

Accelerated Aging Study of Papers Treated with Citrate Solutions

by Madison Brockman

Abstract

Stain reduction with citrate solutions is becoming more commonplace in paper conservation, accentuating the need for basic studies on its various effects on paper. A multimodal accelerated aging study was undertaken at the Los Angeles County Museum of Art's Conservation Center to assess the long-term effects of exposing paper to citrate solutions. A Whatman filter paper and sized antique rag paper were tested with a 1% sodium citrate solution by overall immersion, immersion with rinsing, and local application with rinsing. Aging rates were predicted with microfade testing and samples were aged under UVA light, gallery lighting conditions, and in a thermal aging oven.

In all aging experiments, the citrate-treated samples were found to age at approximately the same rate as untreated samples, and all samples were much less light sensitive than the Blue Wool 4 standard. These results indicate that citrate solutions appear to have no deleterious effects on paper over time.

Introduction

As observed by Antoinette Dwan in her 2015 WAAC article, "staining in paper is varied and complicated."¹ However, over the past five years of experimentation, a singular tool has emerged: citrate solutions.

Citrates have recently gained traction in paper conservation as a cost effective and successful treatment option for stain reduction. However, there are few previous studies² on the effects these reagents can have on paper. More studies are needed to determine the long-term safety of citrate solution treatments.

This study began in early 2019 at the Los Angeles County Museum of Art under the guidance of LACMA assistant scientist Laura Maccarelli. There the author began testing the aging properties of papers treated with citrate solutions during her third year internship as a graduate fellow of the Winterthur/ University of Delaware Program.

Essential Citrate Chemistry

Citrate anions can be found in pre-made salt forms like ammonium citrate (di- or tribasic) or sodium citrate (tribasic). Conservators can also make their own solution

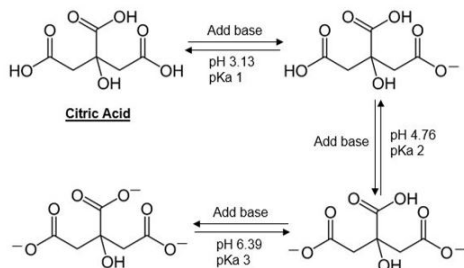


Fig. 1. Molecular structure of citric acid and its three ionization constants (pKa). (Image adapted from https://en.wikipedia.org/wiki/Citric_acid)

with citric acid and the appropriate base (e.g. ammonium or sodium hydroxide), as detailed in Chris Stavroudis' 2015 WAAC article.³ When fully ionized, citrates have three binding locations with which to chelate metals and degradation products (fig. 1). The exact mechanism by which this improved cleaning of organic discoloration occurs is unknown, and the field would benefit from further study into this topic.

Methodology

In order to provide a more complete picture of how citrate-treated papers might age in different environmental conditions, samples were aged in three separate experiments:

- UV illumination
- Gallery (UV filtered) illumination
- Thermal aging oven

Colorimetric analysis was used to measure the rate of change during each experiment.

Sample preparation

Two test papers were selected:

- Whatman Type 1 filter paper (W)
- Sized antique rag paper (A)

Strips (1cm x 4cm) of these papers were treated with 1% w/v sodium citrate solution (adjusted to pH 7 with citric acid) in the following ways:

- Control (C)
- Overall bathing (30 min.), no rinsing (O)
- Overall bathing (30 min.) and rinsing (15 min.) with filtered water (R)
- Local swab application with swab rinse (L)

Colorimetric Analysis

Before any aging experiments began, the colorimetric values of each paper and Blue Wool sample were measured using a portable Minolta Cm-2600d spectrometer and OnColor software (v.5.5.5.3 QC). Measurements were taken at the end of each trial period, and at the completion of each experiment.

Microfade Testing

The control samples were analyzed with microfade testing to predict the rates of change for the all treatment variations of the Whatman and antique papers. The microfade testing was carried out with a Newport FSQ-KG2 heat-absorbing filter in the light path.

The tests were run for 30 minutes, with spectra collected every 10 seconds. To determine the sensitivities of the samples, the curves obtained were compared to those of the ISO Blue Wool standards.⁴

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UVA and Gallery Light Experiment

An example of a sample set for the two illumination sources is pictured in figure 2. A card of Blue Wool standards was included; only Blue Wools 1-4 were monitored as 5-8 do not change at a high rate.

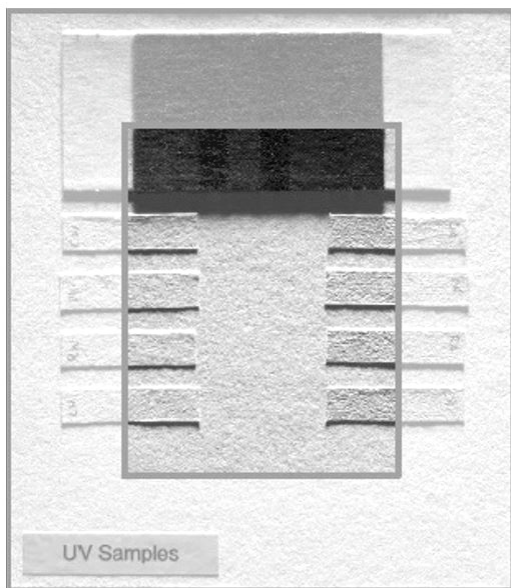


Fig. 2. Schematic of sample set for UV aging (in raking light) indicating how the window mat covers half of the samples. Sample sets for both light aging experiments include Whatman filter paper, antique rag paper, and Blue Wool standards. (Photo: Yosi Pozeilov)

The sample sets included the Blue Wool standards (BW), 4 strips of Whatman filter paper (W), and 4 strips of antique paper (A). Those 4 strips represent one of the citrate application methods: control (C), overall immersion (O), overall immersion with rinsing (R), and local swab application (L). During the experiments, half of each paper sample strip was covered (CV) and the other half was exposed (EX) by a window mat to block the illumination source (fig. 2).

Thus the combinations for light aging are:

BW1	blue wool 1
BW2	blue wool 2
BW3	blue wool 3
BW4	blue wool 4
CW	control Whatman
CA	control antique
OW	overall immersion Whatman
OA	overall immersion antique
RW	overall immersion w/ rinsing Whatman
RA	overall immersion w/ rinsing antique
LW	local swabbing Whatman
LA	local swabbing antique

further designated CV for covered or EX for exposed.

The UV fluorescence analysis cabinet at LACMA uses a Spectroline Model CL 150 light source from Spectronics Corporation that falls in the UVA/B range of 280-400 nm. The samples were exposed to UV radiation for a total of 1203 hours in 16 trials of increasing exposure time.

The gallery light used for the light box is a GE 940Lumen HIR Plus XL 53W 120V (HIR™ Plus XL Halogen Lamp, PAR38). The samples were exposed for 317 hours, until it was apparent that the samples were aging very similarly to those in the UV aging experiment and further aging would not be necessary.

Thermal Aging Experiment

The eight samples aged in the oven had the same W/A and C/O/R/L permutations, without the covered or exposed variations, as the samples are not subjected to light. Rather, the sample strips of paper were clipped to a rack in the Weiss WKL 34/+10 oven, and aged at 80° C and 50% RH for 844 hours in 5 trials of increasing time intervals.

Results

Results from the microfade testing indicated that citrate-treated papers changed at approximately the same rate as their untreated counterparts, and all samples had little color change overall (fig. 3). Interestingly, any citrate treated samples seem to age at a slightly slower rate than the untreated samples, although perhaps not enough to indicate any significant mitigation of color change. This pattern continued through the three different aging experiments.

After 70,000 minutes (116 hours) of UV aging, there was a very slight color change in the Whatman samples, with ΔE values around 1 (fig. 4). This change was not visible to the human eye. There is a more pronounced color change in the antique samples, although these also changed at roughly the same rate (fig. 5). After 70,000 minutes of aging, the ΔE values for the antique samples fall roughly between 5.5 and 7.5. All samples are significantly less light sensitive than Blue Wool 4, which has a ΔE of 18.65.

Gallery light aging produced very similar results. After 70,000 minutes (116 hours), the ΔE values of the Whatman samples are close to 1, while the ΔE values for the antique samples hover around 2. At the end of the experiment, at 19,020 minutes (317 hours), the ΔE values for the Whatman samples range from 1-2 and those for the antique samples remain near 3. For comparison, the ΔE of the Blue Wool 2 at the end of the experiment was just over 8.

Thermal aging caused samples to change in a manner consistent with UV and gallery light aging as well. After 5,000 minutes (83 hours), the ΔE values for the Whatman samples fell between approximately 2 to 3, with the control closer to 3 and the overall immersion sample slightly below 2. The ΔE values for the antique samples had a greater range and fell between 6-12, with the control closer to 12 and the overall immersion sample slightly greater than 6.

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Discussion

Overall, citrate stain reduction solutions appear to be safe for papers. This experiment was designed using “normal conditions” for a citrate stain reduction protocol; the species and concentration the author typically chooses for a treatment. Extrapolations might be made to the performance of ammonium citrate solutions, or to higher or lower concentrations. The effects of such solutions on various modern papers are also yet to be formally assessed.

All three aging experiments indicate that citrate-treated samples age at approximately the same rate as their untreated counterparts. Any reduction in rate of aging may be the result of citrate ions left in the paper support, as the length of bathing does not directly correlate with aging performance (ex. overall immersion at 30 minutes ages better than overall immersion for 30 minutes with 15 minutes of rinsing). The author welcomes ideas on this topic.

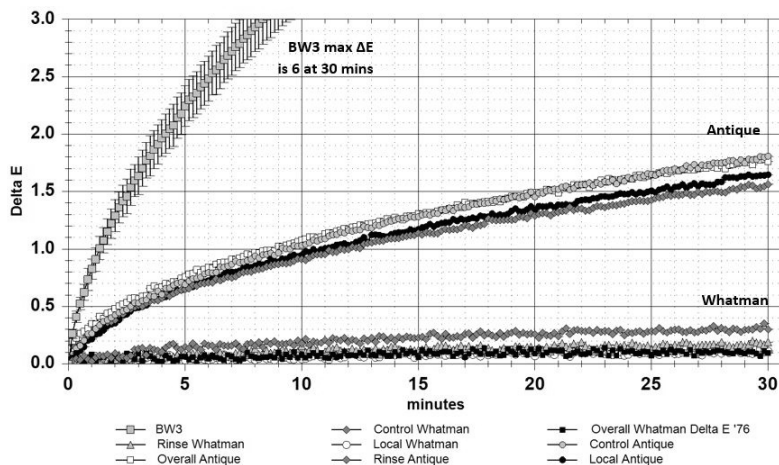


Fig. 3. MFT results showing the ΔE values for the Blue Wool 3 standard, the Whatman samples, and the antique samples

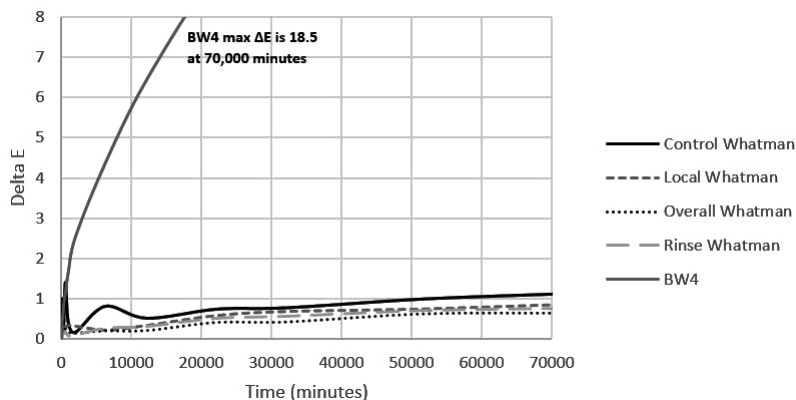


Fig. 4. ΔE values for UV aging of Whatman samples and Blue Wool 4 standard

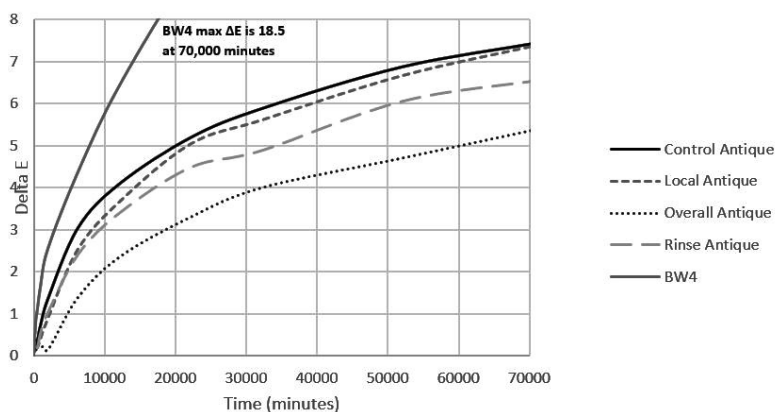


Fig. 5. ΔE values UVA aging of antique samples and Blue Wool 4 standard

Future research topics include instrumentation not immediately available at the LACMA labs: tensile strength, degree of polymerization, etc. This study focused on colorimetric evaluation, yet mechanical analysis would paint a different picture on the health of the paper supports after accelerated aging as well. Again, the author encourages others in the field to continue researching this topic and contribute to our collective body of knowledge.

Conclusions

The results of the microfade testing and the three accelerated aging experiments show that citrate solutions do not appear to cause any deleterious effects to paper supports over time. Paper samples, regardless of fiber composition or treatment with the citrate solution, appear to age at the same rates and are overall much less prone to change than the Blue Wool standards we rely on for indicating light sensitivity. In conclusion, citrate solutions, when used in normal conditions, appear to be safe for continued use in paper conservation treatments.

References

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