

Introduction

Ammonium citrate has been used primarily for the surface cleaning of paintings and in the removal of metallic staining on marble and leather objects. It is a strong chelating agent whose dibasic and tribasic forms are easily adjustable for neutral and basic pH levels. This recommends it for use in paper conservation to solubilize and remove acidic soiling and staining possibly related to a metallic charge. Based on Antoinette Dwan's techniques and studies on the use of ammonium citrate for the removal of these constituents in paper objects, this research was interested in the physical and chemical changes occurring after paper samples were treated with immersion solutions followed by thermal accelerated aging. The research compared the application of excessive w/v solutions of ammonium citrate to established aqueous deacidification and alkalization washing practice. Future research may focus on comparing ammonium citrate applications to solvent and bleaching treatments and their general and desired effects in reducing soiling and staining in paper.

Materials

- Ammonium citrate tribasic A1332 (TAC)
- Saturated calcium hydroxide ($\text{Ca}(\text{OH})_2$)
- Whatman no. 40 filter paper
- Blue-dyed rag ledger paper (c. 1850)
- Newsprint (c. 1915)



Methods of Analysis

- Visual assessment
- Zero-span breaking strength
- Spectrophotometry
- Fourier transform infrared spectroscopy (FTIR)
- X-ray fluorescence spectroscopy (XRF)
- pH measurements

Treatment Designation

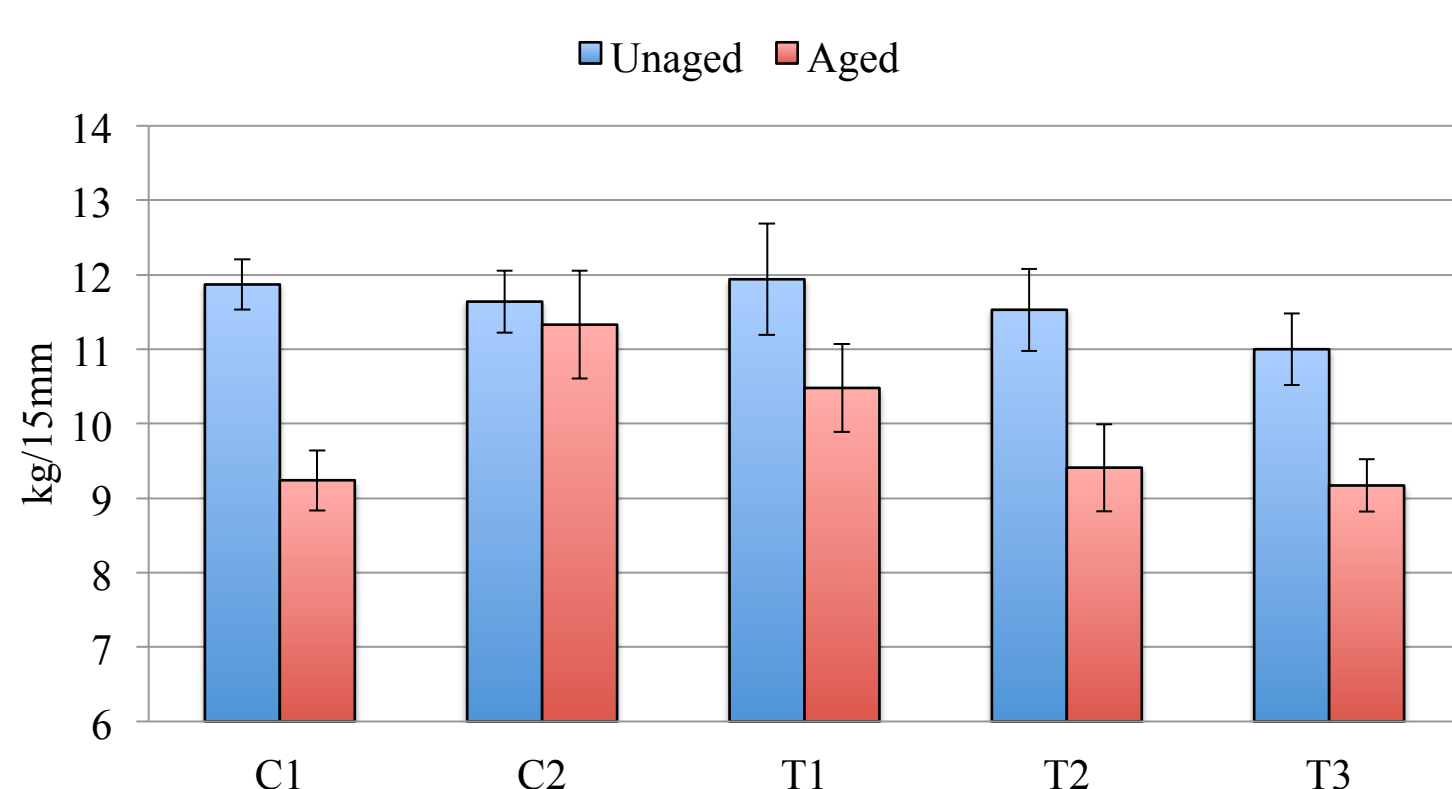
Experiment

Procedure

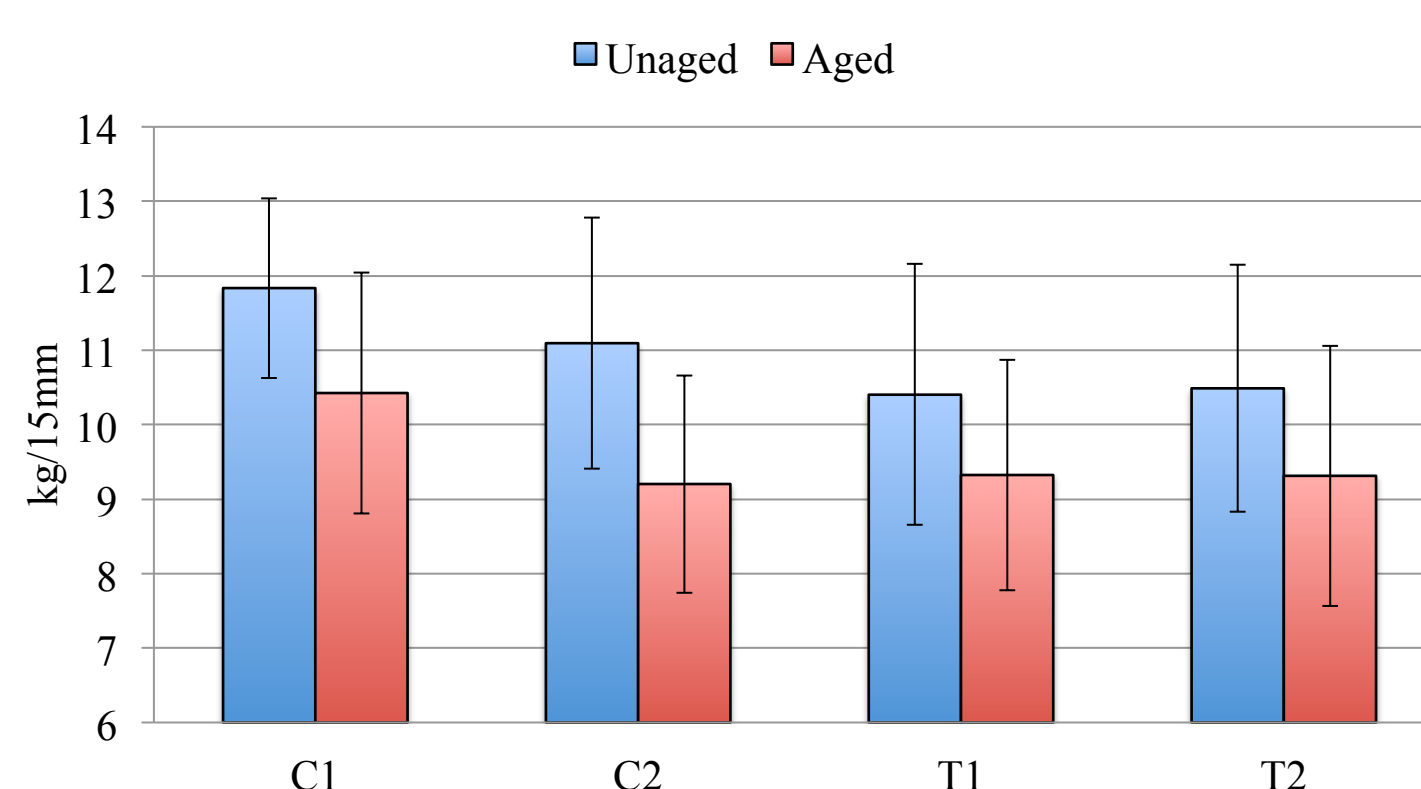
Treatment Designation	Experiment	Procedure
C1	Untreated	Control; half of set aged in tubes 14 days at 90°C
C2	Alkaline wash	Distilled water immersion at pH 8 with $\text{Ca}(\text{OH})_2$; half of set aged in tubes 14 days at 90°C
T1	Alkaline wash + 1% w/v TAC solution	Distilled water immersion at pH 8 with $\text{Ca}(\text{OH})_2$; 1% w/v TAC immersion pH 7-8; clearance with distilled water immersion at pH 8 with $\text{Ca}(\text{OH})_2$; half of set aged in tubes 14 days at 90°C
T2	Alkaline wash + 3% w/v TAC solution	Distilled water immersion at pH 8 with $\text{Ca}(\text{OH})_2$; 3% w/v TAC immersion pH 7-8; clearance with distilled water immersion at pH 8 with $\text{Ca}(\text{OH})_2$; half of set aged in tubes 14 days at 90°C
T3	Alkaline wash + 10% w/v TAC solution	Distilled water immersion at pH 8 with $\text{Ca}(\text{OH})_2$; 10% w/v TAC immersion pH 7-8; clearance with distilled water immersion at pH 8 with $\text{Ca}(\text{OH})_2$; half of set aged in tubes 14 days at 90°C

Results & Discussion

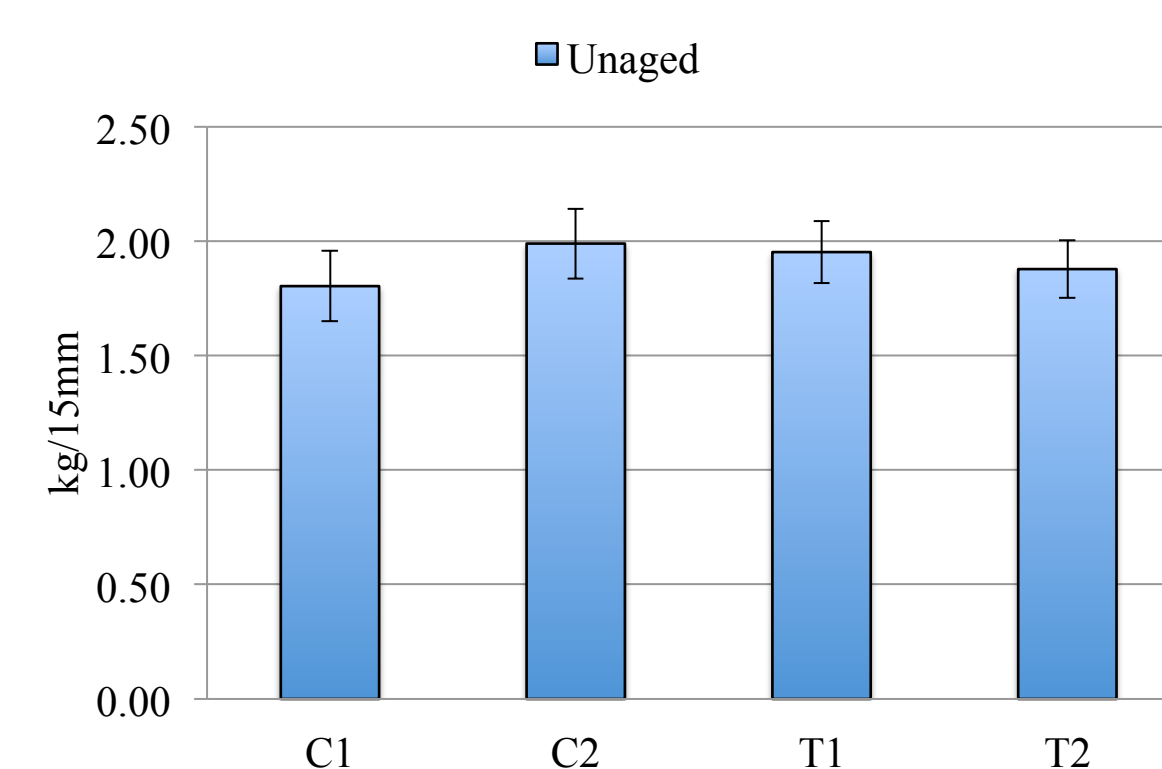
Whatman Zero-Span Breaking Strength



Blue Ledger Zero-Span Breaking Strength

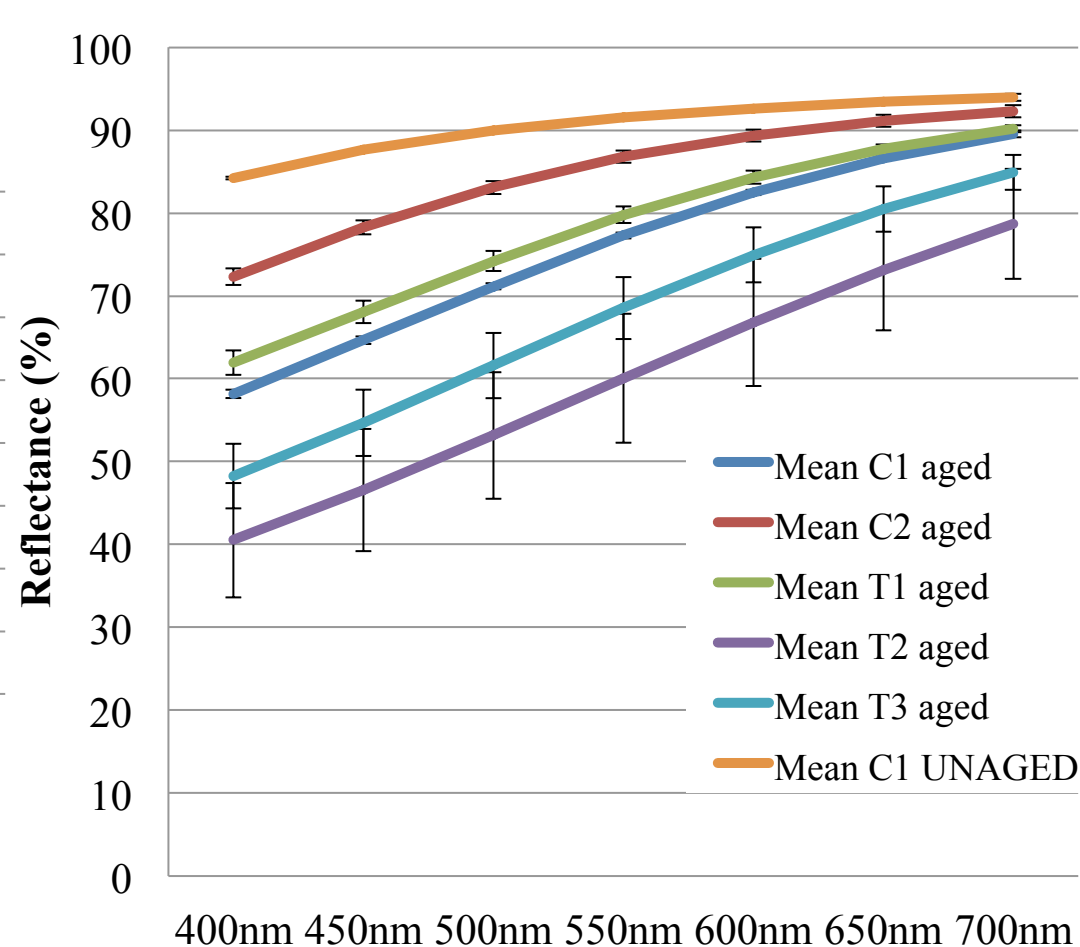
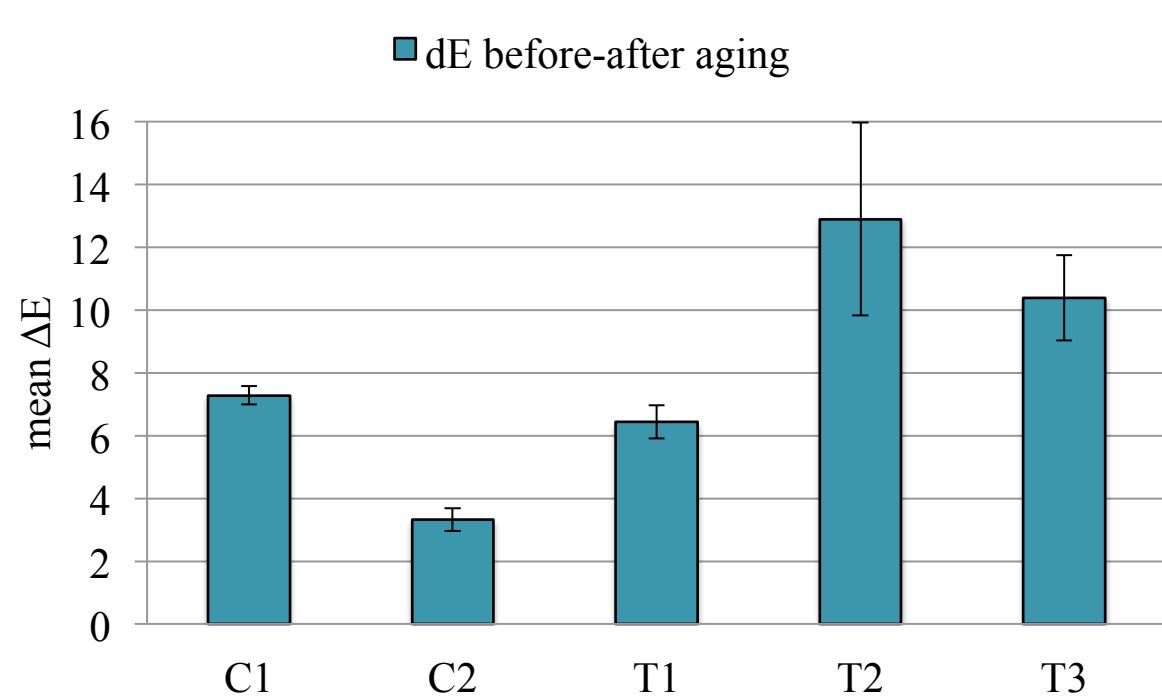


Newsprint Zero-Span Breaking Strength



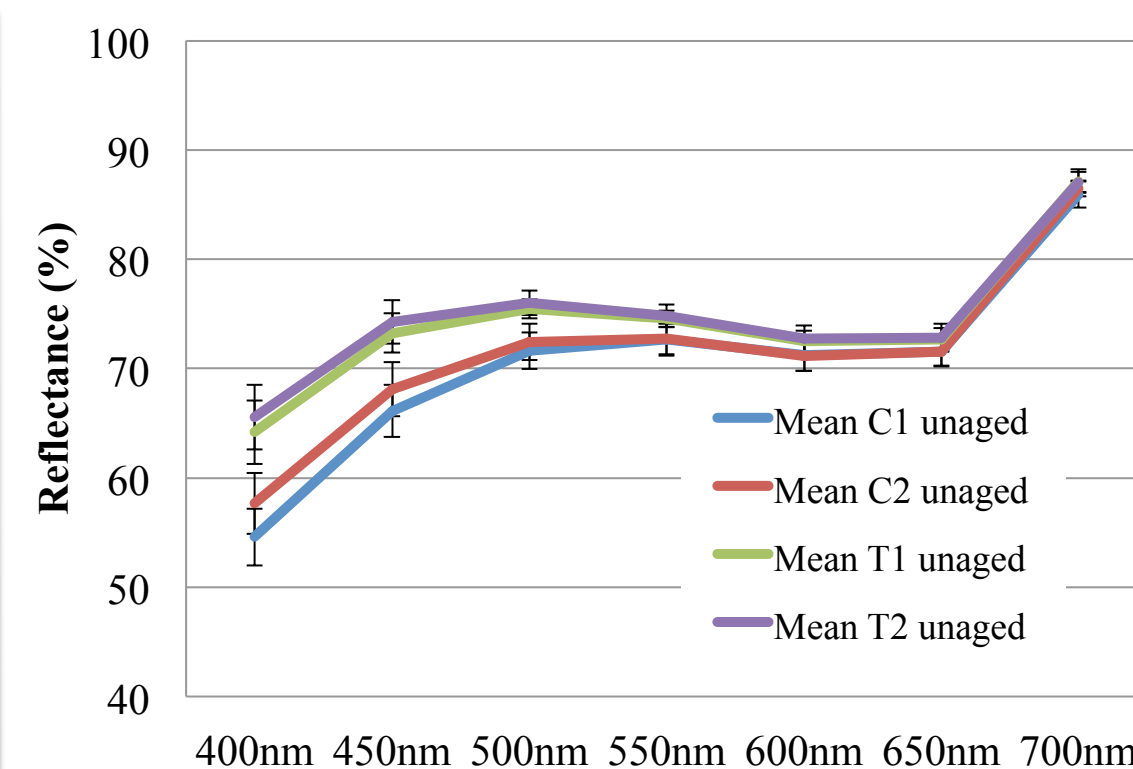
- Average fibre strength for each sample paper type's TAC treatments are comparable or slightly less than both the untreated control and alkaline wash control in both unaged and aged states.
- Evidence of some correlation between a higher surface pH and a greater zero-span tensile strength.

Whatman ΔE 2000



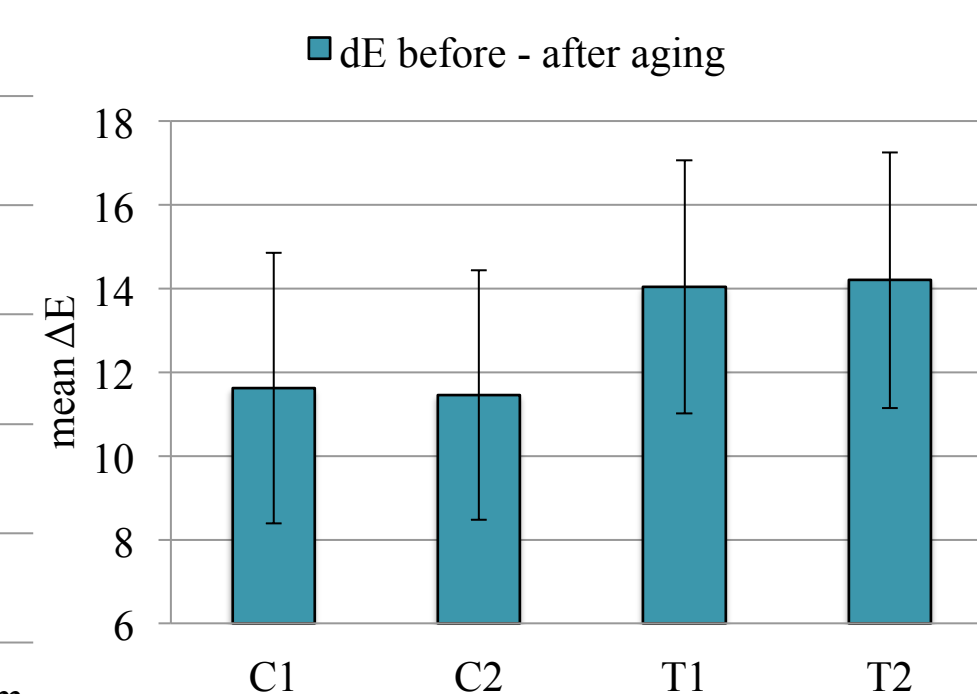
- ΔE for the Whatman samples was complicated by the discolouration observed in aged sample set T2 and T3 from what is believed to be residual TAC that was not removed by the clearance immersion. Replicate experiments, FTIR, and XRF were conducted in effort to determine this.

- ΔE in sample set T1 was slightly less than ΔE of the untreated control, while more than the ΔE of the alkaline wash control, indicating the TAC treatment inhibited the discolouration upon artificial thermal aging.



- ΔE for the unaged blue ledger samples was a dramatic change due to a loss of yellow soiling discolouration (decrease in b^* and increase in a^*), resulting in a visual intensification of blue colour of the paper immediately after the immersion treatments for TAC treatments.

Blue Ledger ΔE 2000



- ΔE before and after aging of the samples was large for the TAC treatments due to the large ΔE observed immediately after the immersions.
- The $L^*a^*b^*$ values between all the aged samples were similar, and the TAC treatments even maintained smaller b^* and larger a^* values than both the control and wash control counterparts.

Conclusions

- 1-10% w/v ammonium citrate tribasic (TAC) treatments did not significantly affect the average fibre strength of various papers of different composition.
- The removal of TAC from within the paper fibres through thorough rinsing with water is paramount, regardless of the TAC solution's concentration.
- ΔE of aged Whatman paper treated with 1% w/v TAC was less than that of the aged untreated control. TAC treatment may have inhibited discolouration potential induced by artificial thermal aging.
- TAC effectively reduced yellowing in the blue coloured ledger paper, enhancing the blue colour, which was partially maintained when the samples were aged.
- Further methods of analysis and TAC treatment in comparison to solvent and bleaching treatments that are similarly artificially aged are necessary.