

## Targeted Cleaning of Works on Paper: Rigid Polysaccharide Gels and Conductivity in Aqueous Solutions

### ABSTRACT

A review of paper conservation literature from the past decade reveals a fundamental shift in the conservator's approach to treatment, an approach that calls for less manipulation, greater control, and targeted cleaning. This two-part paper reviews the use of rigid polysaccharide gels and conductivity-adjusted aqueous solutions as relatively new tools that afford conservators greater control and the ability to tailor treatment.

The first part of this paper provides an overview of rigid gel systems in local and overall cleaning of works on paper, focusing on agarose and gellan gum, two naturally occurring polysaccharides. Both form colorless, rigid gels that may be cut to shape, qualities that make them appealing to paper conservators for a variety of treatment applications: aqueous and solvent-based poulticing to reduce adhesives, stain and tideline reduction, and overall bathing. Dependent upon the specific polymer, these gels may be prepared with deionized water or aqueous solutions, which utilize chelators and other buffers to adjust pH and conductivity. Following a discussion of the advantages of gel treatment and rationale for selecting a gel, the properties of agarose and gellan gum as well as factors that impact their performance will be addressed. These factors—casting thickness, concentration, and additives among others—may be modified to optimize treatment. Several examples are illustrated.

The second part of the paper aims to clarify both the theory and chemistry of conductivity in the context of paper conservation practice. Via combined chemical and physical effects acting on the microscopic and molecular level (for example: diffusion and osmotic effects), a salt in aqueous solution may be exploited to mitigate or to encourage the movement of soluble ions—not only through the fiber web, but also through the walls of individual paper fibers and fibrils. This research addresses the effects of one such electrolyte, aqueous ammonium acetate (a volatile, neutral salt), on discolored paper

substrates. The effects of conductivity-adjusted solutions are distinctly advantageous for moisture-sensitive papers and can improve the performance of local wet treatments when using swabs, poultices, and rigid polysaccharide gels.

### INTRODUCTION

Over the past two decades, a movement towards object-tailored conservation treatment has emerged, reflecting a desire for greater control at both the physical and the chemical level. This evolution began with the work of Richard Wolbers, who promoted the use of modified aqueous solutions to chemically target treatment, and the use of gels for greater specificity in application (Wolbers 2000). These concepts were disseminated in Wolbers' courses at the University of Delaware and in workshops and seminars throughout the world. The Modular Cleaning Program, developed by Chris Stavroudis, translated this concept of chemical targeting into an accessible tool, which employs engineered cleaning solutions through pH- and conductivity-adjustment, as well as by the addition of surfactants and chelators. Traditionally, these methods have been used more frequently in the fields of paintings and objects conservation. This paper will delve into their application to paper conservation.

The first half of this paper reviews two rigid polysaccharide gels that have gained popularity among paper conservators—agarose and gellan gum—outlining the properties of each and the ways in which they may be optimized for greater control in a variety of paper conservation treatments. The second half of this paper reviews the principles of conductivity. It will describe the modification of aqueous solutions using conductivity to enhance cleaning and, at the same time, minimize change to paper objects during treatment.

### RIGID POLYSACCHARIDE GELS

#### GEL POLYMERS AND PROPERTIES

Agarose and gellan gum are both naturally occurring polysaccharides (figs. 1 and 2). Agarose is derived from the cell wall

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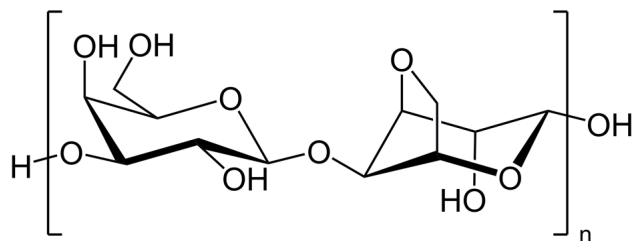


Fig. 1. Agarose monomer, [https://commons.wikimedia.org/wiki/Category:Agarose#/media/File:Agarose\\_polymer.png](https://commons.wikimedia.org/wiki/Category:Agarose#/media/File:Agarose_polymer.png)

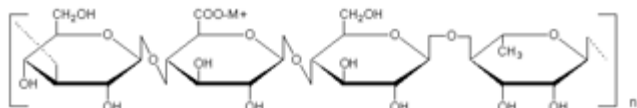


Fig. 2. Gellan gum monomer, [https://commons.wikimedia.org/wiki/File:Gellan\\_gum\\_structure.png](https://commons.wikimedia.org/wiki/File:Gellan_gum_structure.png)

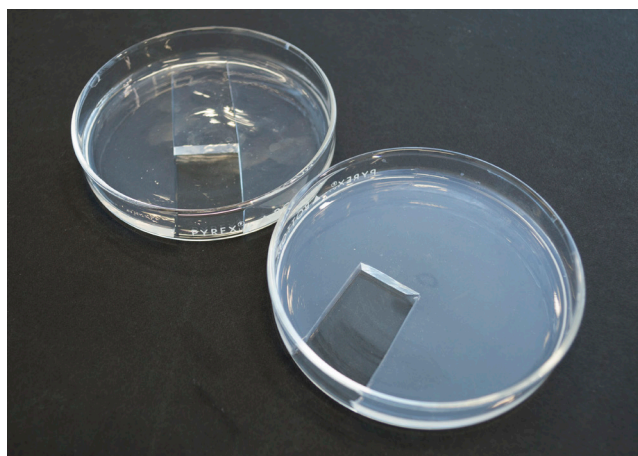


Fig. 3. Gellan gum (left) and agarose (right) prepared at 2% (w/v).

of *Gelidium* and *Gracilaria*, species of red algae, or *Sphaerococcus euchema*, seaweed (Armisen 2000). Along with agarpectin, it is one component of agar-agar. Gellan gum is the product of *Sphingomonas elodea*, a bacterium found on lily pads, and is available in two forms: low-acyl and high-acyl (CP Kelco 2007). When prepared, low-acyl is typically more brittle. This is the type more commonly used in paper conservation.

While agarose is electronically neutral, gellan gum is anionic with negatively charged carboxyl groups, which are available to complex with cations (Sworn 2000 and Mao et al 2001). Agarose and gellan gum are available in powder form and are prepared by dispersing dry polymer in pure water—or modified aqueous solution—and heating until clear and boiling. At this point, the polymers are fully hydrated. Upon cooling, both gels will be colorless, however gellan will remain clear while agarose will become slightly turbid (fig. 3). Some additives, such as volatile salts and enzymes, must

be incorporated once the gel has cooled somewhat to prevent evaporation and denaturation, respectively.

As the polymer dispersions cool, both agarose and gellan gum form helical structures. These helical structures proceed to form aggregates, which define a porous network (Armisen 2000 and Valli and Miskiel 2001). These aggregates form in agarose by hydrogen bonding. In the case of gellan gum, hydrogen bonding also occurs, but the gel network is more robust when prepared with an aqueous solution that contains cations that crosslink at the negatively charged carboxyl groups. Both gels are thermo-reversible and can sustain numerous heating-cooling cycles, transitioning between liquid solution and solid gel (CP Kelco 2007).

#### ADVANTAGES OF GEL TREATMENT

A review of paper conservation literature of the past ten years reveals steadily increased interest in both agarose and gellan gum, for targeted cleaning. This surge in interest among paper conservators is understandable given the numerous advantages afforded by treatment with rigid polysaccharide gels:

- Precise application and restricted lateral flow to confine cleaning
- Increased dwell time, allowing reagents and solutions to work longer in a discrete area
- No mechanical action as with a brush, swab, or spatula
- Colorless and clear, allowing the conservator to monitor the course of treatment
- Unlike viscous gels, they can be removed immediately should a sudden, undesirable change occur

#### MODIFYING GELS FOR PAPER CONSERVATION

With an understanding of how agarose and gellan gum can be modified to achieve a specific result, conservators may tailor gels to suit the needs of a specific treatment. The primary methods for modifying gels include:

- Altering concentration
- Altering casting thickness
- Increasing contact with light pressure
- Changing the aqueous solutions used to prepare the gels
- Adding organic solvents

Rigid polysaccharide gels are typically prepared at concentrations ranging from 1% to 10% depending upon application. Gel polymer concentration and pore size are inversely related. As concentration of the gel increases, pore size decreases (Tukivene 2007).<sup>1</sup> This results in a gel with relatively greater capillary action, that is, a gel that pulls solutions and solubilized materials into its network more vigorously. Figure 4a and b illustrate the increased capillary action of higher-concentration gels. Moving from left to right, the gels increase

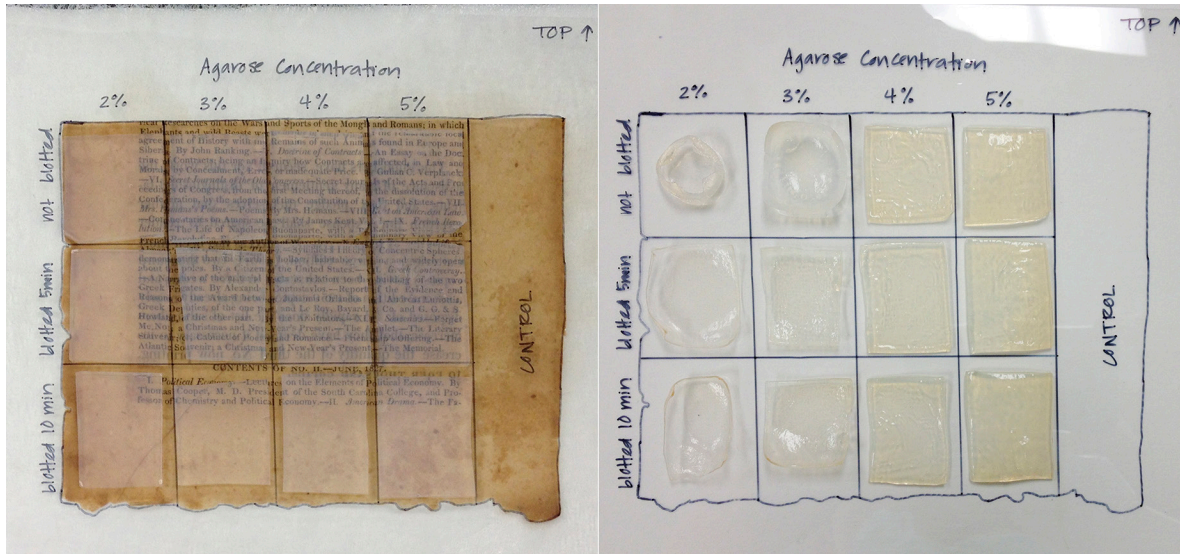


Fig. 4.

LEFT TO RIGHT

- Gels of increasingly higher concentration, from 2% to 5%, placed on an antique book page.
- Gels removed from the page and discolored with solubilized degradation products.

in concentration from 2% to 5% (w/v). Once removed from the sheet of paper, it is clear that the 4% and 5% gels with smaller pores are more discolored and have extracted a greater amount of solubilized degradation products than the 2% and 3% gels with larger pores.

In addition to concentration and pore size, casting thickness can be managed to control diffusion of solvent into paper objects. Thinner gels may be preferred to control tideline formation when working on paper objects that cannot be made wet overall. In other instances, thicker gels may be used to provide a larger reservoir of water, as when washing a print overall.

To target cleaning on a chemical level, gels may be prepared with modified aqueous solutions, that is, water that has been treated before addition of the dry polymer. The most common methods for modifying aqueous solutions are pH and conductivity adjustment and the addition of chelators, enzymes, or reducing agents.

Finally, aqueous gels may be converted into solvent gels by soaking pieces of agarose or gellan gum in a solvent or solvent mixture for approximately 24 hours. During this period, water and solvent exchange and the gels become more rigid. It is advisable, therefore, to cut the gels into useful shapes for treatment prior soaking. Given the chemical structure of polysaccharide gels—full of hydroxyl and carboxylic acid groups—this preparation works best with polar solvents like acetone and alcohols rather than non-polar ones.

Modifications as described above make it possible to use polysaccharide gels for a wide variety of paper conservation treatments, including but not limited to:

- Backing and attachment removal
- Aqueous and solvent-based adhesive reduction
- Local stain reduction
- Overall bathing of paper objects
- Measuring surface pH and conductivity of paper

#### CASE STUDY 1: LOCAL STAIN REDUCTION

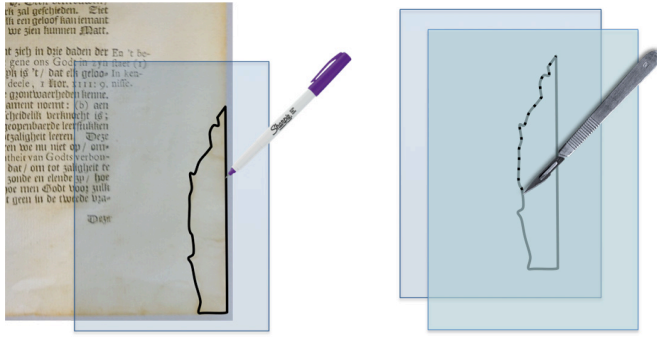
Thinly cast, higher concentration agarose or gellan gum may be used to reduce stains or tidelines in a paper object that cannot be wet overall such as a drawing with sensitive media or a page in a bound volume. The following example illustrates this procedure (figs. 5a-c and 6).

To begin, a template of the area to be treated was created using Mylar® and a permanent marker. Gel cast onto another sheet of Mylar® was placed on top of the template and a scalpel was used to cut the gel to shape. Using tweezers, the shaped gel was placed directly on the stain and a microscope slide was used to improve contact and to slow evaporation of solvent. Multiple applications of fresh gel were required to achieve the desired result, and the treated area was dried between applications to prevent overwetting and tideline formation.

#### CASE STUDY 2: OVERALL BATHING

A number of experiments related to gels and paper conservation treatment have been undertaken at the National Gallery of Art in Washington, DC (NGA), including a study that compared traditional blotter washing to bathing on a sheet of gellan gum. In figures 8 and 9, the sheet on the left in each

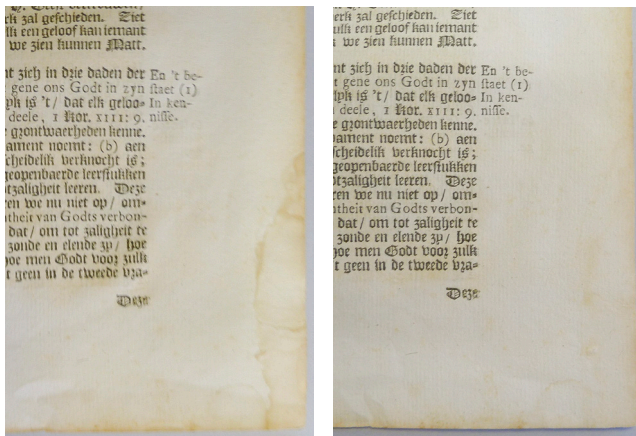




CLOCKWISE FROM TOP LEFT  
 Fig. 5a-c. Stepwise preparation and application of shaped gels for local stain reduction.



Fig. 6. Schematic diagram of gel application for local stain reduction.



LEFT TO RIGHT  
 a. Lower-right corner of antique book page before local treatment with thinly cast 6% (w/v) agarose gel to reduce tideline.  
 b. Lower-right corner of antique book page after treatment.

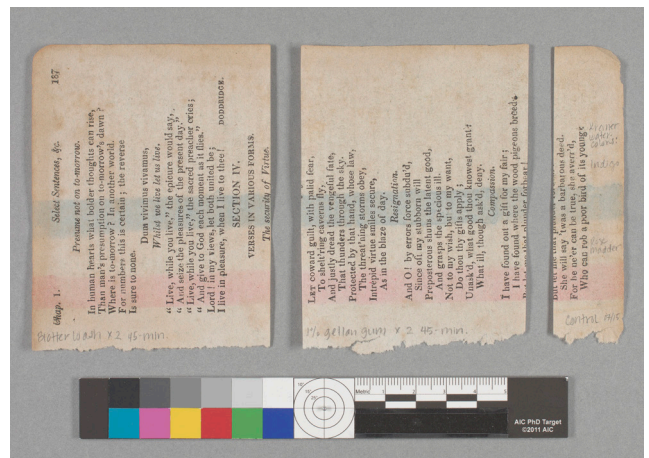
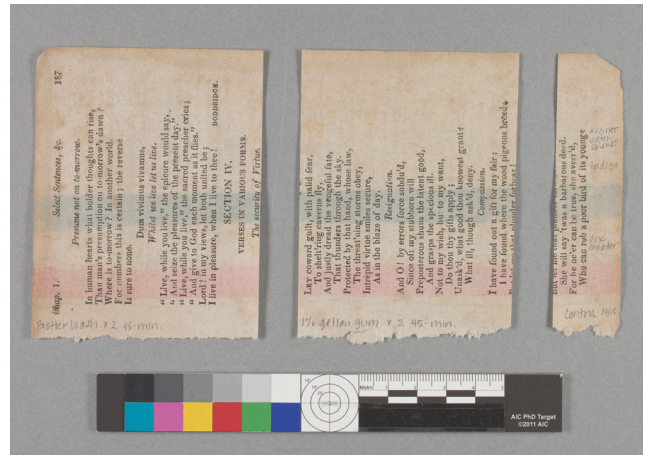


Fig. 8.  
 TOP TO BOTTOM  
 a. Antique book page before treatment, comparing blotter washing to gel washing.  
 b. Antique book page after treatment.

image was blotter washed; the sheet in the middle was washed with 2% (w/v) gellan gum prepared with a dilute aqueous solution of calcium acetate (0.4g/L); and the strip on the right was retained as a control. Both the blotter-washed and gellan sheets were exchanged after 45 minutes and the papers were washed for an additional 45 minutes.

Under normal illumination, improvement to the washed sheets is subtle. Gel washing was more efficient, however, as the sheet washed with gellan appears somewhat brighter (figs. 8a and b). When the samples were viewed under ultraviolet radiation, changes from bathing were more obvious (figs. 9a and b). Both the blotter-washed and gel-washed sheets absorbed more strongly due to the removal of fluorescent, oxidized degradation products. Removal of solubilized degradation products, however, was much more even in the gel-washed sheet versus the blotter-washed sheet. This difference is likely attributed to the gel's ability to conform and

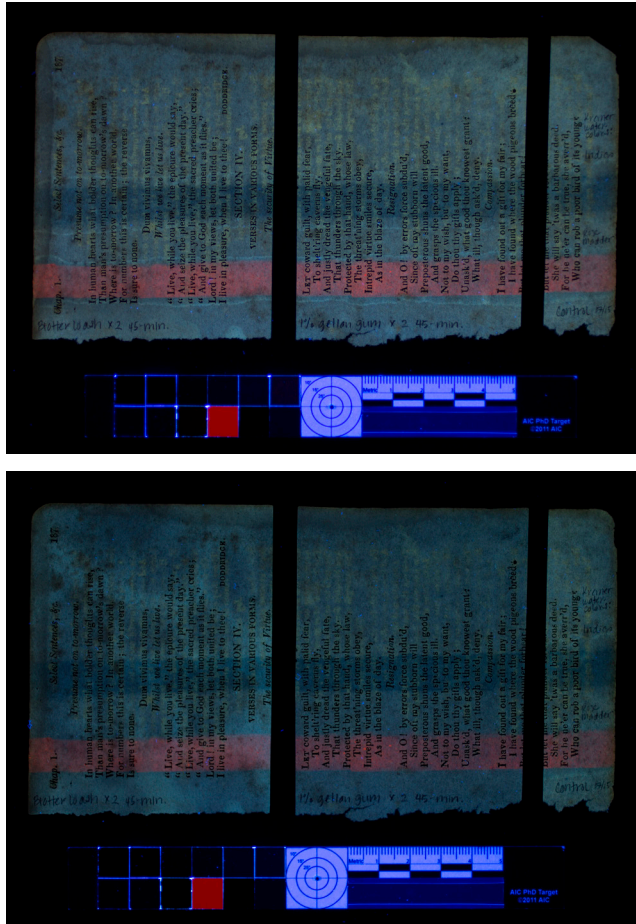


Fig. 9.  
 TOP TO BOTTOM  
 a. Antique book page under UV radiation before treatment.  
 b. Antique book page under UV radiation after treatment. Note the uneven removal of fluorescent degradation products in the blotter-washed sheet (left) versus the gel-washed sheet (center).

make excellent contact with the paper, as noted by others who have published on bathing with gellan gum (Iannuccelli and Sotgiu 2010, Botti et al 2011, and Mayheux 2015).

In light of the positive results of the experimental gel baths, the treatment was scaled up and applied to an object from NGA’s permanent collection. Together, the paper conservators treated a chine collé engraving, *Heart of the Andes* by William Forrest (Scottish, 1805 – 1899) after Frederick Church (American, 1826-1900). This print is a laminate paper object that could not be subjected to full aqueous treatment by immersion or float wash for fear of layer separation, but reduction of overall discoloration and strong tidelines throughout was desired. The print’s sensitive structure made it an ideal candidate for gel washing for its high degree of control and even cleaning. Gellan gum was prepared as described above and was cast into several heat-resistant, flat-bottomed trays (figs. 10a and b). The resulting sheets of gel were joined to create a sheet of gel large enough to accommodate the print, which measures approximately 20 x 30”. A scalpel was used to trim the edges of the cast gel to ensure smooth joins. The gel fused together seamlessly (figs. 11a and b).

Following a period of chamber humidification, the print was transferred to the gellan gum on a sheet of medium-weight *seikishu* Japanese paper. Through spun-polyester web, a smoothing brush was used to ensure contact between the print and gel. During treatment, the print was covered with an inverted Mylar® tray to prevent the surface of the print from drying out. In total, the print was treated with three separate gel washes, each approximately 45 minutes in duration. Periodically, a light mist of slightly alkaline water was applied with a dahlia sprayer to encourage continued movement of water-soluble discoloration into the gel.<sup>2</sup>

The treatment was considered a success. The print’s appearance was improved with markedly reduced staining and overall discoloration. Further, no adverse effects, such as



Fig. 10.  
 LEFT TO RIGHT  
 a. Preparing gellan gum by dispersing powdered polymer into dilute calcium acetate solution (0.4g/L).  
 b. Casting fully hydrated dispersion into heat-resistant tray.



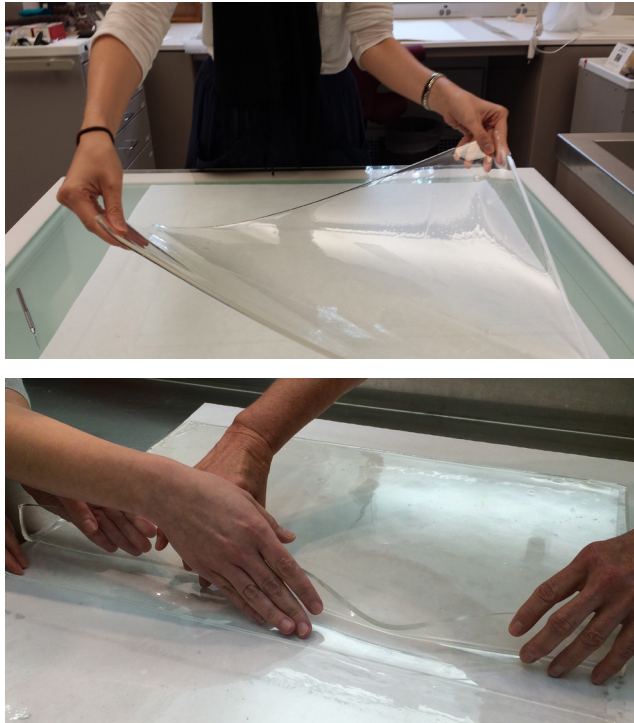


Fig. 11.

TOP TO BOTTOM

- a. Sheet of gellan gum released from heat-resistant tray.
- b. Joining two sheets of trimmed gel.

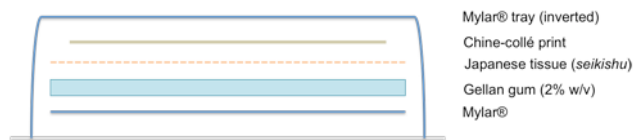


Fig. 12. Schematic diagram of arrangement for overall washing with a sheet of gellan gum.

Water	Conductivity (µS/cm)
Absolute Water (H <sub>2</sub> O)	0.055
Distilled Water	0.5
Dasani® Bottled Water*	50
Tap water (New York City)*	95
Maximum for Potable Water	1055
Ocean Water (Mid-North Atlantic)	53,000

Table 1. Conductivity of common water sources, in microsiemens/cm. \*From laboratory measurements using a Horiba B-771 LAQUAtwin Conductivity meter. Other values from *The pH and Conductivity Handbook*. Stamford, Conn: Omega Engineering, Inc, 1990.

delamination or bubbling of the chine collé, were observed as a result of treatment.

CONDUCTIVITY IN AQUEOUS SOLUTION

The following section addresses the theory and chemistry of conductivity in the context of paper conservation. With an awareness of the properties of electrical conductivity in solution, paper conservators may design aqueous treatments that are more sensitive to the specific needs of objects at hand, achieving stain reduction goals while minimizing swelling of the paper fibers. Many of the concepts surrounding conductivity and ionic strength have been taught in workshops led by Richard Wolbers, Chris Stavroudis, and other paintings conservators.<sup>3</sup> One recent study by Dillon, Lagalante, and Wolbers (2014) addresses specific ionic species and their effects on swelling of acrylic painted surfaces. These concepts have also begun to be published and introduced into wider practice by paper conservators within the last five years (Keynan and Hughes 2013). While conductivity adjusted solutions may be delivered by any familiar method, they are particularly well-suited for local treatment techniques and can be used with swabs, brushes, sponges, loaded into rigid polysaccharide gels, or applied over a suction table.

CONDUCTIVITY

Conductivity, simply put, is that measurement which describes how well a given substance conducts electricity (Atkins, Jones, and Laverman 2016). Electrical charge in aqueous solution flows only in the presence of ions. Therefore, an electrically conductive solution must contain at least one electrolyte, or substance that dissolves into cations and anions. Electrolytes may be acids, bases, or salts—strong or weak, depending on their ability to ionize, or dissociate, in solution.

Conductivity is expressed in the unit siemens (S). Pure water, such as deionized or distilled water, is a poor conductor and yields conductivity values of nearly zero siemens/cm. Table 1 lists conductivity values for familiar types of water. Conductivity is unspecific and merely a broad measurement of ionic content. A conductivity value is a combination of all the ionic species present in a given solution, and typically correlates to the salinity of the water and to total dissolved solids (TDS). In the following section, references to conductivity are primarily used to describe the concentration of salts present in the aqueous solutions used for treating works of art on paper.

Paper conservators already employ numerous salts in their work, although these chemicals are not always recognized specifically as such. Calcium hydroxide, calcium carbonate, and magnesium bicarbonate, to take three examples, are all salts employed in very dilute solutions for the purposes of deacidification (Smith 2011). Sodium borohydride, a salt with high ionic strength, is used in bleaching processes.

Chelators such as disodium ethylenediaminetetraacetic acid (EDTA) and the citrates are frequently used salts as well. Calcium phytate, otherwise known as phytic acid calcium salt, has been employed for several decades to sequester damaging iron ions during treatment of documents bearing iron gall ink (Burgess 1991). Of course, not all salts are equally efficacious, and several salts used for treatment in the early 20<sup>th</sup> century have been shown to contribute to paper degradation over time (Lienardy and Van Damme 1988; Henniges and Potthast 2009). The safety and efficacy of specific salts, and even specific cations and anions, remains an open venue of inquiry for conservators and conservation scientists alike.

Today, aqueous steps taken during the course of a paper treatment are typically carried out using laboratory-purified water with added ionic species. This is because deionized water is a strong solvent; it has been called “ion-hungry” for its capacity to corrode metals such as copper, and to take up carbon dioxide from the atmosphere. In the late 1970s, Tang and Jones demonstrated that washing paper with deionized or distilled water alone could leach beneficial ions such as calcium and magnesium from the paper matrix, contributing to reduced tensile strength after aging (Tang and Jones 1979).

On the other hand, it is possible that washing with purified water may sometimes be preferable for papers with large amounts of damaging impurities, such as degraded papers with alum-rosin sizing or chemically pulped groundwood papers (Burgess 1986). Results from scientific studies such as those of Burgess, and Tang and Jones, indicate that paper conservators ought to exercise individualized care when tailoring their aqueous treatments. Those ionic species that conservators introduce into wash water, and those already present in paper structure, are significant to long term aging, and will affect tensile strength, optical brightness, and degree of polymerization of cellulose.

When washing paper objects, conservators often condition wash water with an alkaline agent in order to neutralize acids in the paper and to buffer against the post-treatment formation of acids. The most commonly employed alkaline agent is likely calcium hydroxide, which must be used in very low concentrations in order to achieve pH levels appropriate to both paper fibers and media. For example, the conductivity of a dilute solution of pH 8.5 calcium hydroxide intended for washing measures 5  $\mu\text{S}/\text{cm}$  and has been diluted over 1720 times (0.013mmol/L) from its saturated state (Smith 2011, 366). Such a dilute salt solution is effective for neutralization and alkalization, but for purposes of neutralization and stain reduction, more concentrated salt solutions may often be preferable. Detailed below will be examples of these alternatives, salt solutions for cleaning that may be adjusted to specific pH and conductivities, ranging from 1,000  $\mu\text{S}/\text{cm}$  (0.1 molar concentration) to upwards of 6,000  $\mu\text{S}/\text{cm}$ .

In the early 2000s, Bogaard and Whitmore (2001) introduced a theory of applying salt solutions to oxidized papers.

In one of their experiments, they investigated the addition of a concentrated solution of neutral pH calcium chloride to wash water. The object of this approach was to speed the rate of diffusion and ion transport into and out of the fibers, with the goal of neutralizing acids in the sheet prior to further aqueous treatment (Bogaard, Morris, and Whitmore 2005). The increased ionic strength (and high conductivity) of the saline water enabled free acids to be drawn out of the fiber interiors more quickly and more thoroughly, leading to improved paper stability after accelerated aging when followed by a rinsing step. Similar findings were presented by Season Tse (2001) of the Canadian Conservation Institute, indicating that deionized water alone cannot wash out significant quantities of acids from cellulosic materials, and that adding a salt enhances the benefits of washing.

#### MECHANISMS OF TRANSPORT: DIFFUSION, OSMOSIS, AND THE DONNAN EQUILIBRIUM

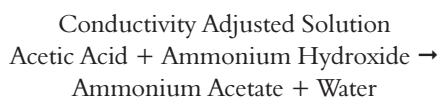
The chemical principles of diffusion and osmosis ought to guide a paper conservator’s choice of conductivity level for treatment. Diffusion is “the most important mechanism in washing paper,” according to Vincent Daniels (2011, 294), from the invaluable resource *Paper and Water: A Guide for Conservators*. Diffusion describes a kind of movement of molecules or ions, which is both constant and random. Particles move from areas of high concentration to low concentration in order to establish equilibrium within a system. During washing, acids and associated colored compounds are gradually removed from paper by the mechanism of liquid diffusion.

There are several factors that alter rates of diffusion when washing paper. Temperature, pressure, permeability, and concentration gradient are each frequently manipulated by conservators during washing for just this reason. Of these, concentration gradient bears a great deal of relevance to issues of conductivity. Concentration gradient is commonly manipulated during aqueous treatment by exchanging wash water or wet blotters as they become yellow from the extraction of ionic compounds (Lienardy and van Damme 1990). This introduction of fresh water (with lower conductivity) disrupts the established equilibrium and creates a new concentration gradient. Alternatively, and in certain cases, conservators might choose to use high conductivity water to disrupt the concentration gradient in order to speed up the rate of diffusion and stain reduction during treatment. It is important to keep in mind that paper fibers possess cell walls that act as semi-permeable membranes in aqueous solution, meaning that osmotic forces above and beyond simple diffusion are present when washing paper.

Yet another object might call for a gentler aqueous intervention—the creation of a solution that agrees with the ionic content of the paper at hand, in order to lower the osmotic pressure in the system of fibers and to reduce swelling. When

introducing water to paper, the bulk aqueous solution has a tonicity in relationship to the localized water that has penetrated into and swollen the fibers. It is the concentration of ionic species, or conductivity in aqueous solution, that determines tonicity—that is, whether a solution is hyper-, hypo-, or isotonic. Along with pH, conductivity is critical to managing the swelling of paper fibers during treatment. In an uncomplicated biological system, hypertonic solutions will result in cell shrinkage, while hypotonic solutions will cause cellular swelling. An isotonic solution, however, is in equilibrium with the interior contents of the cell wall, creating a stable aqueous environment with no net movement of water. For paper objects vulnerable to swelling, such as highly oxidized papers or papers with calendared surfaces, tailored isotonic aqueous solutions may allow for aqueous treatment with fewer risks of surface alteration.

To achieve isotonicity (or near isotonicity) in solution, the pH and conductivity of a paper support must first be measured and recorded. These measurements may be achieved with handheld pH and conductivity meters, using agarose plugs as the vehicle for ionic content, according to the method demonstrated by Chris Stavroudis in a video published by the Getty Conservation Institute.<sup>4</sup> A weak acid and a weak base should then be combined to create a salt in aqueous solution with precisely calibrated pH and conductivity to match the paper object. The two reactants originally proposed by Chris Stavroudis, Richard Wolbers, and others as part of the Cleaning of Acrylic Painted Surfaces (CAPS) workshop are acetic acid and ammonium hydroxide, a weak acid and a weak base, respectively, that react to form ammonium acetate salt.<sup>5</sup> By adding either excess acid or base, the solution's pH may be adjusted to the value desired by the conservator. Ammonium acetate salt has many attractive qualities for the purpose of paper conservation. It is neutral pH, highly soluble, and decomposes into its volatile components upon evaporation.



By exploiting the effects of conductivity when washing paper, conservators may enjoy greater control over the effects of water on paper. Sometimes it may be desirable to encourage swelling, or to speed up the rate of diffusion for more efficient removal of discoloration products, by creating a hypo- or hypertonic solution. In many other cases, however, it is more important to minimize the extent of physical change, to safeguard sensitive media, and/or to retain paper texture, through use of an isotonic solution.

Additional processes are at work in the application of a moderate conductivity salt solution to a sheet of paper when the goal is to limit swelling and to draw out discoloration. It may seem counter-intuitive to many paper conservators, but

the very same solution that limits swelling of paper fibers will also release discoloration efficiently when working in a higher conductivity aqueous environment. In the paper-making industry, studies have shown that electrostatic forces and “Donnan-like” equilibrium effects occur when cellulose fibers are immersed in electrolytic solution (Scallan and Grignon 1979). This may help to explain the mechanism of reduced fiber swelling in moderate to high conductivity solutions. The Donnan effect is similar to osmosis, but with the distinction of trapped or “fixed” charged molecules on one side of a semi-permeable membrane. These charged molecules create an electrical imbalance in the aqueous system and influences the diffusion of smaller and more mobile cations and anions in solution to balance the charge.

Donnan-like equilibrium effects have been shown to occur within the nanopores of cellulose, which are so tiny (not much larger than the diameter of a DNA helix) that they exhibit somewhat unusual behavior in solution (Hidayat, Thygesen, Katja 2013). Acidic compounds, bound to the surfaces of cellulose (mostly carboxylic acid groups), cannot dissociate within the small spaces of the nanopores to the same degree that they can on the exposed surface of the fibers. As a result, the pH within the fiber is quite low. In fact, the measurable pH within the wall of a cellulose fiber is significantly lower than what is measurable by traditional pH measurement techniques (Grignon and Scallan 1980). So whereas a bulk paper might measure pH 6.0 by cold extraction, the pH within the interior of its fibers might be as low as 3.0. Upon discovering this discrepancy, Scallan suggests that paper pH extraction measurements be done in a neutral salt solution (like sodium or potassium chloride) to achieve more accurate readings, as the interior and exterior differences in pH are alleviated as the conductivity of the bulk solution is raised (Scallan 1990). The shift in equilibrium provided by the addition of a salt in the solution effectively releases protons and small acid groups from the interior of the nanopores and subsequently out of the paper matrix. The osmotic effect of the added salt allows small charged ions access into and out of the pores while at the same time limiting swelling of the fiber (Alam et. al. 2012).

#### ANALYSIS OF AMMONIUM ACETATE SOLUTIONS

The effects of neutral salts such as ammonium acetate should be investigated more thoroughly to determine their long-term effects on paper aging and on artists' media. Despite the fact that ammonium acetate and its degradation products are volatile, the ammonia and acetic acid volatilize at different rates, with the ammonia evaporating first. Acetic acid remains detectable by its odor in washed paper for up to 5 days after drying, depending on the thickness of the support and the initial concentration of the salt solution. The odor of vinegar is significant at 6,000 microsiemens.<sup>6</sup> Ideally, the use



of pH- and conductivity-adjusted solutions will not require a rinsing step, however this may not be possible if the paper retains significant acid functional groups after treatment.

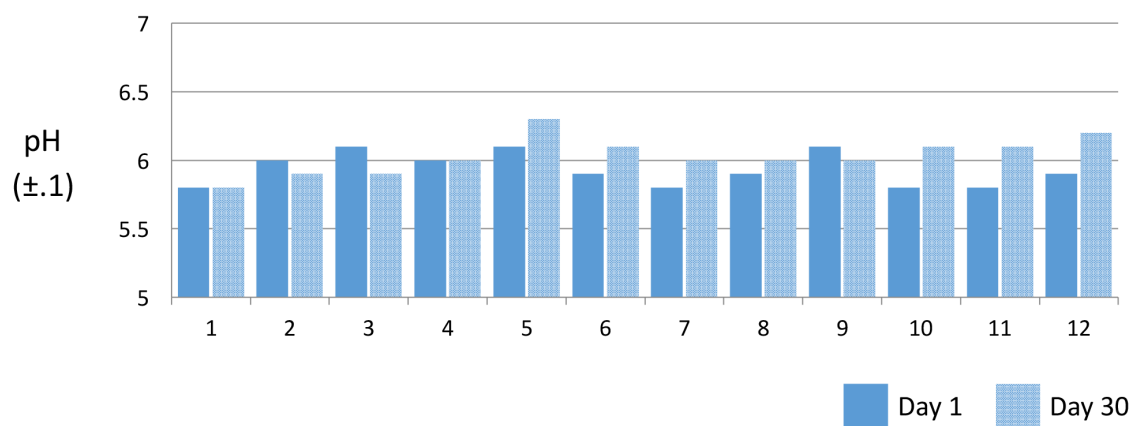
To measure relative amounts of these volatile organic compounds (VOC), Gastec Passive Dosimeters were used to measure time-weighted averages (TWA) of acetic acid and ammonium hydroxide off-gassing from the liquid salt solutions into air-tight containers (Table 2). After testing, it was determined that the Gastec tubes were not sensitive enough to detect VOCs from sample papers treated with these solutions, so the solutions themselves were chosen for the measurements. Gaseous acetic acid evaporating from the slightly acidic solution (pH 6.5 at 6,000 $\mu$ S/cm) was found to be less than one half the volume of acetic acid off-gassing

	Ammonia	Acetic Acid
pH 6.5/6,000 $\mu$ S	1.0 PPM	0.5 PPM
pH 8.5/6,000 $\mu$ S	16 PPM	Under detection limit

Table 2. VOCs as determined using two types of Gastec Passive Dosimeters: Acetic Acid (81D) and Ammonia (3D). Measurements obtained inside an air-tight 1.7-liter polypropylene container.

measured inside solander boxes according to a study by Dupont and Tétreault (2000). These researchers found that such low levels of acetic acid had no statistically significant effect on the degree of polymerization (DP) of cellulose after artificial aging. However, they measured a slight decrease of pH (0.22 units) after 80 days of exposure to the vapors in an enclosed vessel.

Therefore, pH tests were performed on samples of Whatman chromatography paper to determine if papers treated with ammonium acetate solutions would prove more or less acidic over time as compared to unwashed controls and to papers washed using alkaline solutions. The Whatman paper was divided and washed in 12 different aqueous solutions to represent a practical range of the pH- and conductivity-adjusted waters in comparison with more traditional washing solutions (Table 3). After washing the papers, the pH of each sample was measured according to the TAPPI T 509 cold extraction method using a Horiba B-713 LAQUAtwin Compact pH meter. Measurements were performed in duplicate and then averaged. The first round of pH measurements was performed 24 hours after washing the samples and allowing them to air-dry—at this time, the samples washed in 6,000  $\mu$ S/cm ammonium acetate solution



1	Control (unwashed)	7	AW, pH 6.5/18,000 $\mu$ S
2	Deionized Water (approx. pH 5.5/1 $\mu$ S)	8	AW, pH 6.5/18,000 $\mu$ S (rinsed)
3	Deionized Water + Ca(OH) <sub>2</sub> (pH 8.5/6 $\mu$ S)	9	AW, pH 8.5/1,000 $\mu$ S
4	Deionized Water + NH <sub>4</sub> OH at (pH 8.5/9 $\mu$ S)	10	AW, pH 8.5/6,000 $\mu$ S
5	Adjusted Water (AW), pH 6.5/1,000 $\mu$ S	11	AW, pH 8.5/18,000 $\mu$ S
6	AW, pH 6.5/6,000 $\mu$ S	12	AW, pH 8.5/18,000 $\mu$ S (rinsed)

Table 3. pH cold extraction measurements of Whatman Grade 1 cellulose chromatography paper washed in 12 aqueous solutions, measured one day after treatment and 30 days after treatment.

retained a slight vinegar odor. The second round of pH measurements was done 30 days after washing. During the 30-day interval, the washed papers were stored together, uncovered, and loosely stacked in a tray. The measured pH values of all the washed papers, both day-one and day-30, are either equal in pH or more alkaline than the slightly acidic unwashed control samples. This preliminary testing indicates that washing with the ammonium acetate salt may be beneficial to the pH of paper fibers. However, more thorough testing is required to determine how these solutions affect mechanical strength, optical properties, degree of polymerization, as well as pH after longer periods of aging.

## CONCLUSION

The advancements to paper conservation treatment discussed here have been afforded by the pioneering work and cross-specialty interests of Richard Wolbers and his many devoted colleagues. In the interest of moving the conservation profession forward—towards increasingly tailored and object-specific treatments—it is critical for practicing conservators to not only become familiar with the scientific principles that underpin these inventions but to continue the search for the most efficacious methods of putting them into practice. Treatments employing rigid polysaccharide gels and/or conductivity adjustment hold much promise for the future of paper conservation treatment; however these techniques are still in their nascent stages and deserve more comprehensive study and development.

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## NOTES

1. In Tukivene's article, SEM images of agarose prepared at three different concentrations—2%, 6%, and 16%—illustrate the inverse relationship between polymer concentration and pore size. At higher

concentrations, the pore sizes are visibly smaller and the gel networks more compact.

2. Alkaline water was prepared by adjusting deionized water to pH 8 with a saturated solution of calcium hydroxide.

3. Richard Wolbers has been teaching paper-specific workshops since 2007 (personal communication, 2016).

4. This video demonstrates the method as appropriate for acrylic painted surfaces. The method for measuring the surface pH and conductivity of paper is similar, but typically requires a longer dwell time of the agarose plug (up to 10 minutes) to achieve realistic measurements depending on the type of paper and its surface sizing. Surface conductivity measurements reflect the concentration of ionized solutes imbibed by the agarose plug at the test site. Measuring Surface pH and Conductivity Using Water Drop and Agarose Plug Methods. YouTube. The Getty Conservation Institute, Los Angeles, CA. Accessed July 9, 2016. <https://youtu.be/bOqZEE7Kb8Y/>

5. Further resources, including recipes, may be found on the Getty's webpage for CAPS. Conserving Modern Materials. The Getty Conservation Institute, Los Angeles, CA. Accessed July 9, 2016. [http://www.getty.edu/conservation/publications\\_resources/teaching/conserving\\_modern.html/](http://www.getty.edu/conservation/publications_resources/teaching/conserving_modern.html/)

6. The human olfactory system is nearly 35 times more sensitive to the odor of acetic acid than it is to ammonia (Hamilton and Arogo 1999). Thank you to Alan Phenix for this suggestion.

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## MATERIALS

Agarose LE (#A1700)  
Benchmark Scientific, Inc.  
P.O. Box 709  
Edison, NJ 08818  
(908) 769-5555  
<http://www.benchmarkscientific.com/Agarose.html>

Kelcogel LA Gellan Gum  
CP Kelco U.S., Inc.  
3100 Cumberland Boulevard, Suite 600  
Atlanta, GA 30339  
(800) 535-2687  
<http://cpkelco.com/products/gellan-gum/>

Calcium acetate hydrate (#5743-26-0)  
Fisher Scientific  
300 Industry Drive  
Pittsburgh, PA 15275  
(877) 885-2081  
<https://www.fishersci.com/shop/products/calcium-acetate-acs-mp-biomedicals-100g/icn19382180>

Heat-resistant fiberglass trays (#870008)  
Molded Fiber Glass Tray Company  
6175 Route 6  
Linesville, PA 16424  
(800) 458-6050  
<http://www.mfgtray.com>

Glacial Acetic Acid (#A38-500)  
Fisher Scientific  
<https://www.fishersci.com/shop/products/acetic-acid-glacial-certified-acs-fisher-chemical-9/p-20006/>

Ammonium Hydroxide (#A669-500)  
Fisher Scientific  
300 Industry Drive  
Pittsburgh, PA 15275  
(877) 885-2081  
<https://www.fishersci.com/shop/products/ammonium-hydroxide-certified-acs-plus-fisher-chemical-7/p-212671/>

Horiba Laqua Pocket Tester, pH (#UX-05754-10)  
Cole-Parmer  
625 East Bunker  
Court Vernon Hills, IL 60061  
(800) 323-4340  
[sales@coleparmer.com](mailto:sales@coleparmer.com)  
[http://www.coleparmer.com/Product/Horiba\\_Laqua\\_Pocket\\_Tester\\_pH\\_Range\\_2\\_to\\_14\\_pH/UX-05754-10](http://www.coleparmer.com/Product/Horiba_Laqua_Pocket_Tester_pH_Range_2_to_14_pH/UX-05754-10)

Horiba B-171 Twin Conductivity/Salinity Pocket Tester (#UX-05751-10)  
Cole-Parmer  
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Court Vernon Hills, IL 60061  
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Miltex® Biopsy Punch with Plunger, 3.0mm (#15110-30)  
Ted Pella, Inc.  
P.O. Box 492477  
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