80°C resulted in conversion of verdigris to copper oxide; these results may not be representative of natural aging. In terms of retention of fiber strength after heat aging, the only treatment that showed some benefits was EMIMBr+BK. Any benefits from other deacidification treatments, with or without antioxidants, were not clearly evident, despite the neutral to alkaline pH of the treated samples.

The atacamite samples showed very little change in color or appearance after treatment. After heat aging, the WT+EMIMBr, TBAB+BK, and EMIMBr+BK samples showed the least color change. Deacidification alone, with Wei T'o or Bookkeeper, increased the pH from 6 to 10, but there was no improvement in paper strength after heat aging. The addition of antioxidants improved paper strength after heat aging. Samples treated with Bookkeeper and an antioxidant had the highest strength retention.

CONCLUSION

The Haggadah manuscript has been mechanically stabilized, and it is being stored at 40% RH and 18°C in the dark, with restricted access. Results from this study show that, for iron-gall inks, the benefits of the two antioxidants studied are not expected to be evident when the inks are still acidic. However, the Wei T'o treatment in 1987 is believed to have significantly slowed the rate of corrosion by neutralizing some of the acids. This study also showed that TBAB and EMIMBr are effective in protecting paper with atacamite. The method of application would be important to ensure that sufficient antioxidant remained in the affected area.

This study has added to the body of knowledge available on treatment using antioxidants. However, the results do not show clear benefits from using the two antioxidants to treat iron-gall inks or verdigris. Further research and confirmation of their efficacy is needed before they can be used in treatment of the Haggadah.

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