Article: Investigating the Effects of Rigid Polysaccharide Gels on Several Paper Sizings
Author: Karissa Muratore and Haley Carter
Source: Book and Paper Group Annual 41, 2022
Pages: 85-104
Editors: Kimberly Kwan, Managing Editor, and Roger S. Williams, Assistant Editor
Editorial Office: bpgannual@gmail.com
ISSN: 2835-7418

The *Book and Paper Group Annual* is published once each year by the Book and Paper Group (BPG), a specialty group of the American Institute for Conservation (AIC). It was published in print from 1982 to 2021, and transitioned to a digital publication in 2022. All issues are available online at https://culturalheritage.org.

Print copies of back issues are available from AIC. All correspondence concerning back issues should be addressed to:

American Institute for Conservation
727 15th Street NW, Suite 500
Washington, DC 20005
info@culturalheritage.org www.culturalheritage.org

KARISSA MURATORE AND HALEY CARTER

Investigating the Effects of Rigid Polysaccharide Gels on Several Paper Sizings

INTRODUCTION

Since about 2003, rigid polysaccharide gels have been an area of interest and experimentation in the library and paper conservation specialties. Despite a growing body of studies and publications, this new material still requires research.

Based on the lead author's personal experience and an anecdote told by Michelle Sullivan at the 2017 *Gels in Conservation Conference* (2017, 19.1 min), concerns were raised about potential interactions between gellan gum and gelatin-sized papers. Contact with gellan gum seemed to be correlated with paper discoloration and darkening after artificial degradation despite the use of interleaving papers during treatment. Conversely, discoloration and darkening were not observed where agarose gel blocks were used for spot testing. These observations were made under conditions that did not allow for conclusions to be drawn.

Goal/Rationale

The initial goal of this research was to determine if contact with gellan gum negatively affects the long-term preservation and aging characteristics of gelatin-sized papers when compared to agarose treatment. However, during this experiment's development, it was discovered that the brand of gellan gum being sold was affected by supply chain issues that have not been communicated to the conservation field. In addition, the literature review revealed that gel-specific interactions with common paper sizings had not been previously researched. As a result, the project expanded from focusing on potential reactions between gellan gum and gelatin sizing to the potential effects of various rigid polysaccharide gels on several common paper sizings. Effects were evaluated with commonly used techniques and instruments to make the experiment easier to reproduce and compare with other experiments and similar data sets.

Papers presented during the Book and Paper Group Session, AIC's 50th Annual Meeting, May 13–18, 2022, Los Angeles, California

Literature Review

Book and paper conservators began experimenting with rigid gels because of their many preparation, modification, and application advantages. Rigid gels have been used successfully for local stain reduction, overall bathing, humidification, backing and attachment removal, aqueous and solvent-based adhesive reduction, and measuring surface pH and conductivity (Warda et al. 2007; Iannuccelli and Sotgiu 2010; Möller 2014; Sullivan, Brogdon-Grantham, and Taira 2014; Maheux 2015; Kwan 2016; Hughes 2017; Prestowitz 2017). Research has been conducted on their molecular structure, formulation, application, mechanism, cleaning efficacy, residues, compatibility with various additives and interleaving, and effects on certain physical and optical properties (Armisén and Galatas 2000; Sworn 2000; Tuvikene et al. 2008; Miyoshi 2009; Iannuccelli and Sotgiu 2010; Botti et al. 2011; Picone and Cunha 2011; Casoli et al. 2013; Isca 2014; Mazzuca et al. 2014a, 2014b, 2014c; Micheli et al. 2014; Cremonesi 2016; Hughes and Sullivan 2016; Kavda et al. 2016; Barbisan and Dupont 2017; Bertasa et al. 2017; Cremonesi and Casoli 2017; Sullivan et al. 2017). However, research focusing on the potential interactions between rigid gel and paper sizings is limited.

Related published research on paper sizing found gellan gum extracted significantly less gelatin sizing than immersion bathing when treating 16th-, 17th-, and 18th-century papers, which is potentially due to gel pore size and protein morphology (Isca 2014, 137–155). Other articles incidentally mention sizing: Hughes (2017, 62) states the type and amount of sizing disproportionately affects traditional surface pH readings. Iannuccelli and Sotgiu (2010, 34–35), Möller (2014, 44–45), and Micheli et al. (2014, 7) all note the amount of sizing has a crucial impact on the efficacy of rigid gel treatment and/or most effective gel concentration. Warda et al. reiterate advice shared by others that rigid gels should not be directly applied to unsized papers to prevent tide lines (2007, 274). Sullivan et al. observed that the hydrophobicity of sized papers reduces residue deposition, and the removal of gelatin sizing was observed as decreased autofluorescence in handmade rag paper that included samples with a barrier tissue (2017, 47–49). Möller et al. note that gelatin- and

Treatment Type			Paper Type				
Gel Type	Application	Artificially Degraded	Whatman	Antique Gelatin	Modern Gelatin	Alum Rosin	Starch-based AKD
Controls	No Gel	No	5	5	5	5	5
		Yes	5	5	5	5	5
	Water	No	N/A	N/A	N/A	N/A	N/A
		Yes	5	5	5	5	5
2% Ticagel Gellan Gum	Direct	No	5	5	5	5	5
		Yes	5	5	5	5	5
	Interleaved	No	5	5	5	5	5
		Yes	5	5	5	5	5
2% Kelcogel Gellan Gum	Direct	No	5	5	5	5	5
		Yes	5	5	5	5	5
	Interleaved	No	5	5	5	5	5
		Yes	5	5	5	5	5
5% Agarose	Direct	No	5	5	5	5	5
		Yes	5	5	5	5	5
	Interleaved	No	5	5	5	5	5
		Yes	5	5	5	5	5
Total Samples of Each Paper Type:			75	75	75	75	75

Table 1. Breakdown of experiment paper-treatment-application groups

synthetic-sized papers exhibited similarities in Delta E and morphological changes as opposed to unsized papers (2014, 44). Warda et al. found discoloration occurred after artificially degrading gelatin-sized watercolor papers treated with Carbopol and Laponite without interleaving but not in papers treated with agarose or methylcellulose (2007, 274).

Warda et al. also suggest reactions between poultice residues and paper components, such as sizing or fillers, could cause discoloration after artificial degradation (2007, 274). Sullivan extrapolates on this during her *Gels in Conservation Conference* presentation and postulates the discoloration seen in gelatin-sized papers treated with gellan gum may be caused by the two materials interacting with each other (Sullivan 2017, 19.4 min). This is plausible, since they are easily combined at 80°C–90°C (Shim 1985, 2; Kwang et al. 2003, 796; Yueyuan et al. 2018, 4767)—a common temperature range for artificial degradation of paper (Porck 2000, 16–18). Huber presents the Maillard reaction as another possible cause of browning in papers aged at 180°C–200°C and treated with gellan gum containing particular fermentation residues; however, the study did not take sizing into account (2016).

EXPERIMENTAL DESIGN

Five paper types with different sizings were treated using four treatment types—three different rigid polysaccharide gels and water. Treatments were applied directly to the paper samples or with an interleaving tissue. This resulted in 40 paper-treatment-application combinations. Half the paper samples for each treatment combination were artificially degraded (table 1).[1]

At each stage, visible and ultraviolet (UV) induced visible fluorescence light images were taken, and color, pH, and ionic conductivity were measured. The documentation methods described below were chosen since they are easily repeatable in most labs and easily compared to both past and future research.

Materials

Paper and sizings

The five paper types were selected to determine if age and/or sizing type were significant factors. Fiber analysis, using polarized light microscopy and micro-chemical spot testing, was done to confirm the characterization of the chosen paper samples and their sizings before experimentation (table 2). Each paper type was cut into 75 3 × 3 inch samples, which provided enough space to take all measurements while leaving an untreated 1/2 inch margin to prevent contamination during handling. Each sample received a unique number for record keeping.

Rigid gels & water

Each paper type was treated with one of three different rigid polysaccharide gels or water. Kelcogel and agarose were

Paper Type by Sizing	Name	Date	Fiber	Microchemical Testing
Whatman (unsized control)	Whatman Chromatography 1CHR	c. 2016	Pure cellulose cotton linters	Graff "C" Stain
Antique gelatin	handmade paper	pub. 1752, Paris	High cellulose bast	Graff "C" Stain; ninhydrin test
Modern gelatin	Canson Ingres	bought in 2020	Mixed wood, bast, and cotton	Graff "C" Stain; ninhydrin test
Alum rosin	LC Blue Book-keeper Test Book	1993	Highly purified pulp	Graff "C" Stain; aluminon test
Starch-based Alkyl ketene dimers (AKD)	Stonehenge Aqua Watercolor	bought in 2020	Highly fibrillated cotton	Graff "C" Stain; iodine/potassium test

Table 2. Paper Sample Identification

initially chosen because they are the most commonly used and researched rigid gels in the field. During this project's development, however, the lead author learned the vendor TALAS has been selling Ticagel by TIC Gums, Inc., as Kelcogel by CP Kelco since at least 2020 without clearly changing the online description and labeling. Since it is likely many practitioners have unknowingly used this different brand of gel, Ticagel was added to the experiment to compare its performance against Kelcogel. Water was included as a treatment to determine if reactions were gel specific or simply due to the introduction of water.

All three rigid gels were cast to ~3.0 mm thickness (Sullivan 2017, 45) and made per the standard literature preparation recommendations (table 3) (CP Kelco 2007; Iannuccelli & Sotgiu 2010; Isca 2014; Möller 2014; Sullivan 2017). The lowest typical concentration for each gel was chosen to maximize moisture release while still being representative of real-world use (Möller 2014, 8; Huber 2016; Sullivan, pers. comm., 2021). Each gel type was cut into 2 × 2 in. squares and centered to leave an untreated 1/2 in. margin on each paper sample. The water treatment was delivered via 2 × 2 in. Whatman chromatography papers soaked in DI water and blotted before application.

Interleaving

Interleaving is commonly used in the gel-bathing process of paper. To control for its potential effects on the gel-paper interactions, half of each paper-treatment combination (i.e., 5 out of 10 samples) were interleaved to determine if the degree of residue had a demonstrable effect on the resulting measurements and trends. HM-54 Usu-Gami Thinnest (9 g/m^2) tissue was selected to follow previously used protocols (Sullivan 2017; Muratore 2018). The tissue was cut into 3 × 3 in. squares and placed between the gel and paper sample during treatment.

Treatment Type	Percent	Recipe
Deionized water	N/A	deionized water
Ticagel L-6 Gellan Gum	2%	0.4 g/L calcium acetate in deionized water
CPKelco KELCOGEL LT100 Gellan Gum	2%	0.4 g/L calcium acetate in deionized water
Stellar Scientific Agarose LE	5%	deionized water

Table 3. Treatment Type Preparation

Treatment & artificial degradation procedure

Application of treatment type

To avoid contamination, all gels were handled with nitrile gloves. Interleaving was placed on half the paper samples—covering the entire paper sample before the moisture source was applied. After the rigid gel or water squares were placed, polyester film was laid on top of each sample set (fig. 1) to slow evaporation and defend against contaminants (Sullivan 2017). An acrylic block and light weights were then added to encourage uniform contact (Möller 2014, 45).

Treatment lasted 20 minutes to approximate a common treatment interval and ensure contact between gels and papers without being longer than proven necessary (Sullivan 2017, 43 and 46). Immediately after treatment, paper samples were placed under Hollytex, blotter, and weights until moved into a blotter stack to dry overnight.

Artificial degradation

Half the samples of each paper-treatment-application combination—200 paper samples in all—were artificially degraded, while the other half are being kept to serve as naturally-aged

Fig. 1. Detail of experiment setup highlighting gel application, using a rigid polyester jig, on paper samples directly and with interleaving.

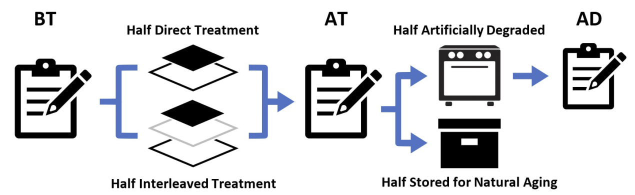

Fig. 2. Diagram of documentation stages.

samples for potential future testing. Samples designated for artificial degradation were sent to the Library of Congress, where they were hung by clips in a large oven and exposed to 80°C +/–2 and 65% RH +/–2% for 21 days. The author recognizes natural aging cannot be accurately predicted by artificial degradation (Porck 2000; Isca 2014, 41–42; Magee, pers. comm., 2020). However, the conditions used in this experiment were chosen to make the results most comparative to specific studies done on these materials (Warda 2007; Sullivan 2017; Muratore 2018). Artificial degradation has also been referred to as "accelerated" and "artificial aging" in the literature (Porck 2000).

Documentation procedure

At each stage—before treatment (BT), after treatment (AT), and after artificial degradation (AD)—samples were measured for color, pH, and ionic conductivity and imaged under visible and ultraviolet induced visible fluorescence (UV) light. Samples that were not artificially degraded were only measured and imaged BT and AT (fig. 2).

Color

The CIE L* a* b* color space, as defined by the International Commission on Illumination (CIE) (X-Rite Pantone 2016), was used to quantitatively track color change. Measurements were taken with an i1 X-Rite Pro Spectrophotometer and i1 Profiler software with the following settings: Delta E/ΔE 2000 (1:1:1), 2° observer angle, and D50 Illuminant. Delta E is a measurement of the total color difference between two samples (Datacolor 2013). Specifically, Delta E is the square root of the sum of the squared differences of each parameter (L*, a*, and b*). L* is the light-dark axis where higher values indicate lightening and lower values indicate darkening; a* is the red-green axis where higher values indicate a red shift and lower values indicate a green shift; b* is the yellow-blue axis where higher values indicate a yellow shift and lower values indicate a blue shift. According to X-rite (Customer Support, pers. comm., March 2021), Delta E values below 1 are not perceptible by human eyes; values between 1 and 2 are perceptible on close observation; and values between 2 and 10 are perceptible at a glance.

Measurements were taken on the same five testing sites on each paper sample at each treatment stage. Polyester film overlays were used to keep sample locations consistent (fig. 3). To avoid the printer's ink on the antique gelatin papers, an

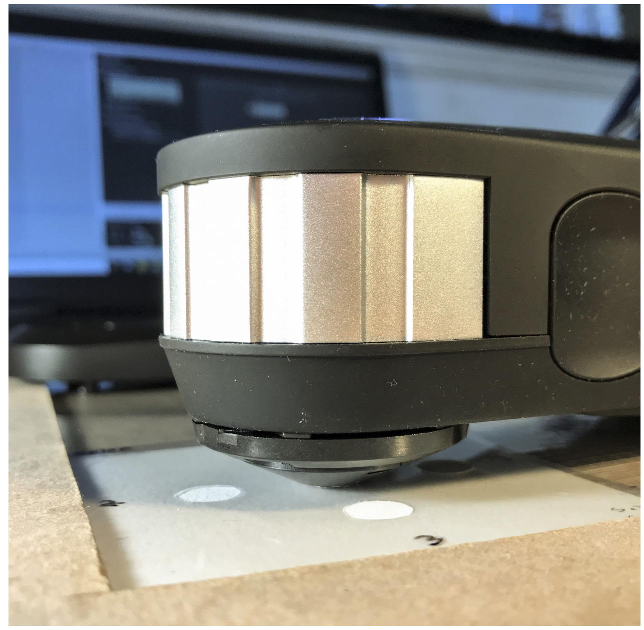

Fig. 3. Spectrophotometer and polyester overlay used to take color measurements of a paper sample.

overlay with an alphanumeric grid was used to identify and record testing sites (fig. 4). This adjustment made the testing sites less consistent and increased their variability when compared to the blank paper samples. Non-inked central and edge testing locations were identified for each antique gelatin paper sample during the planning stages to mitigate variability as much as possible.

All color measurements were taken before pH and conductivity measurements to prevent accidental change in color through proximity of gel blocks and water.

Fig. 4. Polyester film overlay with alphanumeric grid used to avoid the printer's ink when taking color measurements of the antique gelatin paper samples.

pH and conductivity measurements

Conductivity and pH measurements were taken to see if they shared patterns with the color data or other observations, because they are becoming more common characterization techniques in paper conservation. Measurements were taken with a Horiba Twin Conductivity meter and a Horiba LAQUAtwin pH meter, which was allowed to wet up for at least 1 hour prior to use. Before taking measurements, both meters were calibrated using the manufacturer's provided solutions. The pH meter was calibrated using the two-point method and was rinsed with distilled water between each measurement.[2]

pH and conductivity levels were collected with ~3 mm, 5% agarose square gel blocks that were placed on test sites for a minimum of 5 minutes. The gel blocks were rinsed and stored in DI water before use. According to Hughes, differences in concentration, dwell time, diameter, and thickness of gel plug has negligible effects on measurements, and the gel plug method is reliable for papers with a pH between 4.5 and 7—where most collections' materials tend to fall (2017, 65–66). See supplemental material for more details on the measurement process and meter troubleshooting.

During each treatment stage, measurements were taken from three new locations evenly distributed diagonally across a quadrant (fig. 5). To reduce test sites, each gel block was used to measure both pH and conductivity. As a result, conductivity was measured first to avoid the extraction of ions by the pH meter.

Imaging: Visible light and ultraviolet induced visible fluorescence

Photos were taken to capture changes in color and fluorescence of paper samples at different stages to qualitatively support the color data. They were taken with a digital single-lens reflux camera: a NIKON D700, with a 60 mm lens, set on a tripod. All raw images were processed in Adobe Camera Raw in best accordance with AIC standards (Warda et al. 2011). Visible light images were taken under LED 500, 5600K Flolights at approximately a 45° angle with the following camera settings: manual exposure, ISO 800, f-8 aperture, 1/60 seconds shutter speed, and preset white balance. UV light images were taken under long-wave UV (365 nm) lights at approximately a 45° angle, a PECA 918 filter, and the following camera settings: manual exposure, ISO 800, f-8 aperture, 1/8 second shutter speed, and Shade (8000 K) white balance.

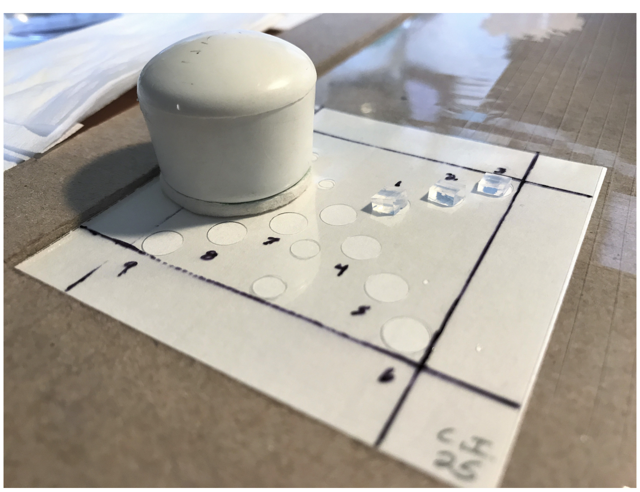

Fig. 5. Detail of agarose gel blocks on sample sites to take BT pH and conductivity measurements.

The gel plugs used for pH and conductivity sampling were expected to cause changes that would be visible in the photo documentation. For this reason, photo documentation was conducted before taking any other measurements.

Data analysis

Across all groups and stages, 4760 color measurements (L*, a*, and b*), 2850 pH measurements, and 2850 conductivity measurements were recorded. Full datasets are available in the supplementary materials. The samples that underwent artificial degradation were used to determine if paper type, treatment type, and/or interleaving affected the response of color, pH, or conductivity to artificial degradation.

Data were analyzed in R (R Core Team 2020) using RStudio (RStudio Team 2018). The R packages tidyverse (Wickham et al. 2019), ggpubr (Kassambara 2020), gtsummary (Sjoberg et al. 2021), kableExtra (Zhu 2021), and colorspace (Zeileis et al. 2020) were used to tidy and visualize data.

L*, a*, and b* values were used to calculate Delta E from BT to AT and BT to AD as a cumulative measure of color change for each paper sample at each of these time points. Linear models were used to assess the significance of interactions between paper sizing and gel treatment on color change AD. Specifically, analysis of variance was used to compare linear models with a response variable of Delta E from BT to AD as follows: intercept only model, paper type only model, paper type and gel treatment additive model, and paper type and gel treatment interactive model.

To determine how color changed AD, the average L*, a*, and b* values were calculated for each paper type BT and AD and tested for statistically significant differences with Kruskal-Wallis ranked sum tests. L*, a*, and b* values, as well as their corresponding colors BT and AD were plotted to get a visual sense of the amount of change in these parameters.

The averages and ranges of the pH and conductivity values were compared overall and analyzed for all paper sizing, gel, and interleaving combinations AD with linear models.

Response variables were modeled by combined gel and interleaving treatments for each paper type. Each treatment's test statistic was compared to that of the control group to identify significant effects of specific interleaving, gel, and paper combinations. Treatments with a p value less than 0.05 were considered to be significantly different from the control. The response variables were: Delta E from BT to AD, and L*, a*, b*, pH, and conductivity AD. Full tables of these results are available in the supplemental materials; statistically significant group averages and treatment effects are reported selectively below. When referenced in the results, SE indicates standard error, and p indicates the probability of the treatment group values being drawn from the control distribution.

RESULTS

Color change—Delta E

Comparison of the Delta E values between all treatment stages show the majority of color change for all paper and treatment types occurred AD (fig. 6). The AD color change was best modeled by including paper type, gel treatment, and their interaction terms as predictive variables, indicating interactions between paper sizing and gel treatments affect color change AD.

The unsized Whatman paper exhibits the least amount of color change AD; many samples have no perceptible change (Delta E < 1) and some show only slightly perceptible change (Delta E < 2) (fig. 7). All other paper types exhibit clearly perceptible color change (Delta E > 2) AD. The antique gelatin-sized papers show the most variation in color change AD; they range from slightly to clearly perceptible (0 < Delta E < 6). However, the antique gelatin samples also began with the most variable amount of discoloration BT.

*Color—L*a*b* (fig. 8)*

How paper color changed AD varied by paper type. The Whatman paper, which showed the least amount of color

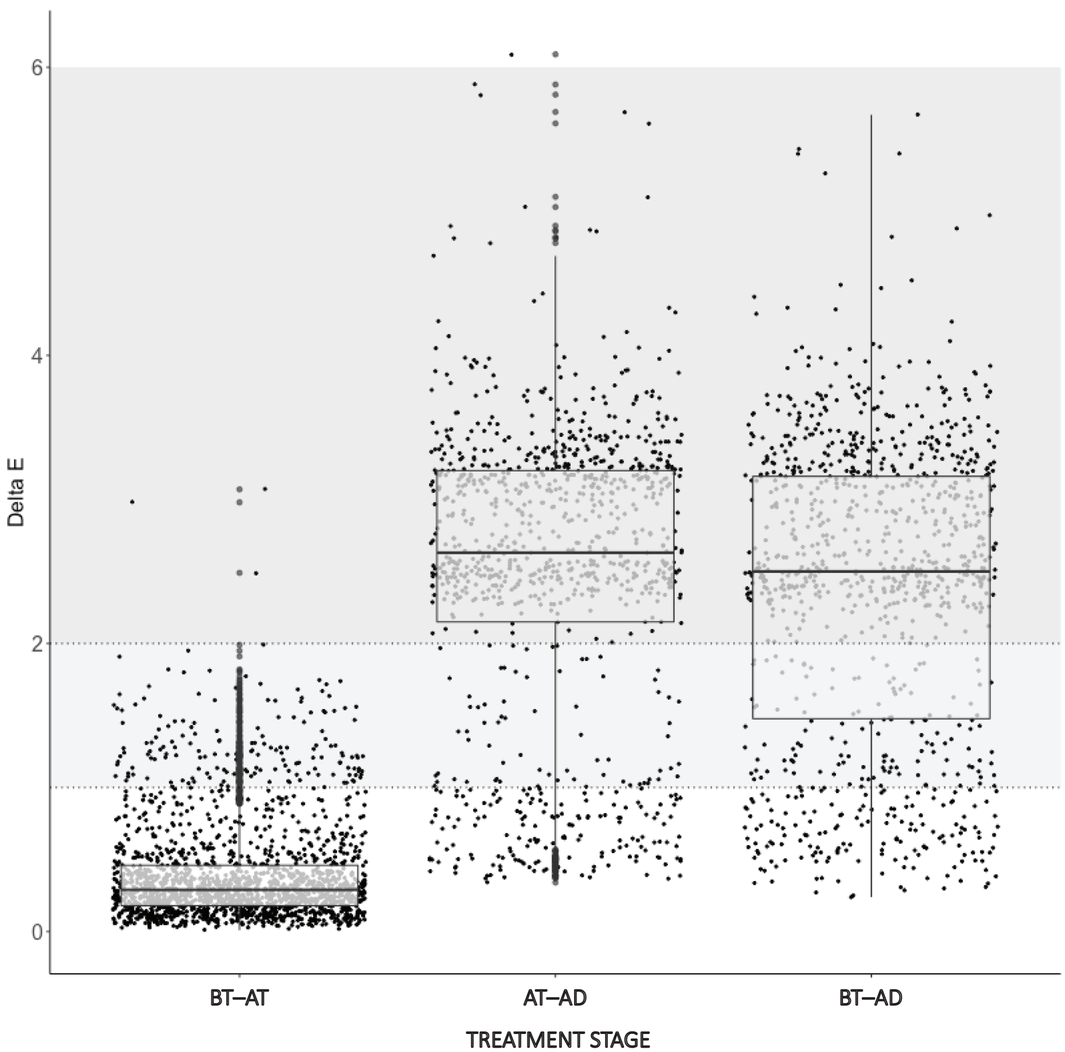

Fig. 6. Boxplots with underlying data points of Delta E for all samples from BT to AT, AT to AD, and BT-AD.

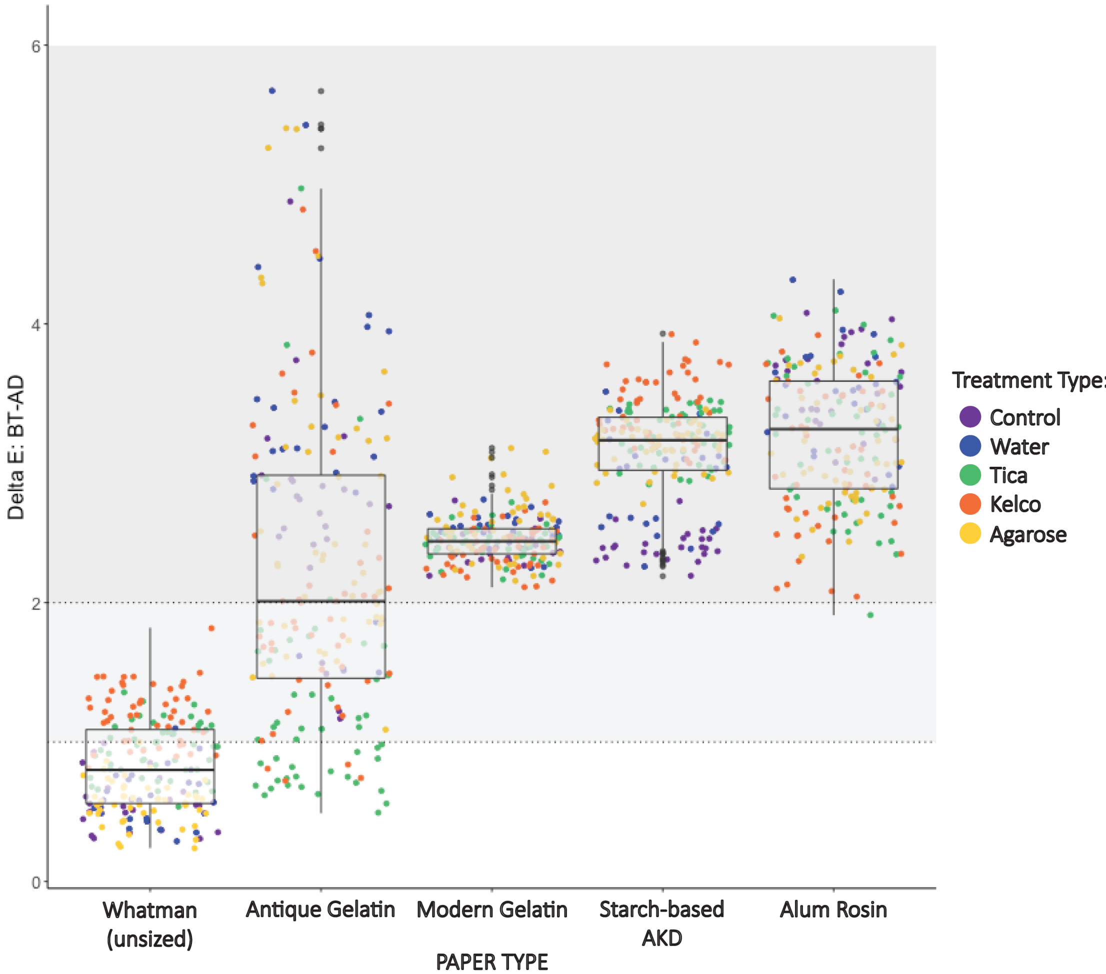

Fig. 7. Boxplots with underlying data points of Delta E from BT to AD for all samples, separated by paper type and colored by treatment type.

change overall, yellowed as indicated by increased b* values AD. This was the only parameter that completely differentiated (no overlap in sample results) between BT and AD in Whatman samples. The antique gelatin-sized paper, which had the most variability in color change overall, got darker (lower L*), redder (higher a*), and yellower (higher b*) AD, though there was overlap BT and AD in all parameters. The modern gelatin-sized paper showed consistent perceptible color change AD. It got darker, greener (lower a*), and yellower, and the BT and AD samples were clearly differentiated by their a* and b* values. The paper sized with starch-based alkyl ketene dimer (AKD) showed two distinct paper sample groups by color BT. Both groups darkened and shifted yellow AD; however, they responded differently in the a* parameter with Group 1 shifting red and Group 2 shifting green AD (G1 and G2 in fig. 8). The alum rosin paper darkened, reddened, and yellowed AD. Though some of the changes in the mean numerical value for each parameter were quite small, all differences between BT and AD were statistically significant for all paper types as tested with Kruskal Wallis test (kruskal.test() function in R) (fig. 9). The b* parameters generally showed the greatest difference AD, which suggests yellowing occurs in all papers, as they degrade, regardless of sizing.

pH and conductivity

Generally, pH level and variability depends on the treatment and paper type (fig. 10). The naturally aged papers (antique gelatin and alum rosin) showed much less variability in pH AD, while the Whatman and new papers (modern gelatin and AKD) show a small change in variability AD. All treatments of the Whatman paper decreased in pH AT including the controls; however, AD the pH of all samples, except those treated with agarose and interleaved Kelcogel, rose to approximately BT levels. The naturally aged papers increased in pH AT with all three gels but remained unchanged after water treatment; they then decreased in pH AD—the antique gelatin paper's pH being similar to BT levels and the alum rosin's pH being notably lower than BT levels. The modern gelatin

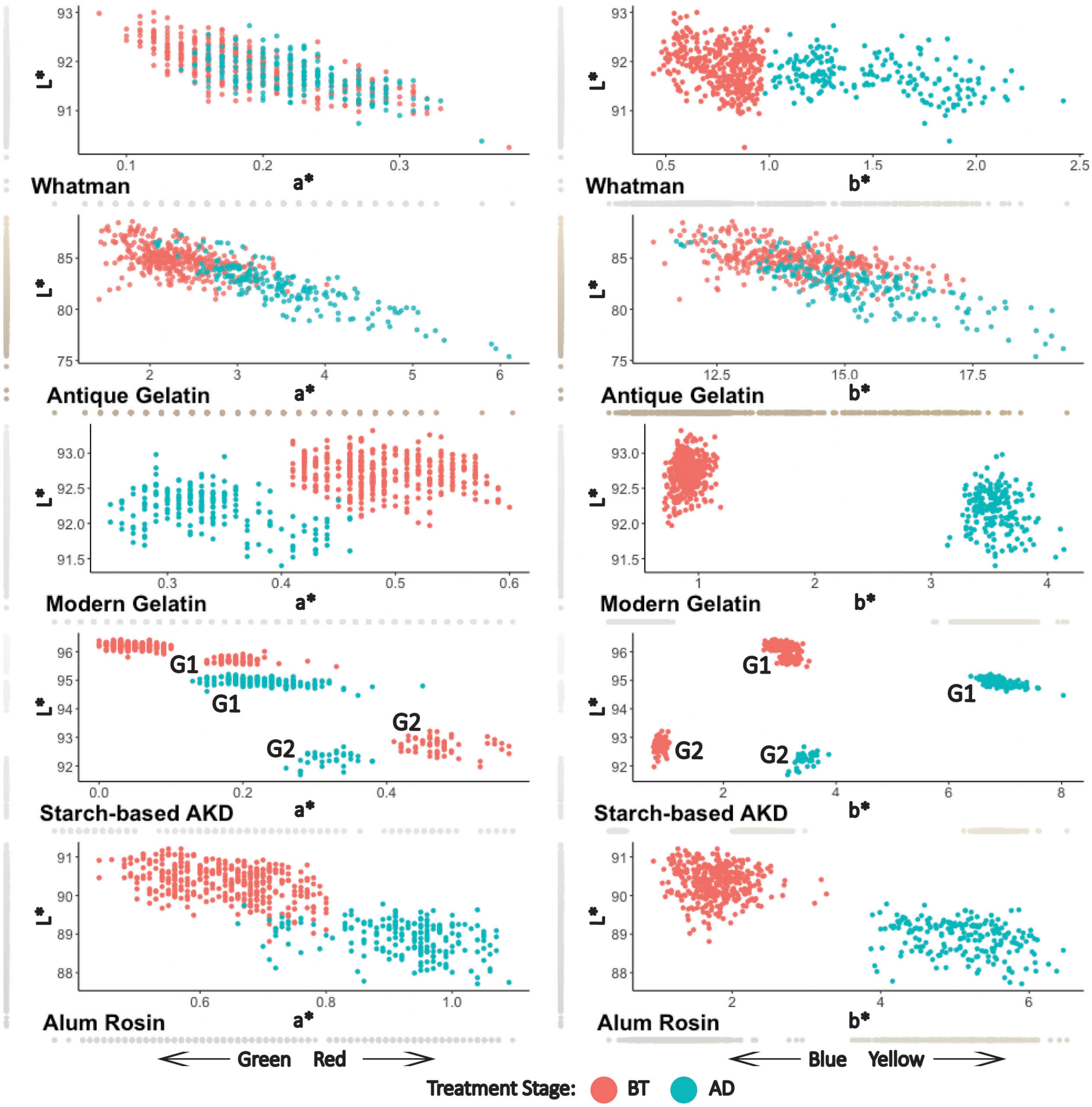

Fig. 8. Scatterplots of L* a* b* values BT (blue) and AD (red) for each paper type. There are two plots for each paper type. The left-side plots have a* on the x-axis and the right-side plots have b* on the x-axis. All plots have L* on the y-axis. Along the axes of each plot are the same sample points plotted in one dimension in their corresponding real-life colors where; the range along the y-axis shows their variation from dark to light, and their range along the x-axis shows their variation from green to red (a*, left side) or blue to yellow (b*, right side). Many changes are imperceptible, even when there is distinct clustering in the scatterplot.

paper showed very little change in pH at the different time points. The AKD-sized paper decreased in pH both AT and again AD.

For the antique gelatin-, modern gelatin-, and AKD-sized papers, conductivity became less variable and lower across time AT and AD (fig. 11). Regardless of time point, the antique gelatin-sized paper was most variable in conductivity, ranging from less than 0.1 mS/cm to just under 0.5 mS/cm, while the Whatman and modern gelatin-sized papers were the least variable. The conductivity of the Whatman paper

Paper sizing	Color parameter	BT mean	AD mean	p value (Kruskal-Wallis test)
Whatman	L*	91.92	91.70	2.4e-09
Whatman	a*	0.19	0.22	1.3e-15
Whatman	b*	0.77	1.49	5.8e-87
Antique Gelatin	L*	84.82	82.33	6.7e-43
Antique Gelatin	a*	2.32	3.48	2.3e-65
Antique Gelatin	b*	14.08	15.25	5.7e-21
Modern Gelatin	L*	92.71	92.20	5.1e-63
Modern Gelatin	a*	0.49	0.34	4.1e-82
Modern Gelatin	b*	0.91	3.55	5.7e-87
Starch-based AKD	L*	95.55	94.48	1.2e-48
Starch-based AKD	a*	0.14	0.24	4.6e-33
Starch-based AKD	b*	2.71	6.29	1.6e-87
Alum Rosin	L*	90.35	88.90	5.0e-84
Alum Rosin	a*	0.64	0.92	1.2e-81
Alum Rosin	b*	1.78	5.12	6.0e-87

Fig. 9. Mean L★ a★ b★ measurements for each paper type BT and AD, and the p values from each Kruskal-Wallis test for significant difference between the means of each measurement for each treatment stage.

was generally less than 0.1 mS/cm, and the conductivity of the modern gelatin-sized paper was generally right around 0.1 mS/cm. There were four individual outliers with conductivity greater than 0.5 mS/cm: two in the AKD samples BT, and two in the antique gelatin samples AD. In order to better visualize the majority of the data these outliers have been removed on figure 8.

Paper, treatment, application interactions AD

Whatman (unsized) paper (fig. 12)

The Whatman paper control samples had a Delta E value of 0.59 that corresponds to imperceptible color change. Both Ticagel and Kelcogel, interleaved and directly applied, showed significantly more color change than the control: all Ticagel treatments increased Delta E by 0.36 on average ($p \leq 5.3 \times 10^{-10}$), direct Kelcogel increased Delta E by 0.58 ($p < 2.2 \times 10^{-16}$), and interleaved Kelcogel increased Delta E by 0.65 ($p < 2.2 \times 10^{-16}$). This puts the Ticagel-treated samples on the verge of slightly perceptible color change and the Kelcogel-treated samples within the range of slightly perceptible color change.

The only type of color change for both the direct and interleaved Ticagel treatments occurred in the b★ parameter, which indicates these samples yellowed more than the controls. All three L★a★b★ parameters were different from controls for the direct and interleaved Kelcogel gel treatments; these samples yellowed, darkened, reddened, and reduced in pH more

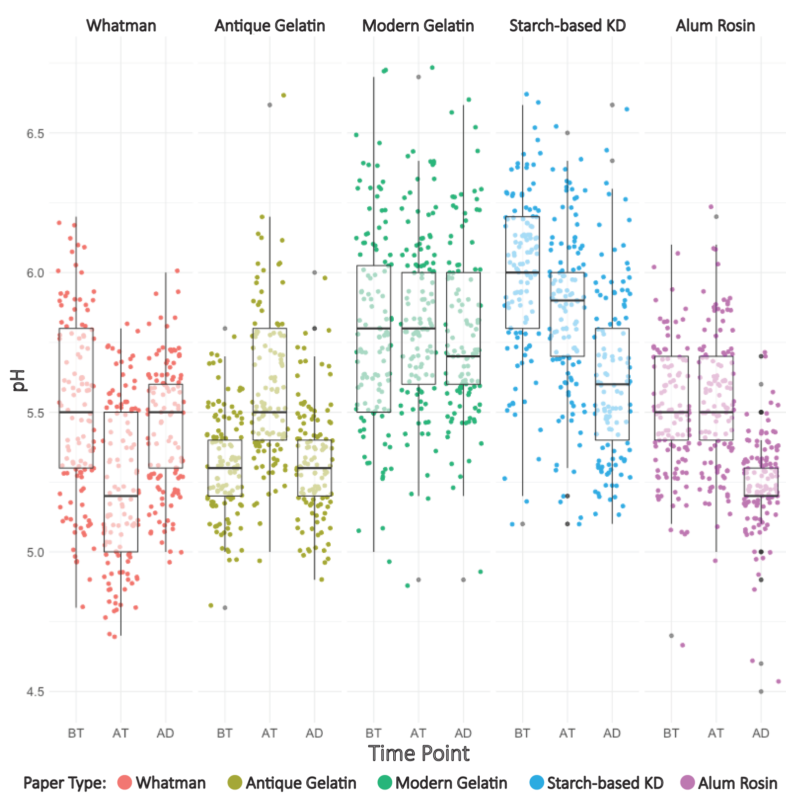

Fig. 10. Boxplots with underlying data points showing pH values at each time point separated and colored by paper type.

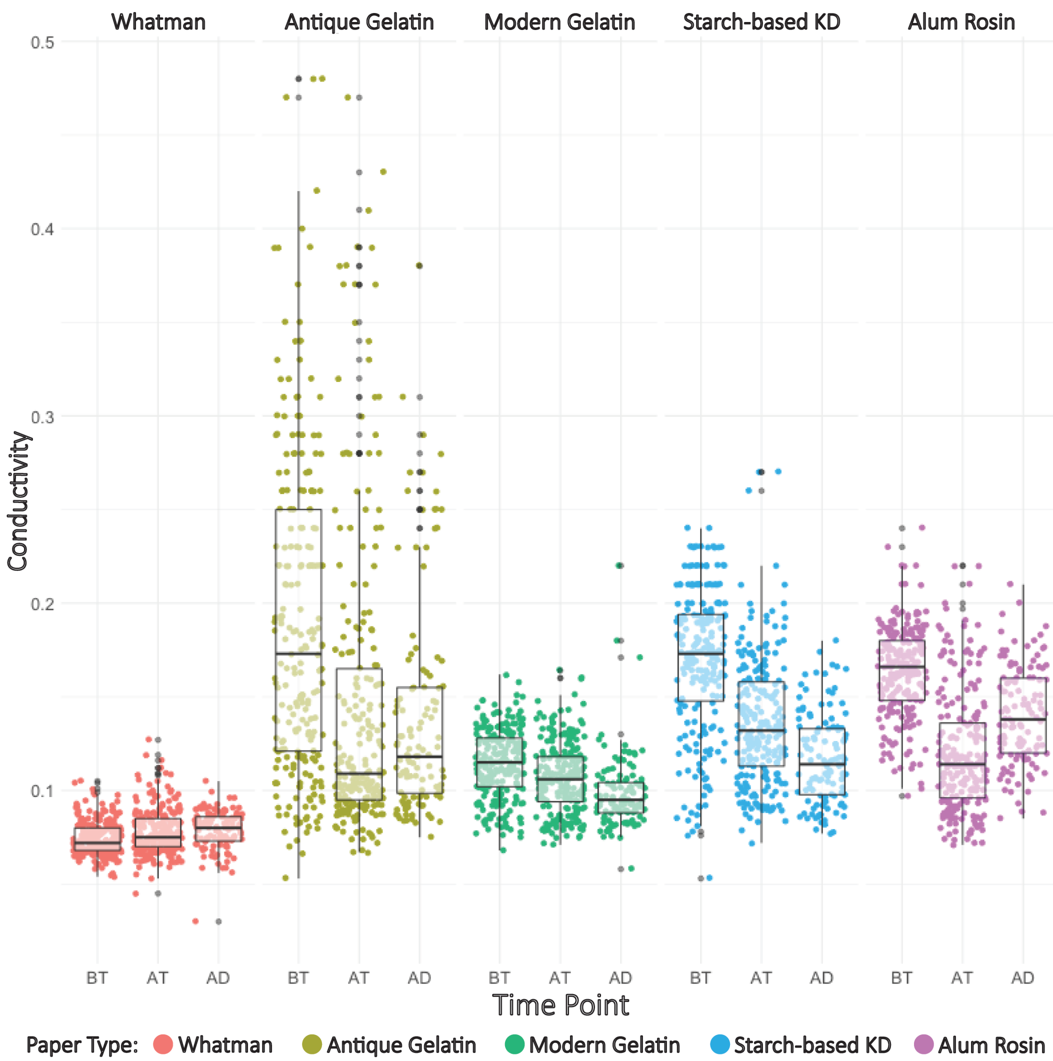

Fig. 11. Boxplots with underlying data points showing conductivity values at each time point separated and colored by paper type (with four outlying samples removed).

than the controls (Direct: –0.13, $p = 0.01$, Interleaved: –0.4, $p = 4.9 \times 10^{-13}$). The water treatment showed no significant difference as compared to the control in any of the color measurements, pH, or conductivity. The agarose gel treatments were not significantly different from the control in terms of Delta E, L★, or b★, but the interleaved agarose treatment showed less reddening (–0.02, $p = 0.04$) and had a lower pH (–0.40, $p = 4.9 \times 10^{-13}$) and conductivity (–0.009, $p = 0.01$). The direct agarose samples only had a reduced pH as compared to the control (–0.39, $p = 9.9 \times 10^{-13}$).

Antique gelatin-sized paper (fig. 13)

The antique gelatin-sized paper control samples had an average Delta E of 2.6, which corresponds to perceptible color change. The water-treated samples had a Delta E significantly higher than the controls (0.7; $p = 0.005$). All of the Ticagel-treated samples and the direct Kelcogel-treated samples had significantly lower Delta E values on average than the controls; they showed only slightly perceptible color change. The direct agarose samples also had a lower Delta E than the controls, while the interleaved agarose samples had a higher Delta E value.

Reduced Delta E values for the Ticagel-treated samples are due to reduced darkening, reddening, and yellowing as compared to the control, though the effect of direct Ticagel on reddening was only marginally significant. The interleaved Ticagel treatment had a much larger effect on average than the direct treatment on each of these measurements as evidenced by larger effect sizes and lower p values; however, there was more variation AD in the interleaved Ticagel-treated samples than the direct samples. Direct Kelcogel-treated samples and direct agarose-treated samples

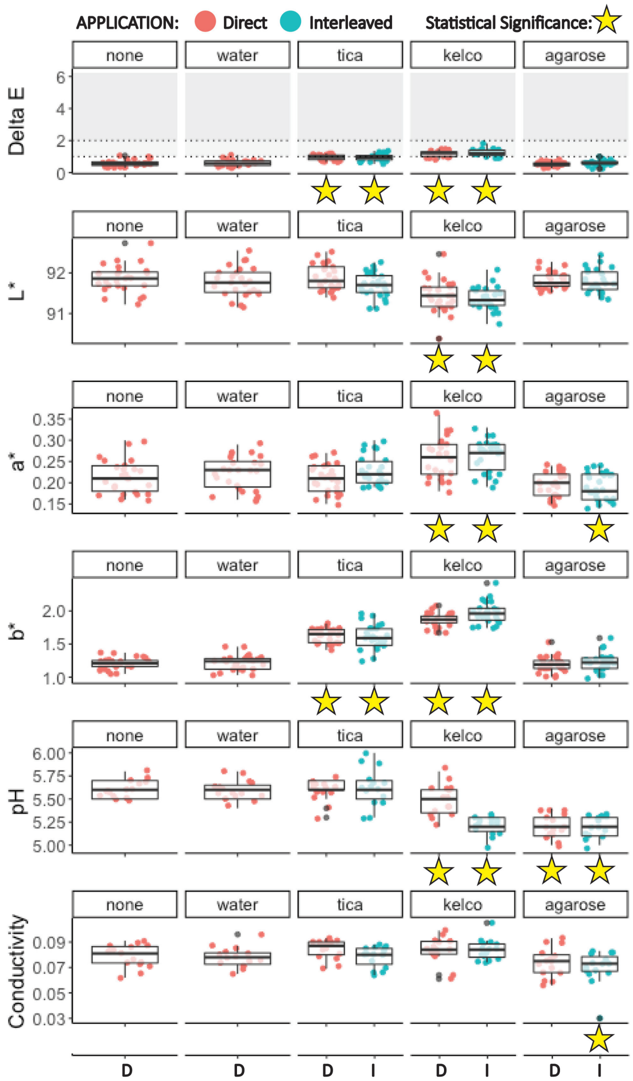

Fig. 12. Boxplots of Delta E, L★ a★ b★, pH, and conductivity AD for the Whatman paper samples, separated by gel treatment and colored by interleaving.

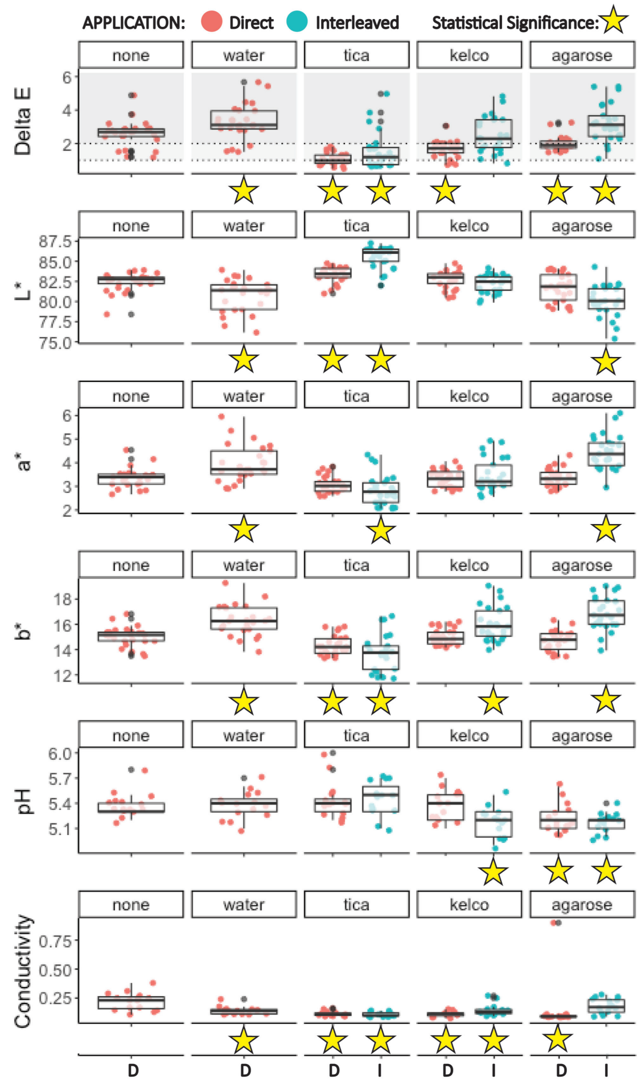

Fig. 13. Boxplots of Delta E, L★ a★ b★, pH, and conductivity AD for the antique gelatin paper samples, separated by gel treatment and colored by interleaving.

showed reduced color change overall as compared to the controls; however, none of the individual color measures were significantly different, which suggests these treatments did not impact any particular color parameter strongly but influenced each enough that their sum was significantly reduced. Though the interleaved Kelcogel treatment did not significantly change Delta E as compared to the control, it did significantly increase b★. The interleaved agarose samples significantly increased Delta E as compared to the controls and increased darkening, reddening, and yellowing. The water treatment showed no significant difference as compared to the control on any of the color measurements.

Both agarose treatments and the interleaved Kelcogel decreased pH, and all treatment types, except interleaved agarose, decreased the conductivity as compared to the controls.

Modern gelatin-sized paper (fig. 14)

The modern gelatin paper control samples showed perceptible color change with an average Delta E value of 2.41. The water treatment increased this average color change by 0.11 ($p = 0.009$), and the interleaved agarose treatment increased it by 0.20 ($p = 5.76 \times 10^{-6}$). None of the other treatments significantly impacted the mean color change; however, some of them did impact an individual color change parameter. All treatments increased yellowing as compared to the controls, and this increase was significant for all treatments except the interleaved Ticagel and Kelcogel. The change in a★ was more directionally variable between treatments; water decreased the reddening seen in the controls and both agarose treatments increased reddening. Both agarose treatments were also darker than the controls.

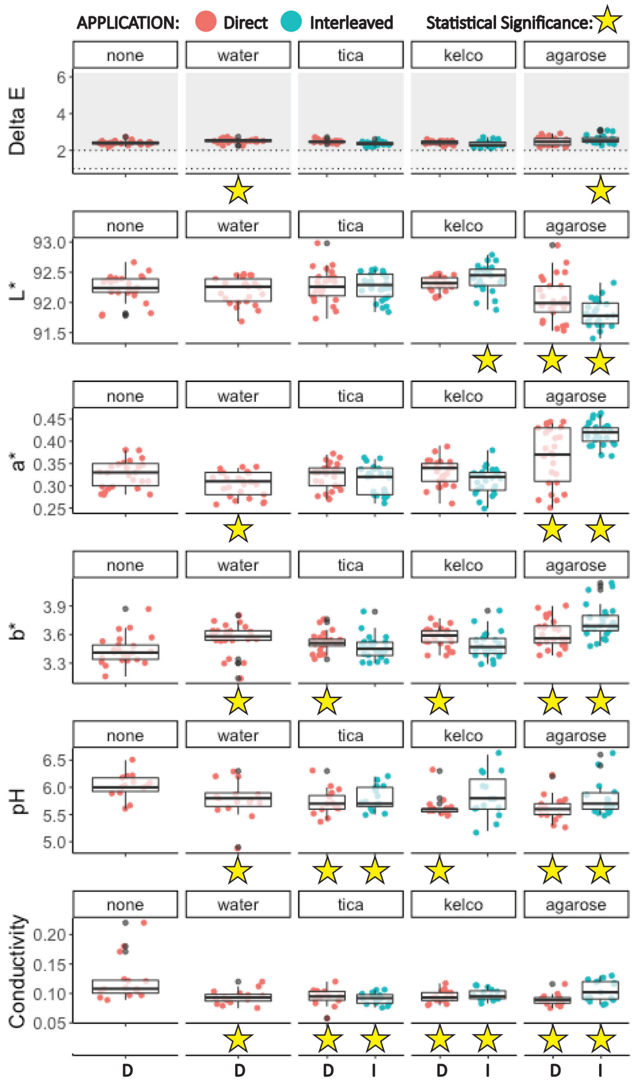

Fig. 14. Boxplots of Delta E, L* a* b*, pH, and conductivity AD for the modern gelatin paper samples, separated by gel treatment and colored by interleaving.

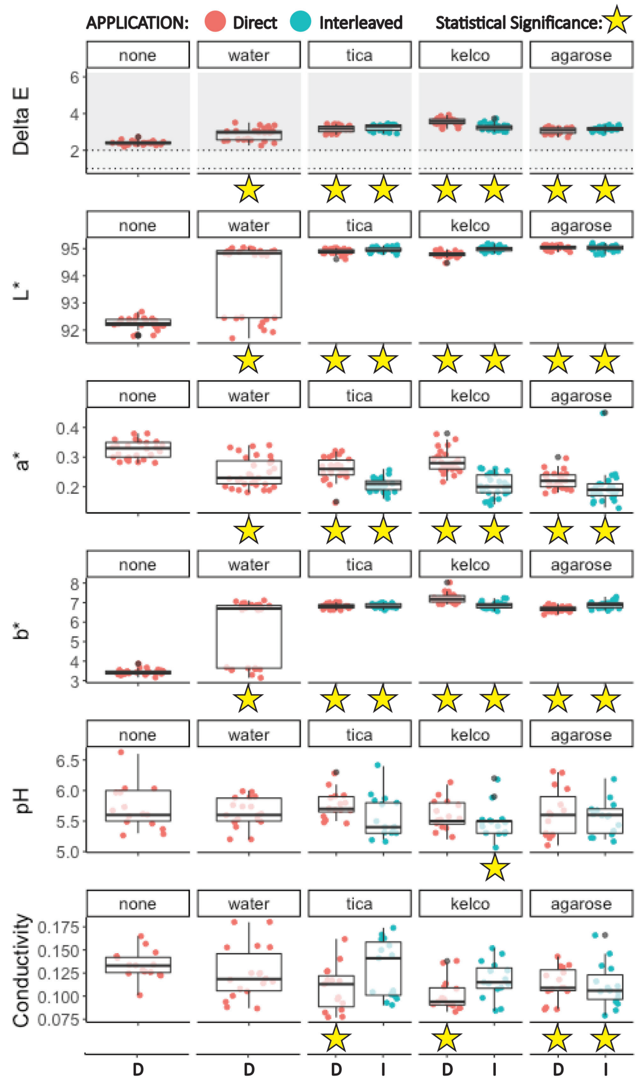

Fig. 15. Boxplots of Delta E, L* a* b*, pH, and conductivity AD for the AKD paper samples, separated by gel treatment and colored by interleaving.

The average pH of the controls AD was 6.03 mS/cm (SE = 0.08), and all treatment groups lowered this average by about 0.4 mS/cm except for the interleaved Kelcogel treatment that showed less of a decrease and was not statistically significant. Conductivity was also reduced by all treatments; direct agarose had the largest effect, and the interleaved agarose had the smallest effect.

Starch-based AKD-sized paper (fig. 15)

The AKD-sized paper control samples had an average Delta E of 2.41 (SE = 0.04), which was increased to various degrees by each treatment group. Direct Kelcogel showed the largest effect with an increase in Delta E of 1.13 as compared to the controls ($p < 2.0 \times 10^{-16}$). Water treatment showed the smallest effect with an increase of 0.48 as compared to the controls ($p = 2.63 \times 10^{-15}$). All treatments decreased darkening, decreased reddening, and increased yellowing as compared to the controls. Interleaved treatments decreased reddening more than the directly applied gels.

Interleaved Kelcogel-treated papers showed lowered pH as compared to the controls ($p = 0.03$). All direct gel and interleaved agarose treatments decreased conductivity as compared to the controls.

Alum-rosin–sized paper (fig. 16)

The alum rosin controls showed perceptible color change with an average Delta E value of 3.57 (SE = 0.07). All treatments lowered this Delta E value; however, that effect was only statistically significant for the direct gel treatments and the interleaved Kelcogel treatment. While the cumulative

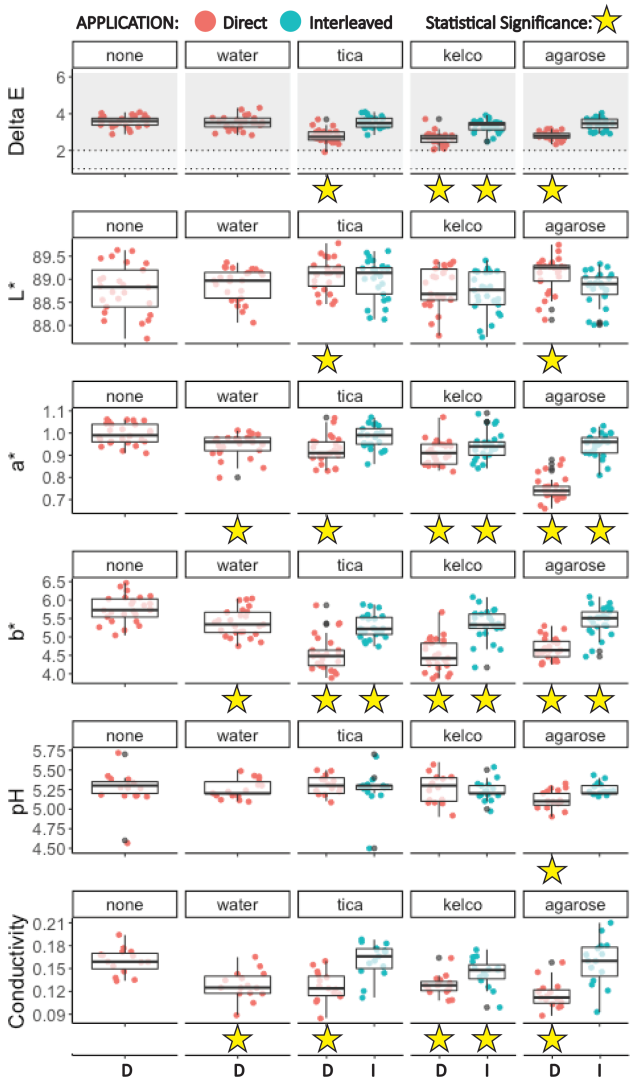

Fig. 16. Boxplots of Delta E, L* a* b*, pH, and conductivity AD for the alum rosin paper samples, separated by gel treatment and colored by interleaving.

color change was greatly reduced by the direct gel treatments, they still showed perceptible color change with average Delta E values greater than 2. All treatments reduced yellowing compared to the controls, with the direct gel treatments having the largest effect. Similarly, all treatments reduced reddening (with the exception of interleaved Ticagel whose effect was not statistically significant), and all direct gels had larger effects than their interleaved counterparts. Darkening was less affected by treatment; only direct Ticagel and agarose statistically differed from the control by 0.3 ($p = 0.01$).

The alum rosin controls had an average pH of 5.27 (SE = 0.04). The only treatment group with a significant effect was the direct agarose which reduced pH as compared to the controls by –0.14 ($p = 0.02$). Conductivity was 0.16 mS/cm on average (SE = 0.01) in the controls, and this was lowered by about 0.03 mS/cm – 0.04 mS/cm by all the direct gel and water treatments and lowered by 0.02 mS/cm by the interleaved Kelcogel ($p = 0.04$).

Visible and UV light photography

Additional photo documentation image files are available in the supplemental material. The images included in this paper were selected to highlight the most notable AD reactions discussed below.

Whatman (unsized) paper (fig. 17)

This paper type did not fluoresce under UV illumination BT. However, paper samples treated with Kelcogel and Ticagel had heightened fluorescence AT and AD that indicates residues were left behind. Interleaving did not prevent the Kelcogel residues from permeating the entire sample but did for the Ticagel treatment samples that exhibited an uneven fluorescent square in treatment areas. Interleaved and direct agarose and water treatments created some faintly fluorescent tidelines around treatment areas, which indicates less lateral flow and deposition of mobile materials. The pH and conductivity

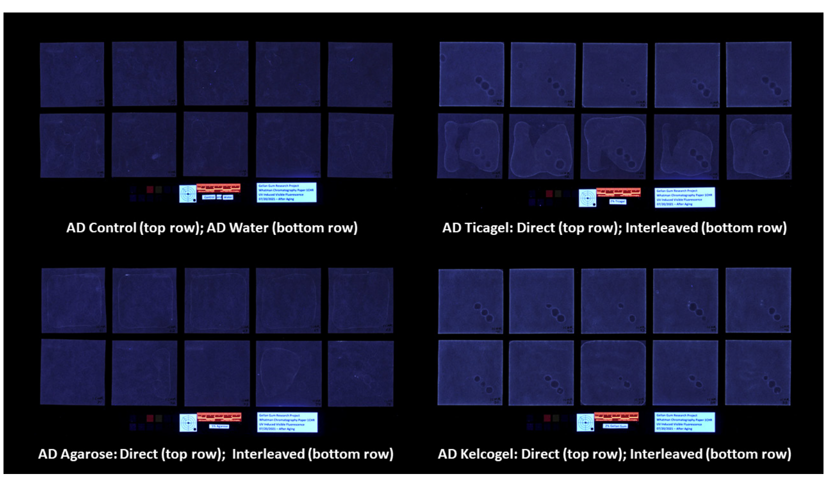

Fig. 17. Whatman paper samples after artificial degradation under UV light.

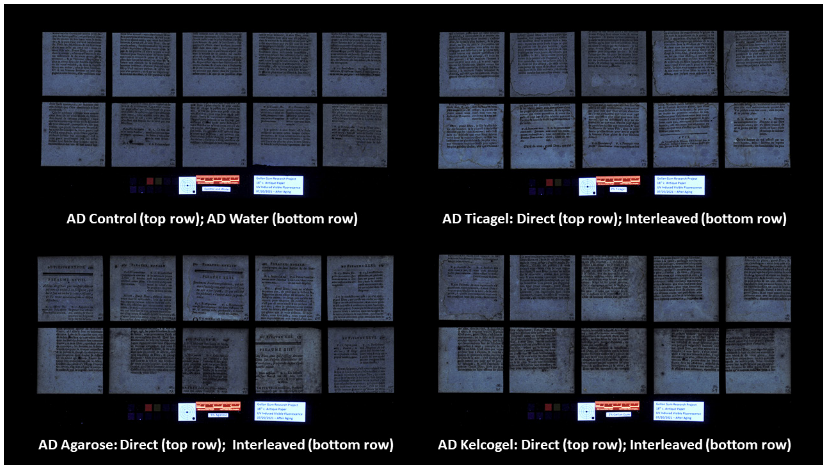

Fig. 18. Antique gelatin paper samples after artificial degradation under UV light.

sample sites taken AT are clearly visible as dark spots AD, which suggests agarose can pick up gellan gum residues. Though difficult to see in the visible light images, overall yellowing is visible with the naked eye around tidelines.

Antique gelatin-sized paper (fig. 18)

This paper type exhibited an uneven greenish-blue fluorescence BT. The directly treated samples have more distinct dark squares in the treatment area than the interleaved samples AT—an indication of greater, more uniform reduction of surface sizing. Treatment areas exposed to Ticagel are lighter than the areas exposed to Kelcogel or agarose. The treatment areas exposed to agarose remained distinctly dark AD; the treatment areas exposed to Kelcogel evened out AD, and the treatment areas exposed to Ticagel remained lighter than their discolored margins AD. This was consistent with color data showing Ticagel reduces darkness AT and mitigates darkening AD the most. Under visible light, most gel treatment areas appear lighter, but the interleaved samples exhibit uneven coloration. Tidelines are clearly visible under both UV and visible light in all gel-treated samples. Water treated samples showed a minor amount of darkening under UV light and a minor amount of visible tidelines under visible light AD.

Modern gelatin-sized paper

The manufacturer of this paper says it does not contain optical brighteners. However, it fluoresces a bright blue inconsistent with protein sizing. The bright blue fluorescence was present BT and persisted AT and AD with no obvious change. The fluorescence may be due to additives such as internal dyes and/or anti-biological agents, and the gelatin sizing may not be visible due to its source and young age. No change was apparent in treatment areas versus the margins of the samples with the naked eye under visible light AD.

AKD-sized paper (fig. 19)

This paper type exhibited a dull fluorescence under UV light BT. The water-treated samples showed no visible change AT or AD, but all three gel treatments caused darkening in

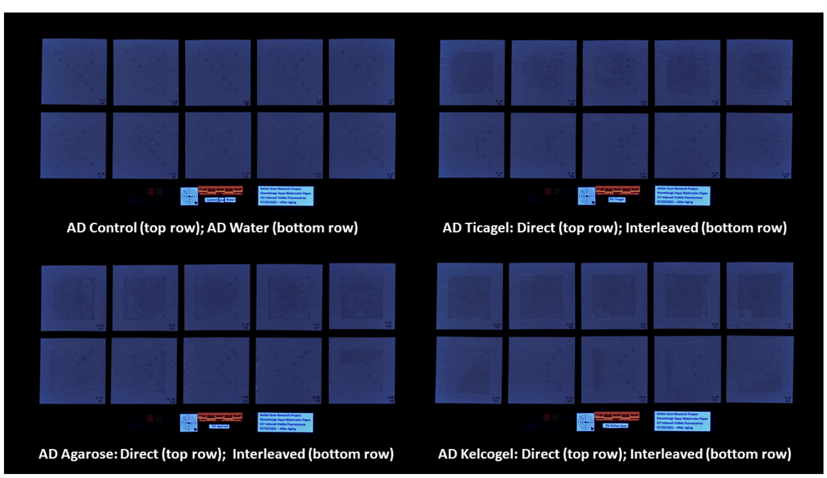

Fig. 19. AKD paper samples after artificial degradation under UV light.

treatment areas, indicating sizing material was removed. The direct application of the gel caused more distinct squares, while interleaving mitigated the sizing removal to varying degrees. In general, agarose and Ticagel removed slightly less sizing material than Kelcogel. Kelcogel also left more apparent green fluorescence along some tidelines. Like the Whatman paper, AT pH and conductivity sampling locations are clearly visible as small dark spots. No change was apparent in treatment areas versus the margins of the samples with the naked eye under visible light.

Alum-rosin–sized paper

This paper type fluoresced a pale blue under UV light BT. The direct agarose treatment caused a slight darkening, and the direct Ticagel and Kelcogel treatments caused a slight lightening AT and AD. The reaction in all cases is faint and is not visible in the interleaved samples. Based on the reactions of the other paper types, the difference in reactions may be the agarose removing sizing while both gellan gums leave behind a fluorescent residue. A slight lightening was apparent in direct Ticagel and Kelcogel treatment areas versus the margins of the samples with the naked eye under visible light AD.

DISCUSSION

All paper-treatment-application combinations experience the greatest degree of color change AD. The Whatman paper shows the least amount of color change while all other paper types exhibit clearly perceptible color change (fig. 7). Since the Whatman paper acts as an unsized comparison to the other paper types, this suggests sizing could lead to reactions that contribute to color change. The antique gelatin paper shows the greatest variability especially in its interleaved samples; this wide distribution is potentially due to the amount of degradation products already in the antique gelatin paper. Support for this theory can be seen in the alum rosin samples, the next oldest paper type, which display the second widest distribution and similar disparity between interleaved and direct application groups (i.e., its interleaved group performed similarly to the water-treated and control groups and less change was observed in the direct-contact samples).

The most notable Delta E result is the antique gelatin paper and Ticagel combination, which exhibits the least change out of all the treatments—meaning it mitigated darkening and discoloration more than other treatments. Kelcogel also mitigated the darkening and discoloration of this paper type but not to a statistically significant degree. Conversely, Kelcogel and Ticagel are the only treatments that caused any visible change in the Whatman paper. The effect of both gellan gums on these two paper types suggests that gellan gum as a material has a subtle effect that the other treatments do not. In addition, the consistency by which Ticagel and Kelcogel act similarly to each other in comparison to the other treatment types is encouraging for the previously untested Ticagel. It indicates the unknowing use of Ticagel for treatment of paper-based objects in the last few years is unlikely to have done any harm and may have even been beneficial. The most concerning trend in this study comes from the AKD paper. This paper type exhibited more statistically significant change than the controls with every treatment (with all three gels showing more change than water). This result suggests that this sizing type is the most vulnerable out of those tested.

Generally, conservators try to mitigate paper change over time; however, the paper's age affects what kind of changes are more or less desirable. Any change in new papers is undesirable, while certain kinds of changes are desirable when older papers are undergoing treatment. While Delta E measures the degree of change, it does not describe what kind of change has happened. For this, the individual $L^\star$, $a^\star$, and $b^\star$ color parameters were analyzed. The analysis found differently sized papers show different color changes AD depending on the use of interleaving and gel treatment. pH and conductivity were investigated to determine if there was a useful correlation. The pH and conductivity analysis showed these parameters have more consistent change AD; smaller differences between treatment types suggest color change cannot be completely explained by these parameters. A more detailed discussion of each paper's unique response is discussed below.

Whatman (unsized) paper

Whatman paper had the least amount of change of all paper types. Only Ticagel and Kelcogel are associated with change, and that change is only perceptible on close observation. The use of interleaving had no statistically significant impact on the color, pH, or conductivity measurements. However, it is clear in the UV images that interleaved Kelcogel treatments flowed further into the sample margins than the interleaved Ticagel treatments by the fluorescent residues. This suggests that interleaving mitigated lateral flow more with Ticagel than Kelcogel. The UV images also show both direct gellan gum treatments penetrated the entire paper sample and caused the entirety of the samples' surface to fluoresce strongly. Generally, for this paper type, all gel-interleaving combinations did not act much differently than the controls in the $L^\star$ and $a^\star$ parameters AT, though agarose seems to be better than the other gels at increasing light and reducing red when compared to the controls. The greatest effect AD was increased yellowing associated with the Kelcogel and Ticagel treatments. Out of the two, Kelcogel is associated with more yellowing than Ticagel in addition to increased darkening and reddening. Based on the fluorescence of these samples in the UV images, it seems likely that it is the gellan gum residues that are yellowing.

Curiously, all samples, including the controls, reduced in pH to a similar degree AT. The reduction of pH in the controls suggests that decreased pH cannot be considered a treatment-induced change for this paper type. However, the pH of interleaved Kelcogel and both interleaved and direct agarose-treated samples remained lowered AD, while direct Kelcogel and both interleaved and direct Ticagel samples performed similarly to the water and control samples. This supports the idea that agarose may be stripping beneficial sizing material away, and the residues left behind by both gellan gums can act as replacement sizing. Conductivity went up in all samples AD except agarose, which was the only treatment to mitigate that increase—perhaps due to its own nonionic quality, minimal residues, and effective removal of existing degradation products. This was the only paper type in which conductivity consistently increased AD, though the amount of change was very slight. The reason for this counterintuitive increase is unknown. Since Whatman paper has no sizing, these reactions may be representative of how the different treatment types interact with unsized papers: water-treated samples behave most like the controls while gel-treated samples have a greater effect on color, pH, and conductivity.

Antique gelatin-sized paper

Of all the paper types, the antique gelatin had the greatest data spread and the most variable amount of color change—ranging from imperceptible to easily perceptible. Water and interleaved agarose showed the most color change AD, and all interleaved application combinations caused more visible and variable change than direct application. Variability among interleaved samples may be due to the quantity of mobile materials, such as degradation products, resulting from 270 years of natural aging. Surprisingly, direct application versus interleaving of Ticagel and Kelcogel caused the least and second-to-least amount of change, respectively. UV imaging shows areas treated with Ticagel are lighter than the water, agarose, and control samples. In contrast, UV imaging reveals that agarose-treated areas remain the darkest. This could mean agarose is removing the most sizing and not depositing residues which would be consistent with the Whatman paper reactions. In this context, the authors postulate that gellan gum residues might be acting as a new "sizing," or protective barrier, rather than leaving the paper matrix stripped of its original sizing and susceptible to increased degradation. If true, this implies the effects of interleaving and gel choice can be used to tailor conservation treatments to suit the needs of an object. For example, to avoid causing areas of distinct change in the future, interleaving may be used to prevent over cleaning and/or gellan gums can be used to impart protective residues when performing spot treatment.

In general, gel treatments follow similar patterns for color, pH, and conductivity (lighter, greener, bluer, increased pH, and reduced conductivity AT; darker, redder, yellower, reduced pH, and reduced conductivity AD). However, Ticagel clearly performs best across all parameters and treatment stages, followed by Kelcogel, and then direct agarose. Interleaved agarose and water tend to perform most similarly to or worse than the controls.

Modern gelatin-sized paper

In direct contrast to the antique gelatin papers, the modern gelatin papers had the least data spread and the least treatment-specific color change across all gel and interleaving combinations. Color measurements identify the change as just above the perceptible threshold for all treatments and the controls AD, but it is difficult to see the differences in visible light and UV images. All treatment types followed the control pattern of getting lighter and greener but remaining unchanged in the b* parameter AT then getting darker, greener, and yellower AD. The most statistically significant differences between the controls and the treatment groups occurred in the a* parameter. This color change was observed both AT and AD, which suggests these treatments might have a greening effect on the paper. Since this is a new paper, any color change is undesirable. In a similar vein, the unchanged b* parameter after all treatment types (except agarose) may be considered the most desirable reaction for a new paper.

There is a slight reduction of pH and its variability with all direct treatment types AD. Interleaved treatments reduced in pH but had a higher variability than the direct applications. All treatment types had lower ionic conductivity AD in comparison to the controls, which show much greater variability AD. Treatment with gels results in similar conductivity AD as treatment with water—suggesting it may be the water and not the gels themselves having this effect. Similar to the antique gelatin, direct agarose shows a lowered conductivity (the lowest of all groups), while interleaved agarose shows a raised conductivity that is more similar to the control group. That direct agarose had the largest reduction in conductivity is not surprising, since it is supposed to be nonionic. In addition, the reduction seen with the interleaved treatments suggests that interleaving mitigates this effect in gelatin-sized papers. The agarose-treated samples show the most undesirable change across most parameters for a new paper.

AKD-sized paper

The AKD-sized papers saw a clearly perceptible color change AD as measured by Delta E and observed in the UV images. All treatments increased the amount of color change by reducing darkening, reducing reddening, and increased yellowing. While this was true of the water treatment as well as the gels, the water had less of an effect than the gels, which suggests the gels themselves are having a unique effect on the paper sizing. Reduced darkening and reddening are common color changes desired from a treatment; however, because this is a new paper, the increased yellowing and greater color change overall observed with the use of gel treatment is concerning. The interleaved and direct gel treatments had similar quantitative results, but the UV images show the gel effects are more uniform with direct contact than the interleaved treatments. Overall, treatment with gels seems to significantly remove the sizing of this paper compared to water, but removal may be mitigated with interleaving.

There were differences in the color measurements of this paper before any treatment, resulting in two visibly distinct groups when graphing the L*, a*, and b* values (fig. 8). The cause of this is unclear: perhaps this paper is not a uniform matrix, or, perhaps, some samples were accidentally measured on the underside, resulting in slightly different values. Where these groups responded differently was noted in the results section above.

While pH and conductivity are reduced with all treatments AT and AD, the interleaved Ticagel and Kelcogel mitigate conductivity reduction. This is potentially due to the calcium acetate in the gellan gum residues.

Alum-rosin–sized paper

The alum-rosin paper had the second greatest data spread, and the degree of color change was clearly perceptible for all treatment types AD. Though, when viewed cumulatively, each gel treatment resulted in less color change than the controls AD, the interleaved and direct gel treatments had different effects on color change. Direct gel treatments decreased the amount of reddening and yellowing much more than the interleaved gel treatments. The interleaved gel treatments still decreased the amount of reddening and yellowing but with a lesser effect that was not statistically significant AD. Since this result is similar to that of the AKD-sized paper, this suggests interleaving can decrease the efficacy of gels. This theory is supported by the UV images of most of the paper types, where distinct squares are perceptible in the direct gel treatment samples and not perceptible in the interleaved gel samples. Also of note: the direct Ticagel and Kelcogel treatment areas appear lighter in UV light compared to the agarose-treated areas which appear darker. Similar to the theory posited for the Whatman and antique gelatin papers, this may be due to the residues left by both gellan gums but not agarose.

Since the alum-rosin paper has already aged for three decades and is known for its poor aging qualities, it may be important to note that interleaving lessens the beneficial cleaning that results from direct gel application.

CONCLUSIONS

This research was initially carried out to determine if treating gelatin-sized papers with gellan gum causes unacceptable darkening or discoloration AD; its scope expanded to investigate the performance of Ticagel and evaluate the reactions between gel treatments and common paper sizings.

The experiment answers the initial question: contact between gellan gum and gelatin-sized papers does not result in a statistically significant degree of discoloration or darkening AD. On the contrary, the results suggest all three gels provide lasting benefits in regard to color change AT and AD. Furthermore, gellan gums perform better than Agarose—with Ticagel clearly performing better than the other gels overall and direct agarose seeming to strip paper of protective sizing. These conclusions are most clearly represented in the antique gelatin versus the modern gelatin paper, which is likely due to differences in their age and manufacture. However, there are several conclusions to draw across both gelatin-sized papers: water-treated samples acted most similarly to, or worse than, the controls; agarose treatment correlates with more extreme reactions; and both gellan gums struck the best balance between the type and degree of change with Ticagel performing better than Kelcogel across most parameters.

While there were some slight differences in their performance across all five paper types, Ticagel and Kelcogel performed similarly to such a degree that any paper treatments unknowingly performed with Ticagel due to mislabeling by Talas is likely negligible. In fact, Ticagel may have ultimately resulted in more beneficial treatments in certain cases.

In terms of reactions between gel treatments and common paper sizings, there are no inherently dangerous interactions between any of the paper types and a specific gel. However, trends and sensitivities do exist and are unique to each paper type (as exhibited by the already discussed gelatin-sized papers). Overall, interleaving mitigates the removal of sizing observed in direct treatment with rigid gels. While interleaving can act as a barrier to reduce negative gel effects on AKD-sized paper, it can also reduce the positive effects of gels on other papers. In the treatment of alum rosin paper, direct gel treatments mitigated undesirable color change to a greater extent than applications with interleaving, while interleaving mitigates over-cleaning in the sensitive AKD-sized papers. Finally, the Whatman paper provides an unsized comparison and illustrates the increased degree of lateral flow, yellowing, and increased conductivity levels of both gellan gums' residues in comparison to agarose and water.

One promising, though unexpected, observation was the detection of gellan gums residues and their potentially beneficial use in conservation. Even though they seem to yellow with age, gellan gum may be preferable over agarose to avoid differential aging in treated areas when performing spot treatments. Alternatively, if more uniform removal of aged sizing is desired or acceptable, such as during bathing, agarose can be used. Furthermore, knowing gellan gum residues impart some of their own qualities (such as conductivity) implies gel formulation can also be used to deliver beneficial components to the paper matrix. Finally, caution should be taken when sampling with agarose plugs, since they may permanently alter papers with certain sizing types to a greater degree than previously assumed.

Due to the size of the collected dataset and limitation in time, the ideas presented here should be understood as the authors' interpretations and theories resulting from an initial analysis. The authors hope this data will continue to be used by other researchers to advance the understanding of gel use in library and paper conservation.

ACKNOWLEDGMENTS

This project was conducted during the lead author's two-year residency in the Northwestern University Libraries conservation lab. The lead author is extremely grateful to Susan Russick, Roger Williams, Tonia Grafakos, Thomas O'Connell, and Kris Green at Northwestern University Libraries for all the support and assistance they provided, which significantly contributed to the successful execution of this project. In addition, this work could not have been done without the vital help of: Dan Paterson, Chris Bolser, and Tana Villafana, who helped to coordinate and/or run the artificial degradation equipment at the Library of Congress; Julianne Murphy and Christina Maimone from Northwestern University Research Computing, who provided crucial assistance in data formatting, analysis, and interpretation; and Michelle Sullivan, Joanna Hurd, Cathie Magee, Catherine Stephens, Joan Irving, and Dr. Melissa Tedone who acted as valued consultants and assisted in troubleshooting along the way. A special thanks to Haley Carter for being a willing partner on this unwieldy project and to Kyle Gies who provided invaluable editorial support.

NOTES

1. Early in the development of this experiment, the water-treated sample set was initially viewed as a second type of control group to identify if reactions were due to water exposure vs. gel contact. From this viewpoint, the inclusion of unaged water-treated samples seemed redundant. In addition, the removal of these samples helped reduce the quantity of measurements required. During analysis, however, it became apparent that water could be viewed as both a control and treatment type. Unfortunately, this also means the artificially degraded water-treated samples will not have naturally aged counterparts available for future study.
2. Early in the experiment, the sensor in the pH meter failed. This was determined via consultation with HORIBA Instruments Inc. The failed sensor was discovered after taking the BT and AT measurements but before taking the AD measurements of the artificially degraded samples. All measurements of the non-artificially degraded samples and the AD measurements of the artificially degraded samples were taken with a new pH meter sensor. Analysis of the data shows no indications that the change in sensor affected the data or results—suggesting the sensor did not fail until after the BT and AT measurements were taken.

REFERENCES

Armisén, R., and F. Galatas. 2000. "Agar." Chap. 4 in *Handbook of Hydrocolloids*, ed. G. O. Phillips and P. A. Williams. Cambridge, UK: Woodhead Publishing. 82–107.

Barbisan, Sophie, and Anne-Laurence Dupont. 2017. "Local Cleaning of Tidelines on Paper Using Rigid Gels: The Influence of ph and Conductivity." In *Gels in the Conservation of Art*, ed. Lora Angelova, Bronwyn Ormsby, Joyce H. Townsend, and Richard Wolbers. London: Archetype Publications. 113–115.

Bertasa, Moira, Oscar Chiantore, Tommaso Poli, Chiara Riedo, Valeria di Tullio, Carmen Canevali, Antonio Sansonetti, and Dominique Scalarone. 2017. "A Study of Commercial Agar Gels as Cleaning Materials." In *Gels in the Conservation of Art*, ed. Lora Angelova, Bronwyn Ormsby, Joyce H. Townsend, and Richard Wolbers. London: Archetype Publications. 11–18.

Botti, Lorena, Aldo Corazza, Simonetta Iannuccelli, Matteo Placido, Luciano Residori, Daniele Ruggiero, Silvia Sotgiu, Lorena Tireni, Michela Berzioli, Antonella Casoli, Clelia Isca, and Paolo Cremonesi. "Evaluation of Cleaning and Chemical Stabilization of Paper Treated with a Rigid Hydrogel of Gellan Gum by Means of Chemical and Physical Analyses." Paper presented at the *ICOM-Committee for Conservation 16th Triennial* Paolo Cremonesi. 2011. "Evaluation of Cleaning and Chemical Stabilization of Paper *Conference*, Lisbon, Portugal.

Casoli, Antonella, Paolo Cremonesi, Clelia Isca, Roberto Groppetti, Stefano Pini, and Nicola Senin. 2013. "Evaluation of the Effect of Cleaning on the Morphological Properties of Ancient Paper Surface." *Cellulose* 20: 2027–2043.

CP Kelco. 2007. *KELCOGEL Gellan Gum Book*. 5th ed. Atlanta: CP Kelco.

Cremonesi, Paolo. 2016. "Surface Cleaning? Yes, Freshly Grated Agar Gel, Please." *Studies in Conservation* 61 (6): 362–367.

Cremonesi, Paolo, and Antonella Casoli. 2017. "Thermo-Reversible Rigid Agar Hydrogels: Their Properties and Actions in Cleaning." In *Gels in the Conservation of Art*, ed. Lora Angelova, Bronwyn Ormsby, Joyce H. Townsend, and Richard Wolbers. London: Archetype Publications. 19–28.

Datacolor. 2013. Color Differences & Tolerances: Commercial Color Acceptability. Accessed August 21, 2022. https://industrial.datacolor.com/support/wp-content/uploads/2013/01/Color-Differences-Tolerances.pdf.

Huber, Corinne. 2016. "Gellan Gum Gels in Paper Conservation-Residue Studies." MA thesis, Bern University of the Arts.

Hughes, Amy, and Michelle Sullivan. 2016. "Targeted Cleaning of Works on Paper: Rigid Polysaccharide Gels & Conductivity in Aqueous Solutions." *Book and Paper Group Annual* 35: 30–41.

Hughes, Amy. 2017. "Measurement of Surface pH of Paper Using Agarose Gel Plugs: A Feasibility Study." In *Gels in the Conservation of Art*, ed. Lora Angelova, Bronwyn Ormsby, Joyce H. Townsend, and Richard Wolbers. London: Archetype Publications. 62–66.

Iannuccelli, Simonetta, and Silvia Sotgiu. 2010. "Wet Treatments of Works of Art on Paper with Rigid Gellan Gels." *Book and Paper Group Annual* 29: 25–39.

Isca, Clelia. 2014. "The Use of Polysaccharide Rigid Gels in Cleaning Treatments: Multi Analytical Approach for the Study of Their Performance, Effectiveness and Interference with Paper Artworks." PhD diss., University of Parma.

Kassambara, Alboukadel. 2020. *ggpubr: 'ggplot2' Based Publication Ready Plots*. V. 0.4.0. Alboukadel Kassambara. PC. https://CRAN.R-project.org/package=ggpubr

Kavda, Stefani, Nishad Dhopatkar, Lora V. Angelova, Emma Richardson, Stravroula Golfomitsou, and Ali Dhinojwala. 2016. "Surface Behavior of PMMA: Is Gel Cleaning the Way to Go?" *Studies in Conservation* 61: 297–299.

Kwan, Kimberly. 2016. "Batch Treatments Within a Limited Timeframe." *Icon News* 64: 33–36. https://www.icon.org.uk/resource/icon-news-may-2016-issue-64-pdf.html.

Kwang Yeon Lee, Jaeyong Shim, In Young Bae, Jaeho Cha, Cheon Seok Park, Hyeon Gyu Lee. 2003. "Characterization of gellan/gelatin mixed solutions and gels." *Swiss Society of Food and Technology* 36 (8): 795–802.

Magee, Cathie. 2020. Personal communication. Conservation Division, Library of Congress, Washington, DC.

Maheux, Anne F. 2015. "Cross-Disciplinary Uses for Gellan Gum in Conservation." *The Book and Paper Group Annual* 34: 69–79. https://cool.culturalheritage.org/coolaic/sg/bpg/annual/v34/bpga34-10.pdf.

Mazzuca, Claudia, Laura Micheli, Marilena Carbone, Francesco Basoli, Eleonora Cervelli, Simonetta Iannuccelli, Silvia Sotgiu, and Antonio Palleschi. 2014a. "Gellan Hydrogel as a Powerful Tool in Paper Cleaning Process: A Detailed Study." *Journal of Colloid and Interface Science* 416: 205–211.

Mazzuca, Claudia, Laura Micheli, Eleonora Cervelli, Francesco Basoli, Claudia Cencetti, Tommasina Coviello, Simonetta Iannuccelli, Silvia Sotgiu, and Antonio Palleschi. 2014b. "Cleaning of Paper Artworks: Development of an Efficient Gel-Based Material Able to Remove Starch Paste." *ACS Applied Materials & Interfaces* 6 (19): 16519–28.

Mazzuca, Claudia, Laura Micheli, Federico Marini, Marta Bevilacqua, Gianfranco Bocchinfuso, Giuseppe Palleschi, and Antonio Palleschi. 2014c. "Rheoreversible Hydrogels in Paper Restoration Processes: A Versatile Tool." *Chemistry Central Journal* 8 (10).

Micheli, Laura, Claudia Mazzuca, Eleonora Cervelli, and Antonio Palleschi. 2014. "New Strategy for the Cleaning of Paper Artworks: A Smart Combination of Gels and Biosensors." *Advances in Chemistry*: 1–10.

Miyoshi, Emako. 2009. "Our Recent Findings On the Functional Properties of Gellan Gum." *Osaka University Knowledge Archive*.

Möller, Lotta. 2014. "Cleaning of Watercolour Drawings: A Study Of the Use of Gellan Gum Gel On Water Sensitive Media." MA thesis, University of Gothenburg.

Muratore, Karissa A. 2018. Paper Bathing Seminar Experiment: 2nd Year Paper Minor Report. Unpublished research, Winterthur/University of Delaware Program in Art Conservation, Wilmington, DE.

Picone, Carolina Siqueira Franco, and Rosiane Lopes Cunha. 2011. "Influence of pH on Formation and Properties of Gellan Gels." *Carbohydrate Polymers* 84 (1): 662–68.

Porck, Henk J. 2000. *Rate of Paper Degradation: The Predictive Value of Artificial Aging Tests*. Amsterdam: European Commission on Preservation and Access. https://www.ica.org/en/rate-paper-degradation-predictive-value-artificial-aging-tests.

Prestowitz, Brook. 2017. "An Initial Assessment of Local Stain Reduction Using Chelate-containing Gellan Gum Gels in Paper Conservation." In *Gels in the Conservation of Art*, ed. Lora Angelova, Bronwyn Ormsby, Joyce H. Townsend, and Richard Wolbers. London: Archetype Publications. 142–144.

R Core Team. *R: A language and environment for statistical computing*. V. 4.0.2. The R Foundation for Statistical Computing, Vienna, Austria. PC. 2020. https://www.R-project.org/.

RStudio. *RStudio: Integrated Development for R*. RStudio, PBC., Boston, MA. 2018. http://www.rstudio.com/.

Shim, Jaewon L. 1985. Gellan Gum/Gelatin Blends. US Patent 4,517,216, filed March 5, 1984, and issued May 14, 1985.

Sjoberg, Daniel D., Karissa Whiting, Michael Curry, Jessica A. Lavery and Joseph Larmarange. 2021. "Reproducible summary tables with the gtsummary package." *The R Journal* 13: 570–80.

Sullivan, Michelle, Shannon Brogdon-Grantham, and Kimi Taira. 2014. "New Approaches to Cleaning Works of Art on Paper and Photographs." Paper presented at the *Association of North American Graduate Programs in Conservation Annual Conference 2014.* Buffalo, NY. http://29aqcgc1xnh17fykn459grmc-wpengine.netdna-ssl.com/anagpic-student-papers/wp-content/uploads/sites/11/2016/02/anagpic2014_sullivan_etal_paper.pdf.

Sullivan, Michelle. 2017. "Rigid Polysaccharide Gels for Paper Conservation: A Residue Study." Presented at *Gels in Conservation.* London: International Academic Projects. https://academicprojects.co.uk/archive/gels-conference.

Sullivan, Michelle, Teresa T. Duncan, Barbara H. Berrie, and Richard G. Weiss. 2017. "Rigid Polysaccharide Gels for Paper Conservation: A Residue Study." In *Gels in the Conservation of Art*, ed. Lora Angelova, Bronwyn Ormsby, Joyce H. Townsend, and Richard Wolbers. London: Archetype Publications. 42–50.

Sullivan, Michelle. 2021. Personal communication. Department of Paper Conservation, J. Paul Getty Museum, Los Angeles, CA.

Sworn, G. 2000. "Gellan gum." Chap. 9 in *Handbook of Hydrocolloids*, ed. G. O. Phillips and P. A. Williams. Cambridge, UK: Woodhead Publishing. 204–227.

Tuvikene, Rando, Kalle Truus, Andres Kollist, Olga Volobujeva, Enn Mellikov, and Tõnis Pehk. 2008. "Gel-forming Structures and Stages of Red Algal Galactans of

Different Sulfation Levels." *Journal of Applied Phycology* 20: 527–535.

Warda, Jeffrey, Irene Brückle, Anikó Bezúr, and Dan Kushel. 2007. "Analysis of Agarose, Carbopol, and Laponite gel poultices in paper conservation." *Journal of the American Institute for Conservation* 46 (3): 263–279.

Warda, Jeffrey, F. Frey, D. Heller, D. Kushel, T. Vitale, and G. Weaver, eds. 2011. *AIC Guide to the Digital Photography and Conservation Documentation*. 2nd edition. Washington, DC: American Institute for the Conservation of Historic and Artistic Works.

Wickham, Hadley, Mara Averick, Jennifer Bryan, Winston Chang, Lucy D'Agostino McGowan, Romain François, Garrett Grolemund, Alex Hayes, Lionel Henry, Jim Hester, Max Kuhn, Thomas Lin Pedersen, Evan Miller, Stephan Milton Bache, Kirill Müller, Jeroen Ooms, David Robinson, Dana Paige Seidel, Vitalie Spinu, Kohske Takahashi, Davis Vaughan, Claus Wilke, Kara Woo, and Hiroaki Yutani. 2019. "Welcome to the Tidyverse." *Journal of Open Source Software*, 4 (43): 1686.

X-Rite Pantone. 2016. *A Guide to Understanding Color*. https://www.xrite.com/-/media/xrite/files/whitepaper_pdfs/l10-001_a_guide_to_understanding_color_communication/l10-001_understand_color_en.pdf

Zeileis, Achim, Jason C. Fisher, Kurt Hornik, Ross Ihaka, Claire D. McWhite, Paul Murrell, Reto Stauffer, and Claus O. Wilke. 2020. "Colorspace: A Toolbox for Manipulating and Assessing Colors and Palettes". Journal of Statistical Software 96 (1):1-49.

Zheng, Yueyuan, Yuqing Liang, Depan Zhang, Xiaoyi Sun, Li Liang, Juan Li, and You-Nian Liu. 2018. "Gelatin-Based Hydrogels Blended with Gellan as an Injectable Wound Dressing." *American Chemical Society Omega* 3 (5).

Zhu, Hao, Thomas Travison, Timothy Tsai, Will Beasley, Yihui Xie, GuangChuang Yu, Stéphane Laurent, Rob Shepherd, Yoni Sidi, Brian Salzer, George Gui, Yeliang Fan, Duncan Murdoch, and Bill Evans. 2021. *kableExtra: Construct Complex Table with 'kable' and Pipe Syntax*. V. 1.3.4. Hao Zhu. PC. https://CRAN.R-project.org/package=kableExtra.

AUTHOR INFORMATION

KARISSA MURATORE
Preventive Conservation Librarian
University of Pennsylvania Libraries
Philadelphia, Pennsylvania
Karissa@udel.edu

HALEY CARTER
Data Science Consultant
Northwestern University
Chicago, Illinois
haleycarter2020@u.northwestern.edu

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in *Arch: Northwestern University Institutional Repository* at https://doi.org/10.21985/n2-653y-1294.

All supplemental material listed below will be available via the above DOI:

- Raw data csv files and R analysis code
- Supplemental graphs
- Full bibliography
- Sources of Materials document
- Visible and UV photo documentation in PowerPoint
- Additional experimental design images and notes in PowerPoint
    - Paper type characterization
    - Summary of WUDPAC 2019 accelerated degradation experiment
    - Measurement taking process
    - pH and conductivity measuring process and meter troubleshooting