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

CATHIE MAGEE

# High Acyl Gellan Gum for Parchment Conservation

## INTRODUCTION

### *About Gellan Gums*

The water-soluble anionic polysaccharide known as gellan gum comes in two forms: the more commonly known low acyl gellan gum (LAGG), which is frequently used in paper conservation, and high acyl gellan gum (HAGG). The main difference is the naturally occurring presence or artificially induced absence of an acyl group that repeats on the polysaccharide chain (fig. 1); the high acyl polysaccharide can be "de-acylated" by an alkaline process, producing LAGG (CP Kelco 2007). The presence or absence of that acyl group significantly changes the properties of the gels.

LAGG forms a clear, rigid gel (fig. 2). The polysaccharide chains form a helix around divalent cations such as calcium that allow for a controlled release of moisture and, simultaneously, the removal of solubilized material through capillary action (Iannuccelli and Sotgiu 2010). This action makes the gel useful in cleaning art on paper through both overall bathing and targeted stain reduction. The gel can be soaked in an organic solvent such as ethanol to replace some of the water in the gel, allowing for the delivery of solvent to the object. Paper conservators have also successfully used LAGG to deliver enzymes and chelators to art objects (Iannuccelli and Sotgiu 2010).

In contrast, HAGG is opaque, flexible, and rather elastic (fig. 3). Despite a drapey and soft texture, it maintains its structural integrity. This malleability is key to its success on uneven surfaces, as the softer gel is better able to make the surface-to-surface contact that is required for the gels to function. HAGG retains the ability to disperse liquid and absorb through capillary action (Peranteau 2013). Unlike LAGG, HAGG can be cooked with a component of organic solvents; rather than soaking the made gel in solvent and replacing the water content through solvent exchange, solvent is added to the gel as it is cooked. Moreover, HAGG does not become rigid upon the addition of organic solvents. In theory, the features of flexibility, liquid dispersion, and solvent capacity make HAGG ideal for working on parchment.

Papers presented at the General Session, AIC's 47th Annual Meeting, May 13–17 2019, Uncasville, Connecticut

### *About Parchment Substrates*

Parchment, which is proteinaceous in content, is hygroscopic and very sensitive to moisture. Even slightly elevated relative humidity can cause parchment to cockle. Prolonged exposure to water can cause severe planar distortions, such as overall cockling, pleating, and shrinkage, and cause the membrane to become brittle and difficult to handle. Tide lines form very easily. In the worst-case scenario of moisture and elevated temperature, parchment can become transparent and even gelatinize (Woods 2006). The planar distortions are somewhat reversible, but tide lines and gelatinization are not. In short, wet treatment on parchment is very tricky.

Conservators who work with parchment typically use nonaqueous treatment strategies. Adhesive on book spines is picked off dry with tools, unfortunately resulting in the removal of any parchment fibers stuck in the adhesive. Surface cleaning is done with abrasive methods, such as cosmetic sponges and white plastic erasers. Although loose dirt and grime are easily removed, much remains ingrained and the overall appearance of well-used parchment is rarely improved after dry cleaning. Tide lines generally are left as they are. These common condition issues can be treated with water or humidity, but very often the risk of damaging the parchment substrate is too great. However, when the use of moisture cannot be avoided, adding an organic solvent to water can be one way of introducing small amounts of moisture to parchment without causing damage. Solvents like ethanol and acetone seem to reduce the appearance of tide lines and discoloration.

## MAKING HAGG GELS

### *HAGG with Water*

HAGG has a hydration temperature range of 70°C to 75°C, meaning that HAGG powder will not dissolve in water below this range (CP Kelco 2007). Even within this range, vigorous stirring is required to get all the powder into solution. A

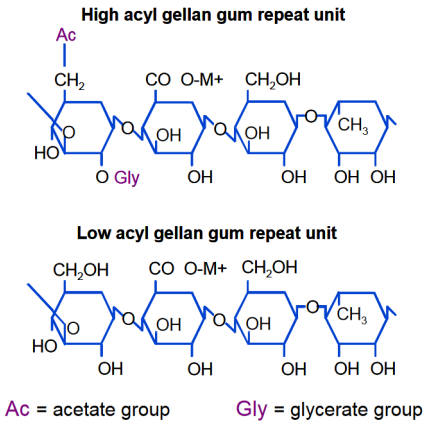


Fig. 1. The gellan gum polysaccharide chain (CP Kelco 2007, 4)

small whisk is a particularly useful tool in breaking up clumps of gellan powder. Cooking HAGG on a hotplate with a stir bar allows for monitoring the cooking gellan for clumps, although HAGG can be made in a microwave.

A divalent cation must be added to the deionized water (before the addition of the gellan) to help the gel keep its structural integrity. A solution of .4 g/L of calcium acetate in deionized water is commonly used in LAGG and is adequate for HAGG.[1] A saturated solution of calcium hydroxide and deionized water seems to be less effective in achieving structural integrity. HAGG made with .4 g/L of calcium acetate in deionized water typically has a pH of 5 to 6 and a rather low conductivity of about 1 mS/cm[2].[2] The pH and conductivity of the gel can be manipulated via the addition of buffering solutions and salts. HAGG can also accommodate chelators and enzymes.

The gelation temperature is about 70°C, meaning that the cooked slurry achieves gelation within seconds of being removed from the hot plate (CP Kelco 2007). The gels can be refrigerated for a few weeks in sealed plastic baggies and still be usable, although they do eventually get moldy. Finally, HAGG almost certainly leaves a residue. A barrier of Japanese

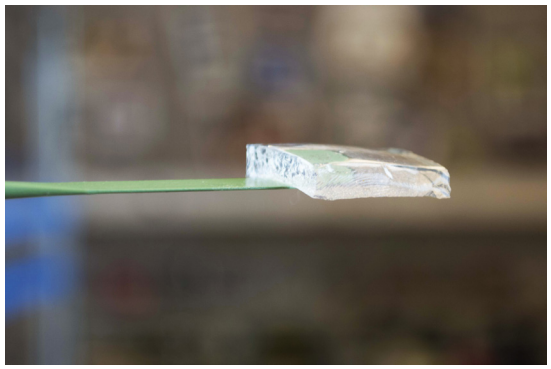

Fig. 2. A 1% LAGG in deionized water (.4 g/L of calcium acetate)

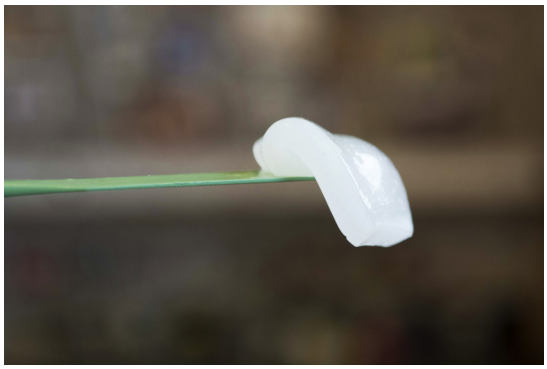

Fig. 3. A 1% HAGG in deionized water (.4 g/L of calcium acetate)

paper can be used to mitigate residue, but it will limit the effectiveness of the gel.

*Recipe for Gel A*
50 mL deionized water with .4 g/L calcium acetate
.05 g NaCl
.5 g HAGG powder

Instructions: Preheat water in a microwave or on the hot plate to above 70°C. Add the NaCl to the water and dissolve. Add the HAGG powder and stir vigorously with a whisk to break up clumps. Insert the stir bar, and cook/stir until completely dissolved. Pour the gel into a Mylar tray. (A total of 50 mL seems to fill a 3 × 5 in. Mylar tray, forming a gel approximately 3 mm thick.)

*HAGG with Water and Ethanol*
HAGG can accommodate up to 50% ethanol—that is, a 1:1 mixture of ethanol and deionized water (with a divalent ion component)—without losing its flexibility or structural integrity. However, HAGG is insoluble in ethanol, and it can be challenging getting the gellan powder to dissolve. Furthermore, if all of the ethanol is added to the gel slurry at once, very large congealed lumps of gel form and take a while to cook down. The author found success in dividing the powder and the ethanol in half and adding the components in stages. Minimizing the cooking time is to be prioritized, as the longer the gellan takes to dissolve, the more solvent is cooked off and lost. (Solvent loss has not yet been quantified.)

*Recipe for Gel B*
25 mL deionized water with .4 g/L calcium acetate
25 mL ethanol, divided
.5 g HAGG powder, divided

Instructions: Add half of the gellan powder to the water on the hot plate. Whisk to break up clumps. Insert the stir bar, and cook/stir until completely dissolved. Add the other half of the gellan powder to half of the ethanol. Slowly add this mixture to the water/gellan on the hot plate. If clumps form, pause and let them cook down. After the ethanol/gellan is sufficiently integrated, use the rest of the ethanol to rinse the gellan powder residue from the little beaker. Again, add this ethanol slowly. It may take 5 to 10 minutes for the gellan powder to fully dissolve. Once there are few or no clumps, pour the gel into a Mylar tray.

## CASE STUDY 1: GEL FOR LIFTING ADHERED PARCHMENT

The first case study is a medieval codex treated by the author as a Mellon Fellow at the Walters Art Museum. The Saint Francis Missal (W.75) is a 12th-century Italian illuminated manuscript that had been rebound during the 15th century into a quarter leather binding with beach wood boards (fig. 4). The spine leather was replaced in the 19th century. The codex was beset by an insect infestation sometime before the spine leather was replaced and required complete disbinding to repair much of the damage. The wooden boards had extensive tunneling and losses, especially to the back board at the spine edge, and required consolidation and some reconstruction.

Standing in the way of that process were two pastedowns adhered to the inside faces of the boards (fig. 5). To have complete access to the damage, these pastedowns needed to be removed. The pastedowns were parchment manuscript waste: two bifolia from a pocket missal that dated to the 11th century. Both sides of the bifolia have writing in iron gall ink and rubrication in red lead. Microchemical tests indicated that the adhesive used to adhere these bifolia overall was animal glue with a starch component. When manuscript

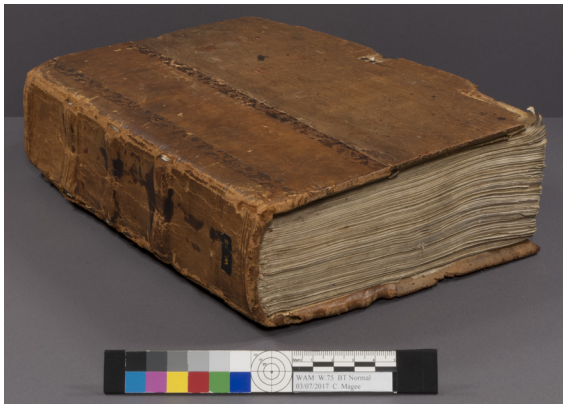

Fig. 4. The Saint Francis Missal (W.75), a 12th-century illuminated manuscript. Before treatment. Image courtesy of the Walters Art Museum, Baltimore.

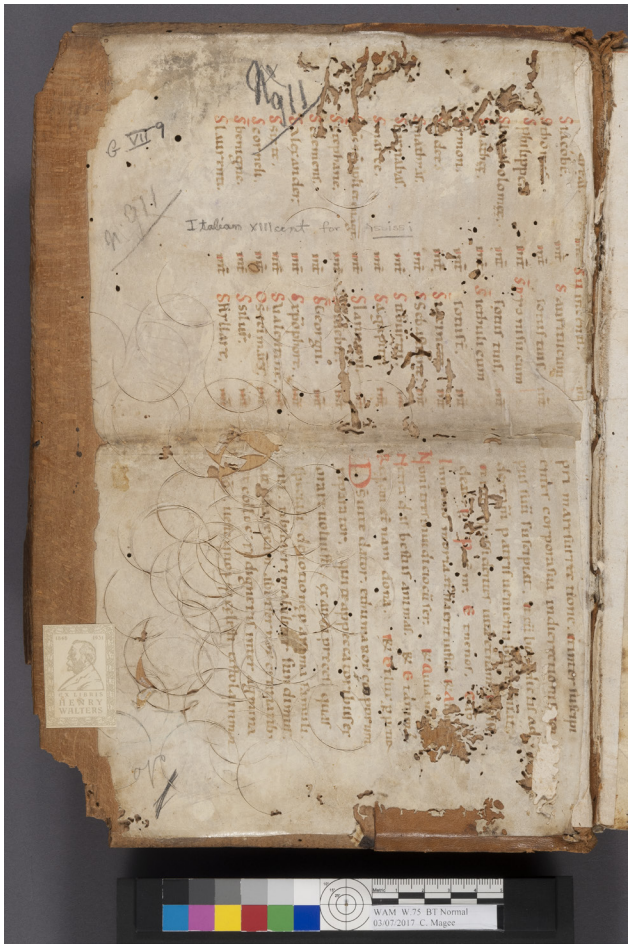

Fig. 5. The front pastedown of the Saint Francis Missal (W.75) is 11th-century manuscript waste, which is adhered to the wood overall with an animal adhesive that has a starch component. Before treatment. Image courtesy of the Walters Art Museum, Baltimore.

waste pastedowns are removed by lifting with a knife or spatula, skinning of the adhered surface of the parchment often occurs, and ink, paint, and the surface layer of the parchment are left behind in the adhesive residues. The pastedowns of W.75 had been partially lifted when the leather was replaced, and some skinning and loss of media had already occurred.

After some trial and error, HAGG with 50% ethanol was determined to be the most effective in lifting the pastedowns (see the preceding Gel B information). The gels were applied directly to the face of the parchment, humidifying the adhesive through the membrane (fig. 6). The flexible, soft texture of this gel ensured sufficient surface contact, which is necessary for the gel to function efficiently. (Feeding the gels underneath a lifting edge of the parchment did not allow the humidity to reach the adhesive still adhering the parchment to the wood.) After allowing the gels to sit on the parchment for about 5 minutes, the gel was removed and pieces of Hollytex and wool felt were placed on the humidified area with a weight on top. This allowed time for the adhesive to become softened

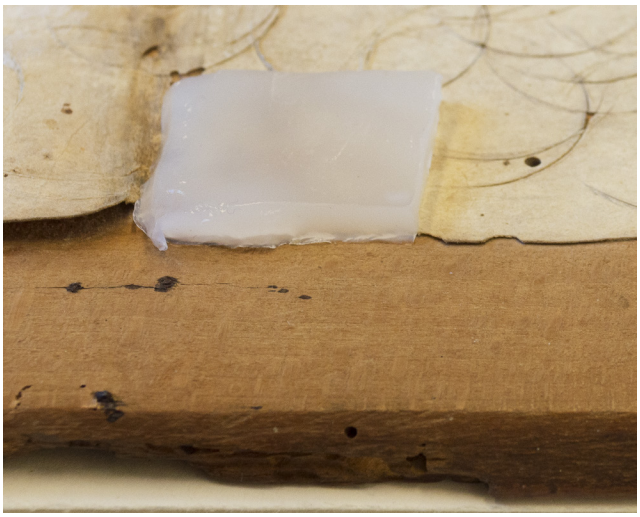

Fig. 6. HAGG with ethanol was applied directly to the face of the parchment without a barrier layer.

while the parchment began to dry. After approximately 10 minutes, the weight, felt, and Hollytex were removed and the parchment could be lifted with a spatula (fig. 7).

Throughout the pastedowns were dozens of overlapping circular cuts, the presence of which has not yet been explained. These cuts presented a challenge during lifting, as dampened parchment is extremely malleable and can be forced out of plane by even gentle manipulation. To prevent distortion, areas with the cuts were temporarily faced with remoistenable tissue before lifting. The parchment was still damp after the initial gel application, and the tissue was set in place and pressed on with finger pressure, then dried under felt and a weight for 10 minutes. This technique was effective in keeping the parchment in plane during lifting.

Fig. 7. After humidification, the parchment was lifted with a Delrin spatula.

Overall, the parchment lifted quite well (fig. 8). Most of the ink was recovered, and the text was in a readable state. The nerve-wracking prospect of using opaque gel over writing media (none of which was observed to be water sensitive during pretreatment solubility testing) was tempered by the ability to effectively deliver moisture and solvent combination without causing tide lines or discoloration.

## CASE STUDY 2: GEL FOR ADHESIVE REDUCTION

The second case study is a medieval codex treated by the author as a Kress Fellow at the Walters Art Museum. The 11th-century German Gospel Book (W.14) is an illuminated manuscript that was also designated to undergo a complete disbinding (fig. 9). After the 19th-century parchment spine lining was removed, it became apparent that the excellent condition of the parchment spine folds provided a good

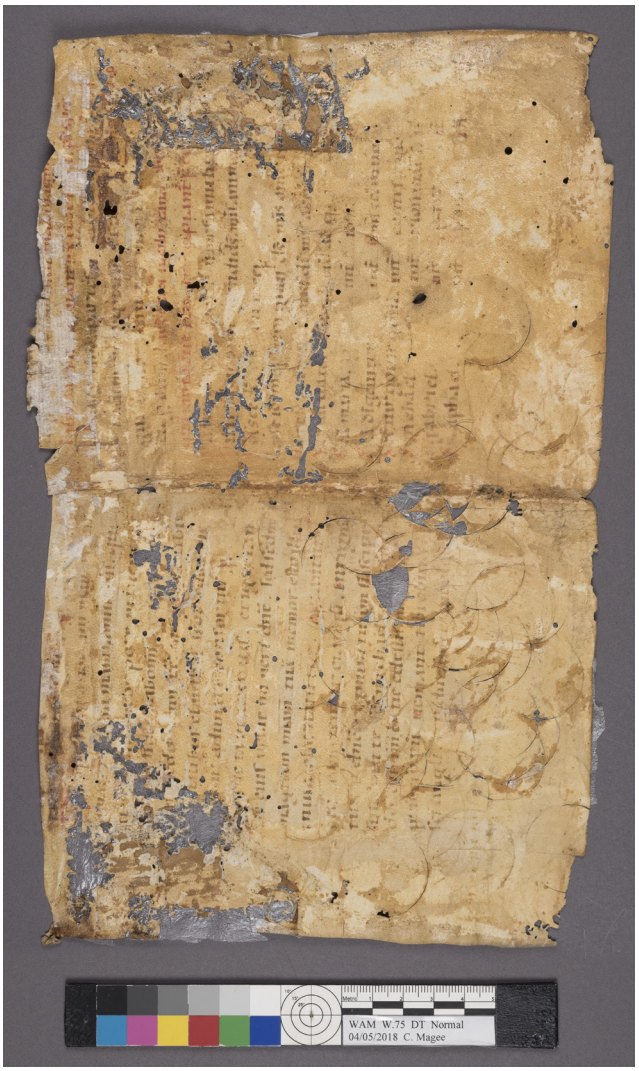


Fig. 8. Adhesive side of the front pastedown after lifting with gels. Image courtesy of the Walters Art Museum, Baltimore.

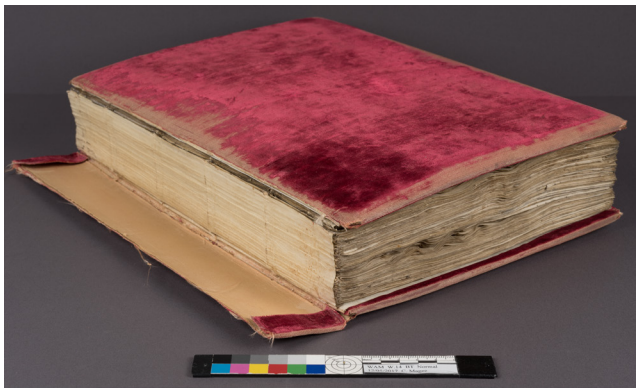

Fig. 9. German Gospel Book (W.14), an 11th-century illuminated manuscript. Before treatment. Image courtesy of the Walters Art Museum, Baltimore.

opportunity to see if gels could be useful in reducing spine adhesive. Microchemical tests indicated that this adhesive was also a mixture of animal protein and starch.

It was thought that determining the pH at which the adhesive was most soluble would quickly facilitate the removal of the spine adhesive. Solubility tests were done with three buffer solutions (pH 4, 7, and 10) on small samples of the adhesive that had been removed from the spine. A few drops of each solution were placed on the samples in a ceramic well dish. Their rates of dissolution were observed under a microscope. All of the samples swelled and became very soft within 30 seconds.

Given the success of the ethanol gels from the pastedowns of W.75, the same recipe was tried first (see the preceding Gel B information). This gel typically has a pH of about 6. The gel was left on the spine adhesive for about 5 minutes and then removed (fig. 10). This amount of time was enough for moisture to begin seeping through cracks or gaps in the adhesive layer, and the parchment underneath had begun to wet out. Only the top layer of adhesive became softened. This layer could be scraped off with a flat wooden spatula, but a layer of hard adhesive was left underneath. It took two or three passes with the gel to fully remove all of the adhesive residue, with the undesirable result of disturbed parchment fibers from the excessive mechanical action. A second gel was tried: 1% HAGG in deionized water (.4 g/L of calcium acetate), pH 6.5. This gel was also unsuccessful in sufficiently softening the adhesive after sitting on the adhesive for 5 minutes.

At this point, consideration returned to the buffer solutions. Perhaps it was not the pH but the conductivity of the solutions that caused the adhesive samples to solubilize so quickly. The buffer solutions of pH 4, 7, and 10 have conductivities of 4.9 mS/cm$^2$, 7.7 mS/cm$^2$, and 9.8 mS/cm$^2$, respectively. Although very different, they are all much higher than the conductivities of both gels (ethanol HAGG, .21 mS/cm$^2$; water HAGG, .99 mS/cm$^2$). To boost the conductivity of the water gel, .05 g of sodium chloride was added, bringing the conductivity up to 2 mS/cm$^2$. Most of the spine adhesive was softened and removed in one pass (fig. 11). Mechanical action was still necessary to remove the adhesive, because even though it was not terribly thick, it was still too much material for the gel to absorb via capillary action.

Removing adhesive with this method left behind adhesive that seeped between the quires, which could not be reached by the liquid expressed from the gel. This adhesive was addressed after the book block was disbound and the quires were separated. Rather than picking it off dry, the same gel was used to soften the adhesive locally while the outer bifolia were unfolded.

## SURFACE CLEANING

Investigations into the use of HAGG for surface cleaning on parchment have only just begun. Gels cannot work as quickly as the parchment requires; one does not simply let the gel soak out the parchment for an hour or two as one could with paper. HAGG can be left on for a few minutes, depending on

Fig. 10. The ability of HAGG to conform to the uneven book spine was instrumental to the success of the gel.

Fig. 11. The adhesive could be removed with a wooden spatula after becoming sufficiently softened.

| Gel | Ingredients | pH | Conductivity |
|---|---|---|---|
| Gel 1 | .5 g HAGG in 50 mL of deionized water | 4.8 | 0.78 mS/cm$^2$ |
| Gel 2 | .5 g HAGG in 50 mL of deionized water (.4 g/L of calcium acetate) | 5.5 | 0.92 mS/cm$^2$ |
| Gel 3 | .5 g HAGG in 25 mL of ethanol + 25 mL of deionized water (.4 g/L of calcium acetate) | 5.8 | .32 mS/cm$^2$ |
| Gel 4 | .5 g HAGG in 50 mL of deionized water (.4 g/L of calcium acetate) + .05 g of NaCl | 5.7 | 2.9 mS/cm$^2$ |
| Gel 5 | .5 g HAGG in 40 mL of deionized water (.4 g/L of calcium acetate) + 10 mL of pH 7.5 citric acid monohydrate | 7.0 | 9.3 mS/cm$^2$ |
| Gel 6 | .5 g HAGG in 50 mL of saturated calcium hydroxide | 7.0 | .61 mS/cm$^2$ |

Table 1. Experimental Gels

the thickness and condition of the parchment. This is enough time for capillary action to begin, but, as with adhesive removal, it cannot be relied on for cleaning. Gel application must be followed by mechanical action via swab. However, that action generally disturbs the parchment fibers and causes the parchment surface to appear rough.

The six different HAGG gels shown in table 1 were applied to a portion of a 16th-century parchment book cover (fig. 12). The gels were left on for 5 minutes before being removed and the areas swabbed. The results vary widely, showing that gels can effectively deliver cleaning solutions to parchment and that not all cleaning solutions are equal. The area cleaned with Gel 1 (.5g HAGG in 50 mL of deionized water, no divalent ion added) seems to have had the best results.

## TIDE LINE REDUCTION

A small scrap of modern goatskin parchment was given an artificial tide line using su-su, also known as "paper extract" or "paper dirt". The same six gels used for surface cleaning were left on for about 5 minutes (fig. 13). In this instance, gel application was not followed by swab action, as the effectiveness of capillary action alone was of interest. In some areas, the gels do seem to have softened the edge of the tide line, but by no means was the stain removed. The most improvement was seen in the area cleaned by gel 3 (.5 g HAGG in 25 mL of ethanol + 25 mL of deionized water [.4 g/L of calcium acetate]).


Fig. 12. Six gels were used in the experimental cleaning of a 16th-century parchment book cover. The numbers by the cleaned areas in the image correspond to the number of the gels in table 1. Image courtesy of the Walters Art Museum, Baltimore.

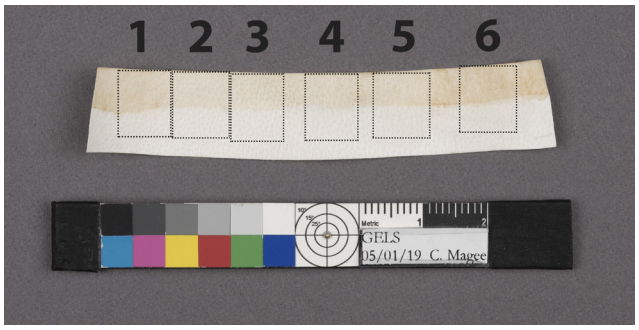


Fig. 13. The efficacy of the six experimental gels (see table 1) were tested in the reduction of an artificially created tide line on a piece of modern goatskin parchment. Image courtesy of the Walters Art Museum.

## ARTIFICIAL "AGING"

Polysaccharides are, in theory, chemically innocuous to parchment. However, exposure to the water, solvent, and salts may cause long-term damage to the protein fibers of the membrane. The six HAGG gels used in the cleaning and tide line experiments were applied to six squares of recently made goatskin parchment (fig. 14) and squares of Whatman filter paper. Control samples of parchment and Whatman

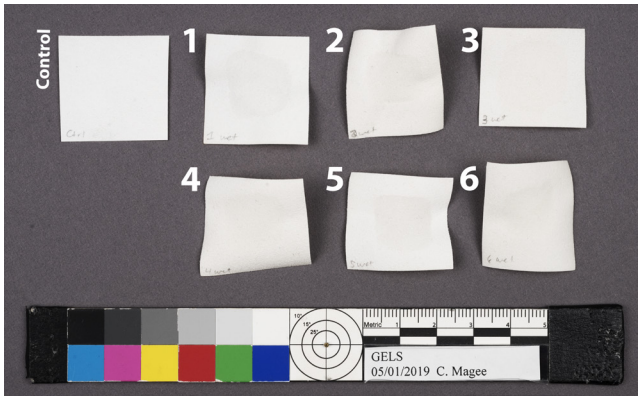


Fig. 14. Squares of modern goatskin parchment were exposed to the six experimental gels and artificially aged in an oven. The control sample was not exposed to a gel. Image courtesy of the Walters Art Museum.

paper that were not exposed to gels were also included in the test. Pieces of each gel (about 1 $cm^2$) were placed on the parchment and paper squares until the substrates wet through, about 5 minutes. Then the samples were allowed to air dry.

Parchment and paper samples treated by the same gel were placed in a small glass jar containing a glass test tube with a dampened cotton ball at the bottom (seven jars total). The mouths of the jars were covered with pieces of aluminum foil, over which plastic lids were screwed on. The jars were placed in an oven at 60°C for 21 days.

Although it is plainly visible where the gels were applied, the samples do not look much worse than before they were placed in the oven. Much of the darkening and distortion were present after the parchment was allowed to air dry. If anything, this experiment demonstrates the need for limited exposure to moisture and controlled drying for parchment rather than being an argument against using gels.

## CONCLUSION

Gels made of HAGG can be successfully used on parchment components in codices for the purposes of softening and reducing adhesives made from animal protein. The gels can deliver cleaning solutions to parchment surfaces, but the removal of surface grime must be done mechanically and may be disfiguring to the surface of the parchment. The gels are also limited in their effectiveness in reducing tide lines. It is possible that a different combination of pH and conductivity modulation in addition to chelators or surfactants may make a difference in the effectiveness of the gels for these purposes.

## ACKNOWLEDGMENTS

The author would like to thank Abigail Quandt, Elisabetta Polidori, Dr. Glenn Gates, Madison Whitesell, and the always supportive conservation department at the Walters Art Museum. Special thanks to Michelle Sullivan for inspiring this research and for continued guidance. Deep gratitude goes the Society of Winterthur Fellows for their support through a Research and Continuing Education Grant. This article is dedicated to Grumpy Cat, who passed away the week that the original paper was presented.

## NOTES

1. The concentration of calcium acetate in deionized water at .4 g/L has been seen in several sources (Iannuccelli and Sotgiu 2010; Hughes and Sullivan 2016), but how this concentration was determined is unknown.
2. The pH and conductivity were measured with Horiba LAQUAtwin meters. Each meter was calibrated with standard solutions before measurements were taken. Slight variations were observed in both the pH and conductivity when measuring different areas within a gel.

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## SOURCES OF MATERIALS

KELCOGEL LT100 Gellan Gum (High Acyl)
CP Kelco US, Inc.
3100 Cumberland Blvd., Ste. 600
Atlanta, GA 30339
800-535-2687
https://www.cpkelco.com/products/gellan-gum/

Calcium Acetate Hydrate (CAS: 114460-21-8)
Acros Organics, via Fisher Scientific
300 Industry Dr.
Pittsburgh, PA 15275
724-517-1500
https://www.fishersci.com/shop/products/calcium-acetate-hydrate-99-extra-pure-acros-organics-3/AC211052500/

Buffer Solutions (pH 4, 7, and 10)
Aldon Corp.
221 Rochester St.
Avon, NY 14414
585-226-6177
https://www.aldon-chem.com/

Sodium Chloride
J. T. Baker Chemical Co.
Phillipsburg, NJ 08865

Horiba LAQUAtwin Compact pH Meter B-71X; Horiba LAQUAtwin Conductivity Meter
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CATHIE MAGEE
Kress Fellow in Book Conservation
The Walters Art Museum
Baltimore, MD
cathie.magee@gmail.com