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Cross-Disciplinary Uses for Gellan Gum in Conservation

ABSTRACT

Gellan gum gel, a high molecular weight polysaccharide, was first introduced to the North American conservation community by Italian conservators Iannuccelli and Sotgiu (Central Institute for the Restoration and Conservation of Archival and Library Patrimony (ICPAL) Laboratory for the Conservation of Library Materials, Rome) at the Book and Paper Session of the AIC Meeting in 2010. Their search for an alternative method of wet- cleaning graphic art that would not alter topographical features—like surface texture, platemarks, and etched/engraved lines—led to early experiments with gellan gum at ICPAL in 2003–2004. The product is used as a thickening or gelling agent in food, pharmacology and personal care product industries. For conservation purposes, gellan gum gradually releases moisture into an adjacent substrate in a controlled way and leaves no residue. When used for cleaning or stain reduction, soluble deterioration components are transferred to the gel through osmosis. Iannuccelli and Sotgiu reported on various treatments carried out with gellan gum, including backing removal, enzyme delivery, deacidification, and reductive bleaching. Inspired by their findings, conservators at Library and Archives Canada (LAC) first attempted to incorporate the use of gellan gum as part of the protocol for the treatment of a large collection of Audubon prints on wood pulp backings. This paper reports on the results of experiments with gellan gum for backing removal, as well its use in a variety of treatments on objects ranging from a book, a three-dimensional map and globe, to a vintage paper dress.

INTRODUCTION

In 2010, paper conservators at Library and Archives Canada (LAC) commenced a long term project that has stretched over several years: the conservation of a dis-bound set of Audubon's *Birds of America*. The majority of the hand-coloured Audubon sheets had been solidly adhered to acidic wood pulp board. The challenge lay in finding the safest, most efficient way of removing the auxiliary supports as a first step in the treatment protocol.

That same year paper conservators Simonetta Iannuccelli and Silvia Sotgiu, from ICPAL, Laboratory for the Conservation of Library Materials in Rome, introduced the use of a rigid polysaccharide gel for wet conservation treatments of works on paper at the AIC meeting in Madison Wisconsin, and at the ICOM-CC Graphic Documents Working Group interim meeting in Copenhagen. (Iannuccelli and Sottgiu 2010).

Sottgiu became interested in exploring agarose gel applications for paper conservation treatments after having attended a cleaning workshop given by Richard Wolbers in Italy in 2003. The search for a more economical alternative to agarose gel led to ICPAL experiments with gellan gum. Results of thorough physical and chemical analysis at ICPAL proved its safety and effectiveness (Botti et al 2011).

Gellan gum, it seemed, might be worth investigating: here was a material that could deliver moisture in a highly controllable way with minimal impact on the paper substrate, and had been successfully used for lining removal, cleaning, deacidification and reductive bleach and enzyme delivery.

The Canadian Conservation Institute (CCI) organized an advanced professional development workshop in Toronto, Ontario in March, 2014 on the wet treatment of graphic art on paper with gellan gum, delivered by Sottgiu and Iannuccelli. A summary session organized by workshop participants from CCI and LAC was held at CCI a few months later for conservators in the Ottawa region to disseminate information about gellan gum. Since then, LAC conservators have found many applications for gellan gum in the course of treating a wide range of objects and continue to experiment with it.

The use of polysaccharide-based rigid gels as the basis for highly controlled cleaning systems for painted surfaces was first introduced by Richard Wolbers in 2000. Altering pH and incorporating a range of other ingredients, like surfactants, chelators and enzymes can produce tailor-made rigid

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gels for specific cleaning applications. Paper conservators have customarily used gels based on cellulosic thickening agents, like methyl cellulose, ethyl cellulose, hydroxy methyl cellulose, sodium carboxy methyl cellulose over the last 40 years as poultices for cleaning, or for mixing with other active ingredients, like bleaches and enzymes. The application of rigid gel treatment systems to paper artifacts is of great interest to paper conservators, permitting a superior degree of control by limiting capillary action and the movement of cleaning agents held within the gel matrix during the course of treatment.

OVERVIEW OF GELLAN GUM

Gellan gum is a high molecular weight polysaccharide (i.e.: complex sugar) produced by the fermentation of the microbe *Sphingomonas elodea*. It finds application as a thickening or gelling agent in the biomedical, pharmacology and food industries, and is biodegradable and non-hazardous. Recently gellan gum has found new applications for molecular gastronomy and modernist cooking applications.

The general chemical structure is a straight chain of four linked monosaccharides (i.e.: simple sugars), including one molecule of rhamnose (plant-derived sugar), one molecule of glucuronic acid, and 2 molecules of glucose (fig. 1).

Studies conducted by Sottgiu and Iannuccelli of various rigid gellan gels (Phytagel gellan, Gelrite and Gelzan CM) concluded that Kelco gellan gum was the most effective and economical product. Gellan gum also compared favorably in tests to agarose gel, with higher transparency and greater water retention properties (Iannuccelli and Sotgiu 2010).

Gel formation is influenced by temperature, concentration, thickness of the cast layer and by the presence or absence of mono or bivalent cations. Gellan gum is available in two grades: high and low acyl content, which form soft and hard gels respectively.

Deacylated gellan gum is used for conservation applications. It forms a stronger gel, and sets at a much lower temperature range—between 30 and 50 degrees Celsius—while high acyl gels set at much higher temperatures. It is the acyl groups that have a significant influence on gel characteristics. The high acyl form produces soft, elastic non-brittle gels, while the absence of acyl groups in the low acyl form produces firm, non-elastic brittle gels.

The ability of gellan gum to gradually release water molecules into the paper, and in turn absorb soluble degradation products is one of its most advantageous qualities. Because of the slow, constant introduction of moisture via gellan gum, the effects of aqueous swelling are minimized, a consideration that is critical when treating works with distinct dimensional qualities, like platemarks, embossings and surface texture. The ideal concentration of gellan gum will depend on the hydrophilic nature of the paper.

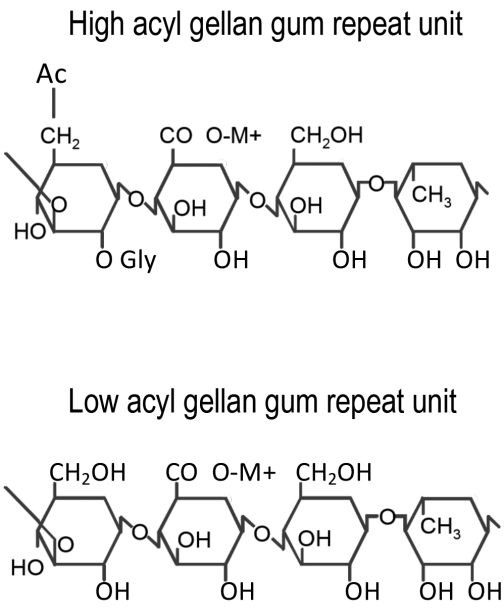

Fig. 1. Gellan gum structure.

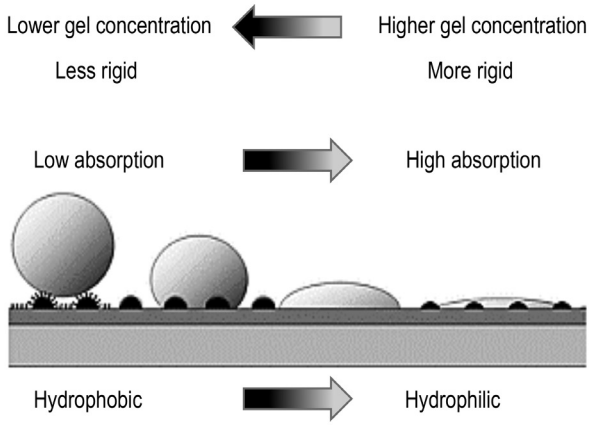

Fig. 2. Calculation of gel concentration.

In order to choose the appropriate gel percentage, the conservator must subjectively assess the wettability of the paper support. This is affected by the porosity of the paper, fiber type, sizings and coatings, and the state of preservation of the paper. The more absorbent (hydrophilic) the paper is, the higher the concentration of gellan gum used, as it will give off less moisture. (fig. 2)

GELLAN GUM PREPARATION

For use with paper artifacts, the gellan gum is normally prepared in the range of 2–4% concentration to make a semi-rigid layer. A saline solution with calcium acetate is prepared, (0.4 g/L calcium acetate), to which the gellan gum powder is added. The gel powder is quickly whisked into the

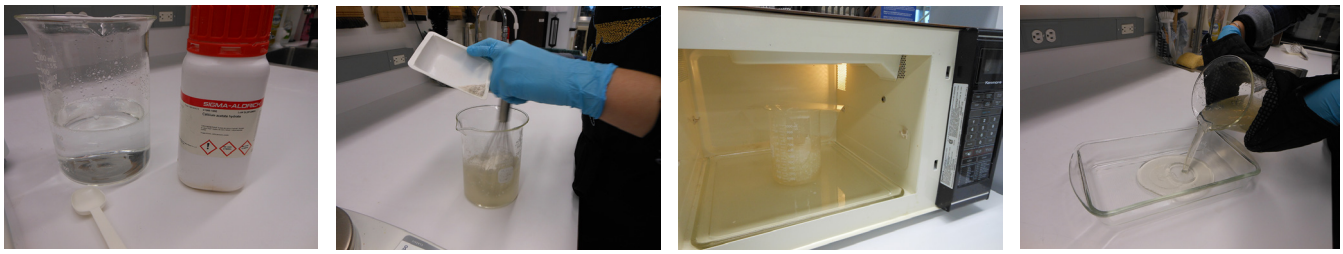

Fig. 3. Preparation of gellan gum gel.

LEFT TO RIGHT

a. A saline solution is prepared with 0.4g/l calcium acetate in reverse-osmosis water.
b. Gellan gum powder is measured according to desired gel concentration and quickly whisked into the saline solution.
c. Gellan gum solution is heated in a microwave until hydrated (allow to boil for a few minutes).
d. Gellan gum solution is immediately poured into heat proof pan to desired thickness.

saline solution to create a colloidal dispersion. It is covered and heated in the microwave until the dispersion turns into a slightly yellow, transparent solution. Complete hydration of the gel occurs at 75–100 degrees Celsius. The solution is poured into a heat resistant tray while it is still hot and runny, and the rigid hydrogel film forms as the solution cools to room temperature. (figs. 3a–d) Gellan gum is susceptible to mold, and can be can be covered and refrigerated for approximately 2 weeks before becoming unusable.

Gellan gum can also be prepared without a saline solution, which reduces the degree of rigidity. The absence of calcium ions in lower gel concentrations, however, may render the cast film too mushy and crumbly to handle. The calcium ions stabilize the gel structure, rendering it more firm and easily manipulated. Similarly, the degree of water purity will also affect the ability of the gellan gum to achieve an adequately rigid form. Depending on the intended use of the gel, a lower concentration of less rigidity may be desired. In early experiments at LAC, gellan gum was prepared with water purified by reverse- osmosis, sometimes made alkaline with the addition of saturated calcium hydroxide, resulting in an easily pliable, semi rigid film.

The range of gel flexibility is illustrated in this image of different gellan gum samples prepared with calcium acetate solution in increasing concentrations. (fig. 4)

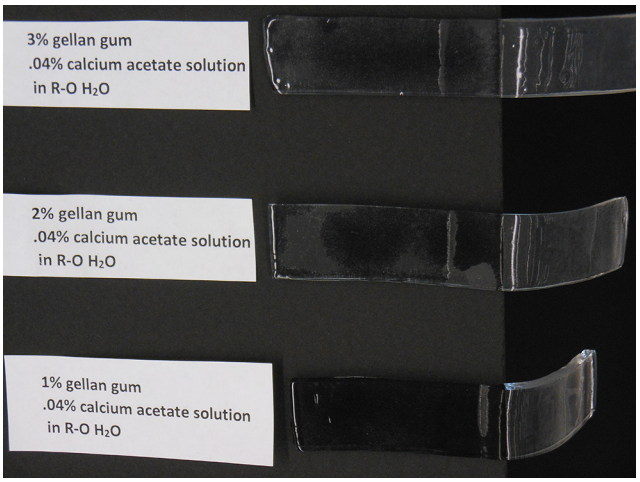

Fig. 4. Comparison of rigidity of gellan gum concentrations incorporating calcium acetate.

GELLAN GUM TREATMENT EXAMPLES

AUDUBON PRINT BACKING REMOVAL

Each Audubon plate had been solidly adhered to wood pulp cardboard. (fig. 5a) Experiments were conducted with different concentrations and thicknesses of gellan gum to try and find the optimal moisture content that would sufficiently release the cardboard secondary supports. The following points were noted:

- Gellan gum works best for backing removals if the object can be thoroughly humidified first.
- Thinner paper and card backings are most easily removed with gellan gum.
- The dense outer cardboard layer impedes the penetration of moisture from the gellan gum.
- Gellan gum was most effective in removing adhesive from the object verso once the cardboard had been removed. (fig. 5b)

In the case of the Audubons, gellan gum did not make the backing removal operation more efficient or less labor intensive.

LOCAL STAIN REMOVAL WITH GELLAN GUM

STAIN REDUCTION ON A VINTAGE PAPER DRESS

A paper dress, with a photographic image of Canadian Prime Minister Pierre Trudeau on both recto and verso, was produced for hostesses at the 1968 Liberal convention. (figs. 6a, b) The highly textured, poor quality wove paper is similar to

Fig. 5.

TOP TO BOTTOM

a. Audubon prints: mechanical backing removal and subsequent treatment takes total of 40 hours per print.

b. Gellan gum cast sheets are used to remove adhesive residue from print verso.

the waffle-like texture of paper towel. The neckline is edged with black broadcloth bias tape. At one time the top of the dress was folded on to the back, leaving a stain on the face of Trudeau that mirrors the black trim along the neckline and along the slit on the verso. The stain has also penetrated through to the recto, where it is visible to a lesser extent. In

Fig. 6. (Untitled) Trudeau Paper Dress, 1968, photomechanical print on wove textured paper, 84.0 x 49.9 cm, Library and Archives Canada, MIKAN 3000168

LEFT TO RIGHT

a. Overall view before treatment.

b. Overall view after treatment.

preparation for removing the stain, a 4% concentration of gellan gum dissolved in alkaline water, with the addition of saturated calcium hydroxide to pH 8.0 was prepared and cast into a 1 cm thick layer.

Initial tests with paper towel, then at the back hem of the dress affirmed that the textured surface was not lost after contact with gellan gum under light weight. Blotting paper and mat board were inserted inside the dress under the stained area.

One of the great advantages of working with gellan gum is the fact that it can be easily trimmed with a scalpel into precise shapes for local stain removal, alleviating the need for producing masks to shield sensitive media. In the instance with the paper dress, the stain was traced onto Mylar and the gellan gum was trimmed to size. The gel was covered with Mylar and lightly weighted for 3 minutes then removed. The paper was highly absorbent, and soluble degradation components were drawn up into the gel, and also moved into the blotter placed beneath the treated area. The surface texture was unchanged. (figs. 7a–d) The process was repeated on the stains until they were almost completely reduced. (figs. 8a, b)

STAIN REDUCTION ON A COLLAGE

A collage suffered damage in a flood. (figs. 9a, b) The main substrate is corrugated cardboard solidly adhered to Masonite, with poor quality paper elements arranged in an overlapping pattern tacked to the surface of the cardboard. Water soaked the bottom of the work, moving soluble degradation components up to the tideline, and leaving the lower portion lighter (and cleaner) than the rest of the support, with no adverse effects on the acrylic paint layer. Since the

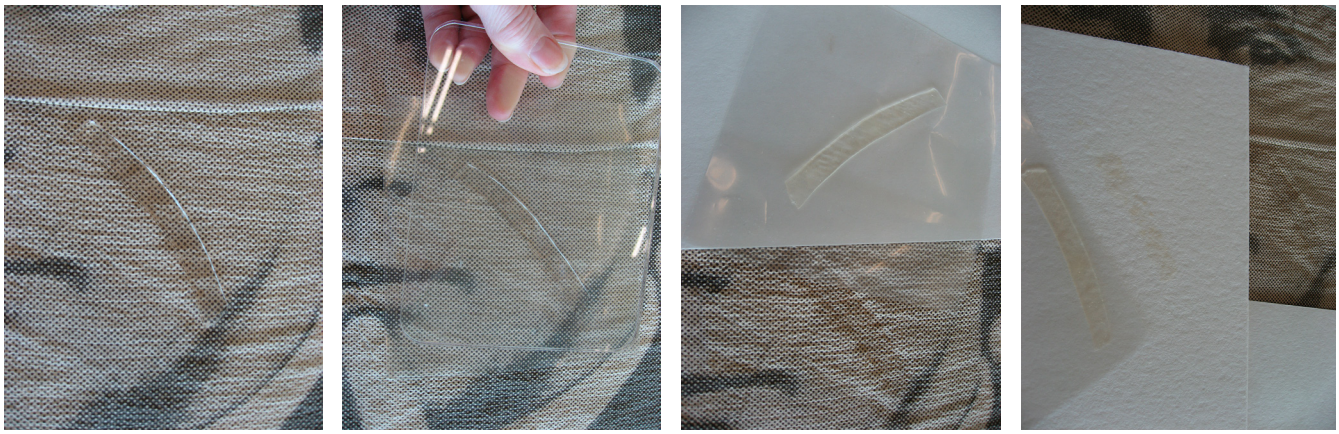

Fig. 7.

LEFT TO RIGHT
a. Trimmed gellan gum gel is placed over stain.
b. Plexiglas weight placed over gellan gum.
c. Removed gellan gum: minimal moisture penetration into paper.
d. Yellowed gellan gum removed from stained area and transfer of stains to underlying blotter.

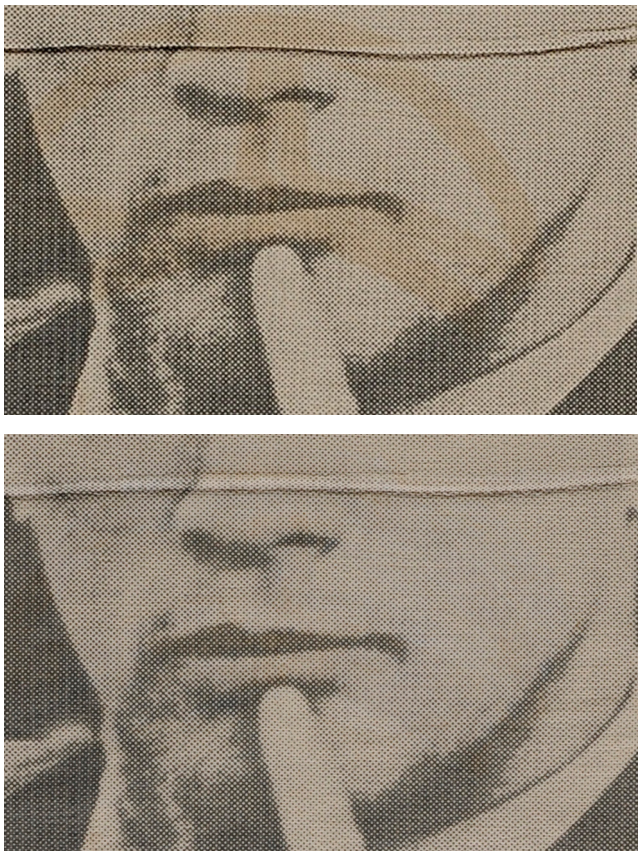

Fig. 8.

TOP TO BOTTOM
a. Trudeau Paper Dress. Stained area before treatment.
b. Right, stained area after treatment.

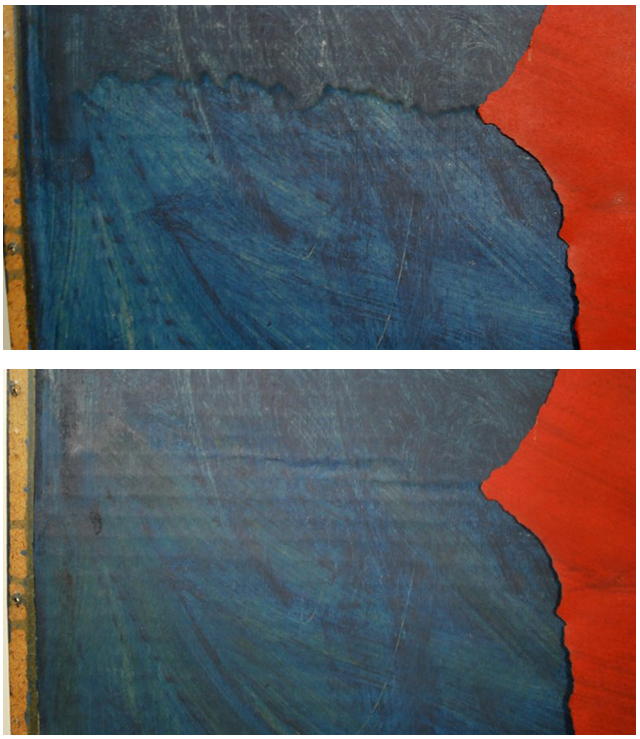

Fig. 9. Detail of water damage to a mixed media collage on corrugated cardboard.

TOP TO BOTTOM
a. Detail before treatment.
b. Detail after treatment.

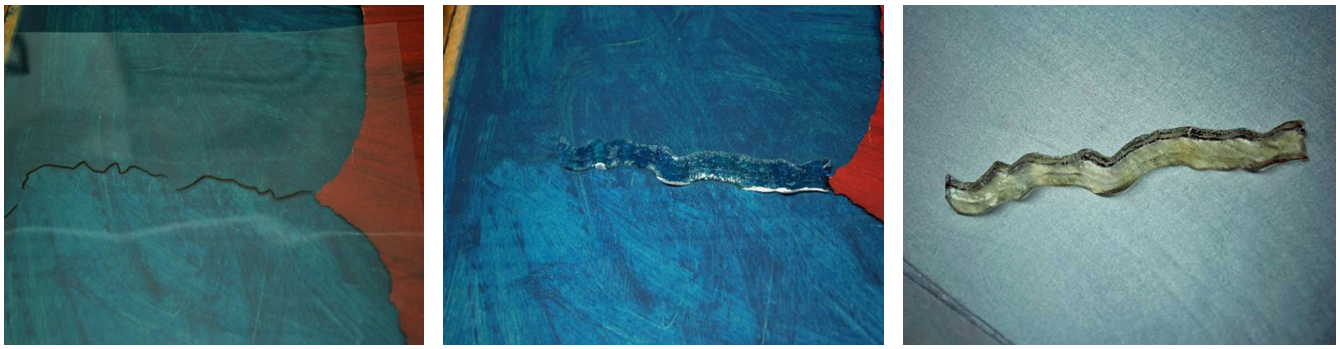

Fig. 10.

LEFT TO RIGHT
a. Stain tideline is traced onto Mylar.
b. Gellan gum is trimmed to the shape of the tideline.
c. Discolored gellan gum after stain reduction.

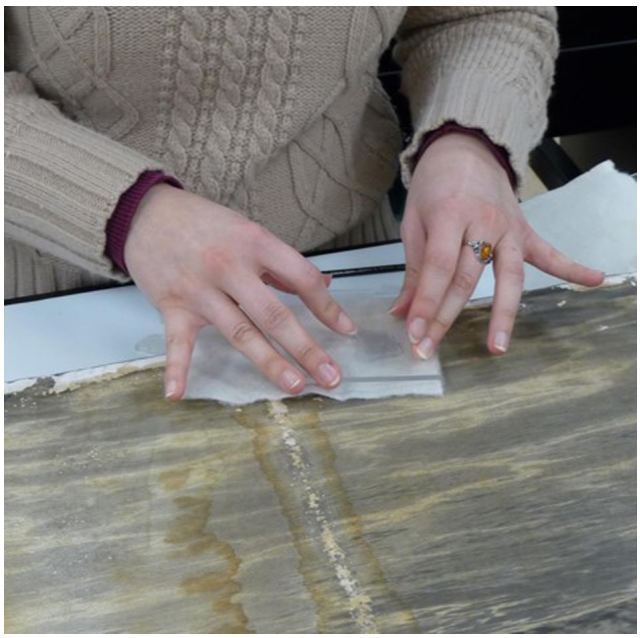

Fig. 11. William Thompson Freeland Panoramas, 1913, silver gelatin on paper, 68.5 x 570.0cm, 1913, Ontario Archives, RG49 243.

TOP TO BOTTOM
(Photographs courtesy of the Canadian Conservation Institute)
a. Conservators working on stain removal with gellan gum.
b. Detail of gellan gum being applied through Japanese paper.

corrugated cardboard was firmly attached to the Masonite, a poulticing method had to be used to reduce the stain. A 3% concentration of gellan gum dissolved in alkaline water (pH 8 with the addition of saturated calcium hydroxide) was prepared. The irregular border of the stain was traced onto Mylar, and gellan gum was trimmed to match. It was placed over the stain, covered with Mylar and light weight and left for ten minutes. The process was repeated several times until the stain was sufficiently reduced. A light wash of watercolour was applied over the cleaned area to restore visual balance. (figs. 10a–c)

STAIN REDUCTION ON A SILVER GELATIN PHOTOGRAPH

Gellan gum has also successfully been used to reduce staining on silver gelatin photographs. Two 570 cm long panoramas of Niagara Falls are currently being treated at CCI. (figs. 11a, b) The images are believed to be the largest single sheet, single exposure photographs produced at that time. Because of the solubility of the deteriorated emulsion, a more rigid 3% gellan gum was prepared in a calcium acetate solution, and an interleaf of thin Japanese paper was used between the surface of the photograph and the gellan gum. The gel was trimmed into circular shapes to avoid leaving hard-edged tide lines. Stains were drastically reduced as a result (figs. 12a, b).

LOCAL REMOVAL OF PAPER LAYERS

REMOVAL OF A PAPER LABEL FROM THE VERSO OF AN OIL PAINTING

Gellan gum works well as a poultice for humidifying and removing paper layers from various substrates. High gel concentrations afford a slow, constant, highly controllable release of moisture. Adding weights to the gellan gum can also increase the rate of moisture release. A paper label was successfully removed from the verso of a painting, with minimal wetting of the canvas. The controlled release of moisture

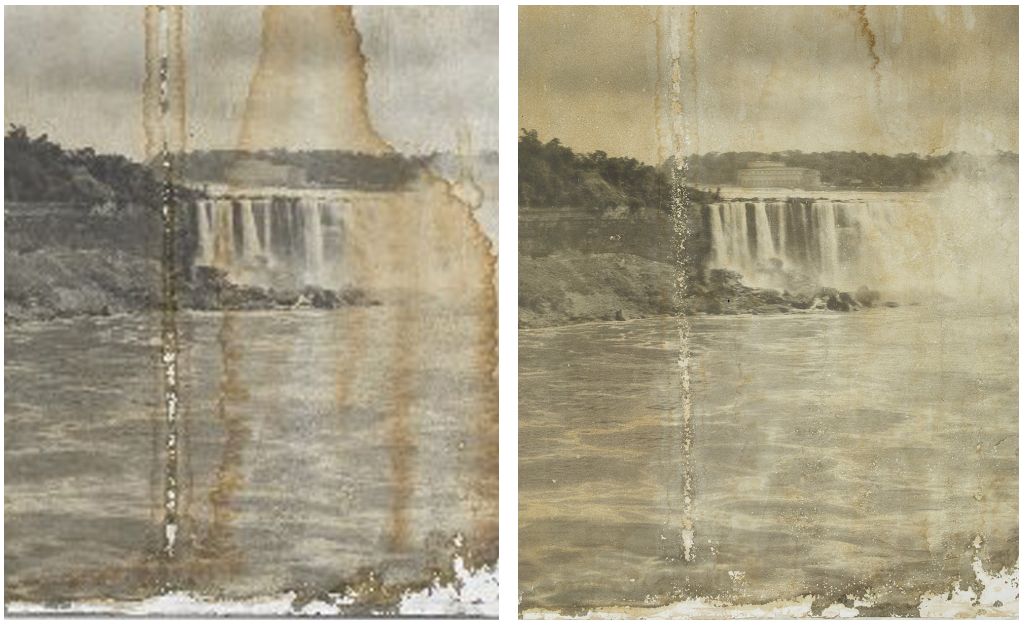

Fig. 12.

LEFT TO RIGHT

a. Detail of panorama before treatment.
b. Detail, of panorama after stain reduction with gellan gum.

Fig. 13. Removal of a paper label from the verso of an oil painting.

LEFT TO RIGHT

a. Gellan gum is trimmed to shape of label, with Mylar barrier beneath the gel to protect canvas surface.
b. After 5 minutes, the gellan gum was removed, and the label was lifted with microspatula.

prevented over-wetting of the substrate, which could have led to serious planar deformations and complications with the paint layer and ground. (figs. 13a, b)

REMOVING LINING FROM BOOK SPINE

In the process of examining the first Bible published and printed in Canada, the conservator discovered that the blue paper covering the spine is a fragment of an advertisement for the Bible. The treatment objective was to remove the fragment and underlying white paper layer in one piece, without over-exposing the spine to moisture, and running the risk of creating tidelines and staining in the text block. 2% gellan gum prepared with RO water was gently pressed into contact with the curve of the blue paper-lined spine, then covered with Mylar and soft weights. After five minutes, the gel was removed and the paper layers were slowly peeled off with the aid of a microspatula (figs.14a–c). The blue printed text was successfully removed in one piece, and the textblock was not affected by moisture. Gellan gum delivered the adequate humidity needed to soften adhesive layers in order to release the paper.

Fig. 14. Henry John White (Printer), The Holy Bible, (King James Version), 1832 or 1833, 28.0 x 22.0 x 6.0 cm, Library and Archives Canada, AMICUS 23024642.

LEFT TO RIGHT
a–c. Removal of paper covering the book spine.

Fig. 15. Relief Map of Canada, Atlas School Supply Co., Chicago, 1909, 80.0 x 114.0 cm., LAC R14016 vol. 2. Cleaning map with gellan gum.

LEFT TO RIGHT
a, b. Cleaning the map with thin cast of gellan gum.
c. Detail of map during cleaning with gellan gum.

TREATMENT OF THREE-DIMENSIONAL OBJECTS

CLEANING THE SURFACE OF A TOPOGRAPHICAL RELIEF MAP

For maximum flexibility, gellan gum can be prepared at a low concentration without a calcium salt solution, and cast into thin layers. 3% gellan gum gel prepared with RO water was used to clean a severely discolored relief school map by pressing it into contact with the irregular surface (figs. 15a, b). To discourage tidelines, gel applications were overlapped as cleaning progressed. Tidelines were subsequently removed by applying 3% gellan gum that was brush coated with ethanol (fig. 15c).

CLEANING A TERRESTRIAL GLOBE

A large terrestrial globe recently underwent extensive treatment at CCI, including varnish and adhesive removal, and overall cleaning and stain reduction. After varnish removal, 5% gellan gum cast in thin layers was applied to selected areas of the paper gores to reduce brown stains and overall discolouration. As with the relief map, the gel was prepared without the addition of a calcium salt in order to produce a more flexible gel layer that would conform to the spherical shape. It was applied in small sections, covered with thin Mylar and removed after several minutes. The number of gellan gum applications varied according to the area and degree of discolouration. In this case, tidelines were avoided by overlapping the wet areas as the treatment progressed (figs. 16a, b).

Gellan gum was also used to reduce degradative soluble copper (II) salts from the greenish brown pigments at the perimeter of the land masses, thus preventing their migration into the surrounding paper. Pieces of gellan gum tested before and after treatment with Ink Cor non-bleeding indicator paper confirmed removal of the copper (II) ions. (McMann 2013).

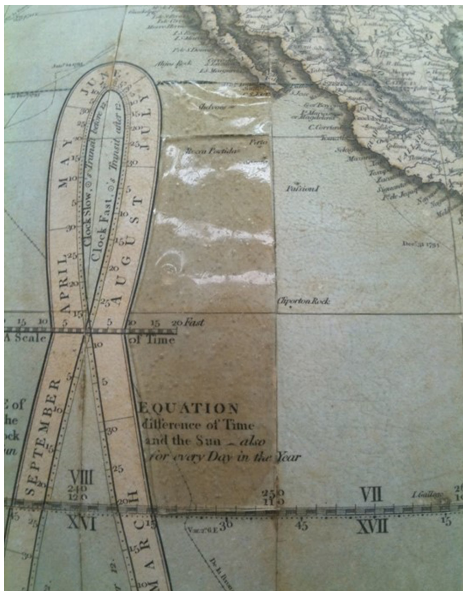

Fig. 16. Cary Terrestrial Globe, 1835.

LEFT TO RIGHT

a, b. Gellan gum used to reduce staining on globe. (Photographs courtesy of the Canadian Conservation Institute)

Fig. 17. Sarony, Major and Knapp, Lithographers, City of Ottawa, Canada West, 1858–61, lithograph on wove paper, 74.2 x 99.7 cm, Library and Archives Canada, R3133-3997894.

LEFT TO RIGHT

a. Stain reduction using gellan gum and Borane reductive bleach.

b. Comparison of map sections: left, before stain reduction, right, after treatment with gellan gum and borane reductive bleach.

REDUCTIVE BLEACHING WITH GELLAN GUM

Sottgiu et al. (2010) reported on the possibility of incorporating reductive solutions into gellan gum gel to expand the range of stain reduction treatments. Borane, a tert butylamine complex ($(CH_3)_3 CNH_2 . BH_3$) (7g/L) is added to a calcium acetate solution (0.4g/L) *after* the gellan gum is added and the colloidal suspension is heated in the microwave. Note that proper personal protective equipment must be used when handling borane tert-butylamine complex, including appropriate gloves, goggles and respirators. Preparation of the solution and treatment should take place under adequate extraction, and the gel must be disposed of as hazardous waste.

A severely deteriorated lithograph of a bird's eye view of Ottawa underwent extensive treatment. After backing removal, bathing and several light bleaching campaigns failed to satisfactorily reduce staining, further bleaching with gellan gum mixed with Borane was considered. A 2% reductive bleaching gel was prepared in calcium acetate solution, to which 7g/L of borane tert-butylamine complex was added. The lithograph was sandwiched between the cast gel sheets for two periods of 60 minutes, with impressive results. Note that the reductive bleaching gel has a milky white, opaque appearance, compared to the more transparent stock gellan gum gel (figs. 17a, b).

Fig. 18. Robert Hood, Cross Fox Catching a Mouse, 1820, watercolor with pen and black ink over graphite on wove paper, 13.4 x 25.0 cm, Library and Archives Canada, R13133–440. Deacidification of a watercolor with gellan gum and calcium propionate.

LEFT TO RIGHT

a. Humidified watercolor is placed on cast sheet of gellan gum with calcium propionate.
b. A second cast gel sheet is placed on the recto of the watercolor.
c. A hole is cut in the gel sheet to avoid contact with soluble areas in the watercolor.

APPLICATION	GELLAN GUM FORMULATION	COMMENTS
Overall cleaning **Local stain removal**	Less rigid gel: 2-4g/L gellan gum powder in H_2O* More rigid gel: 2-4g/L gellan gum powder in saline solution (0.4g/L calcium acetate)	* Quality of water affects rigidity: the lower (or absence of cations), the less rigid the gel
Bleaching	2-4g/L gellan gum powder in saline solution (0.4g/L calcium acetate) AFTER heating gellan gum in microwave, quickly whisk in 7g/L borane tert-butylamine complex	Cast gel layer is milky and more opaque in appearance PPE must be used when preparing borane solution Requires proper disposal as hazardous waste (refer to MSDS)
Deacidification	2-4g/L gellan gum powder in saline solution (0.4g/L calcium acetate) Add 3.5-5g/L calcium propionate* to saline solution BEFORE heating in microwave	*Quantity of calcium propionate dependent on desired alkaline reserve Cast gel layer is milky and more opaque in appearance

Fig. 19. Gellan Gum Applications and Solutions

DEACIDIFICATION WITH GELLAN GUM

Preparation of gellan gum for deacidification is similar to the procedure for reductive bleaching. Calcium propionate (3.5–5g/L is added to a calcium acetate saline solution (0.4g/L), before whisking in the gellan gum and heating it in the microwave. A small watercolour with soluble ink additions to the face of the fox was washed and de-acidified using 3% gellan gum mixed with 3.5g/L calcium propionate. The support was sandwiched between two layers of gellan gum, covered with polyethylene, Plexiglas and light weights for 45 minutes. The soluble media in the fox's face was easily isolated by cutting a triangle out of the gellan gum. Washing and deacidification solutions were effectively delivered from both sides without any compromise to the soluble media. (figs. 18a–c)

CONCLUSION

The table lists the gellan gum applications and solutions that have been described in this article (fig. 19).

Gellan gum has proven to be a valuable addition to the arsenal of materials used in the conservation labs at LAC. The following advantages have been noted:

- Gellan gum is safe; easy preparation and disposal (note exception for Borane gel);
- Provides an even, highly controlled delivery of moisture;
- Retains dimensional qualities, textures and topographical qualities of the object being treated;
- Has variable flexibility, so is effective in cleaning uneven or multi-dimensional surfaces;
- Is transparent to permit observation of object during treatment;
- Does not leave a residue;
- Can be used for local application or overall treatments, and
- Can be used to deliver a variety of chemical treatments.

The preceding examples illustrate the versatility of gellan gum, and the author hopes that the conservation community will use these treatments as a stepping stone and inspiration for continued investigation.

ACKNOWLEDGEMENTS

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MATERIALS

Ink Cor Non-Bleeding Indicator Paper
http://www.universityproducts.com/cart.php?m=product_list&c=598

Gellan Gum
http://www.talasonline.com/
http://cpkelco.com/products/gellan-gum/

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