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Soft Matter: Gel Development for Conservation Treatment Gellan Gum and Nanorestore Gel®

INTRODUCTION

In the field of conservation of cultural heritage, new technologies are developed or adapted to achieve a more gentle, targeted approach to the conservation of artifacts. While gels have been used for decades, recent developments indicate a desire for greater control over the action of the treatment. After reviewing many studies, my interest has focused on two different gels: the Gellan gum and the Nanorestore Gel©. This paper will present the subject of my master thesis "L'utilisation de gel pour le nettoyage d'oeuvre graphique" (*The use of gel for the cleaning of paper artifacts*) at the Paris 1 Panthéon-Sorbonne university.

To begin, we will review the main characteristics we require in gels used for conservation of cultural heritage materials/objects. This will be followed by an examination of how these two gels answer our needs for paper conservation, including details about their properties and their use. Finally we will compare the two gels and see how they complement each other.

WHY USE A GEL?

The word "gel" is commonly used to describe many types of products. In general, we describe "gel" products as having a gel-like appearance, which is thick and sticky. From a chemical point of view, a gel is a polymer, which in small amounts, acts as a thickener liquid. But a gel-like material can be produced from various sources and can have different appearances and characteristics according to the compositions and proportions used.

Gels are used in the food and medical industries. For the conservation of cultural heritage, the gels used are most often an adaptation of these technologies, adjusted to meet the specific needs of the conservator.

Presented at the Book and Paper Group Session, AIC's 44rd Annual Meeting, May 13–17, 2016, Montreal, Canada

Liquid treatments are used for two main purposes, for the introduction of an element, (introduction of water for the purpose of humidification, or introduction of a chemical for de-acidification treatment) or for the extraction of an element, (acidic degradation products in the paper, yellowing, grime and dirt). A gel can be used as a poultice to achieve both of these objectives.

A poultice can be effective for many reasons when conducting treatments involving liquids. By containing the solvent, we can have a better control over the area treated. We can also have better control over the penetration and diffusion of the solvent into the material, by slowing its absorption. Finally, a poultice can limit the evaporation of the solvent. In doing so, a smaller amount of solvent can be used allowing a longer contact time between the solvent and the object/material. When used with a more toxic solvent, a poultice can lower the risks to a conservator's health.

The use of gel as a poultice material for conservation treatment was popularized in the 1980's. Initial characteristics are transparency, stability and versatility. Using a gel should make conservation treatment simpler and safer both for the artifact and conservator.

Some of the most common gels currently used in conservation are the cellulose ethers (Klucel©, methylcellulose), Carbopol©, Laponite©, and different polysaccharides like agar-agar and gellan gum. The final selection of a single material and the proportions used, are made based on the specific requirements for each treatment, the solvent used and the desired texture.

CHOOSING A GEL

For paper conservation treatment, some gel characteristics are more crucial than others. First of all, the solvent retention ability is very important, considering the high absorptivity of the paper surface. For a poultice to be effective, the affinity of the poultice material with the solvent must be greater than with the surface treated, to control the diffusion of the solvent inside the material.

Secondly, when using a gel, there is the possibility of leaving a residue, which may be limited by an additional rinsing step or by the use of an interleaving layer. These residues can be harmful for the artifact in the medium or long term. A poultice that limits the risk of residue is an appreciable advantage.

For the treatment of paper, we should add a high retention capacity and the absence of residues after treatment to the list of desired gel characteristics. These criteria are the basis for the evaluation of gels used in this paper.

The two gels chosen, gellan gum and Nanorestore Gel©, have both a very high retention ability. They also have a rigid form and a strong internal cohesion which allow their use on paper without leaving residues. These two gels, even though they appear similar, have very different compositions and characteristics. Gellan gum is a physical gel, acting as a thickener for the liquid it is added to. Nanorestore Gel©, on the other hand, is an artificial chemical gel, which acts as a sponge to contain a liquid solvent within its structure.

As previously mentioned, gellan gum is a polysaccharide, which forms a physical gel. In low concentration, it forms a rigid gel that can be cut and handled easily. The retention capacity is higher than other physicals gels. By controlling the proportion of the different components, we can easily modify this aspect. Gellan gum is compatible with aqueous solvents and is capable of being prepared using a small amount of alcohol. It can be used for humidification, removal of adhesives, the washing of paper and for some deacidification or bleaching treatments.

Nanorestore Gel© is a chemical gel, meaning that the chemical bonds between the macromolecules are strong, giving the gel a very high internal cohesion. The gel is very flexible and resistant to tears, to a certain extent. Three formulations of the gel are available, with variable retention abilities, all of which are higher than the gellan gum. The chemical gel performs like a sponge and can retain aqueous solvents, including micro-emulsions and micellar solutions of the Nanorestore© product line, but also can be used with pure organic polar solvents, such as ethanol. The very high retention ability allows for use of the gel in local treatment while limiting the risk of creating a tide-line.

GELLAN GUM

Gellan gum has become increasingly more popular since 2010, following various publications and workshops about the material. The recipe and treatment protocols used are those proposed by conservators S. Iannuccelli and S. Sotgiu in the article *Wet Treatment of Works of Art on Paper with Rigid Gellan Gels*[1]. With little adaptation, these protocols have proven to be quite effective.

Gellan gum is purchased in a powder form and is prepared in a water or water solution, in concentrations ranging from 2% to 5% weight / volume. The mixture is heated in a microwave until achieving complete dissolution of the gellan gum, which is then poured into a container with a flat bottom. When the temperature has decreased and the gel has set, it can be cut to the desired form and manipulated easily.

To wash paper using gellan gum, the smooth side of the gel is applied to the surface of the paper. An interleaving layer of Japanese tissue can be used to facilitate the manipulation of a fragile paper or an item with sensitive media. The paper object and the gel are placed between two sheets of clear polyester, with Plexiglas and a light weight on top to ensure an even contact between the paper and the gel. The transparency of the gel allows the conservator to visually assess the document during the treatment.

In a first stage, the paper will absorb water from the gel. Then, an exchange process will occur, and the solubilized products from the paper will be absorbed by the gel. This process is observable by the yellowing of the gel during treatment. The treatment can last from 20 to 60 minutes, and the treatment can be repeated with a clean gel, until there is no longer a yellow coloration present in the gel.

Gellan gum is also a useful tool for the removal of a lining. The gel poultice ensures a slow and controlled humidification, with the artifact placed face-up on the gel. When the adhesive has softened enough, the recto of the artifact can be placed face down against the gel, which will act as a water reserve during the gradual backing removal process, so the object won't dry out as quickly.

In the aforementioned article, the authors compared the amount of water released by two physical gels, gellan gum and agar. When analyzed, the percentage increase in the weight of the paper samples treated with Gellan gum, was much greater than those treated with Agar, indicating a greater retention ability in Gellan gum, though even after 18 hours of treatment with either of the two gels, the samples showed a much smaller weight increase when compared to samples treated by immersion.

NANORESTORE GEL©

Nanorestore Gel© has been developed by the members of the Nanoforart project, which is a collaboration of specialists from various disciplines and countries. The main objective of the project was the development of nano-materials for the conservation of cultural heritage including nano-structured cleaning fluids. The chemical gel has been developed as a carrier for those products. The resulting publication describes the different products and their use in various areas of conservation[2]. The cleaning liquids and gel are now available commercially from the company, CSGI, located in Italy.

Nanorestore Gel© is available in a pre-made sheet, with an approximate size of 7 x 10 cm or 10 x 15 cm. The gel is conditioned in a sealed bag with purified water and is ready

to use. The water content in the pre-made gel can also be replaced by another liquid, such as the cleaning products from Nanorestore©, or by a polar solvent, by immersing the gel for a period of 12 hours. An exchange process occurs between the liquid contents in the gel and the liquid in which the gel is immersed.

Before application of the gel to an object, the two faces of the gel are placed on an absorbent paper to remove the excess solvent. The gel is also visually assessed to make sure there aren't any tears or defects visible such as small tears or air bubbles on the surface of the gel, which may contain additional solvent which could result in an uncontrolled spreading of the solvent during the treatment. Any damaged gel should be discarded.

Once the gel is placed on the surface of the paper, the first stage of the treatment is the humidification of the surface in contact with the gel, followed by an exchange process of the solvent. The solubilized products are then absorbed by the gel. The application can last from a couple of minutes to 30 minutes, and many successive applications can be made.

In another study by Bonelli and Baglioni[3], the three Nanorestore Gel© formulations were compared to Agar and Gellan gum in an examination of the amount of water released by the gels. The results showed that the three chemical gels released approximately half the amount of water compared to Gellan gum.

Nanorestore Gel© was used for the removal of aged adhesive residues from a document at the Bibliothèque et Archives nationales du Québec (BAnQ). The document treated was in 4 four pieces and had previously been repaired with pressure sensitive tapes. The aged rubber based tape had lost its adhesive properties, so the carrier had fallen off and the adhesive components had migrated into the paper, resulting in a strong brown discolouration and a loss in opacity of the paper. Residues on the surface were dry and shiny in appearance. In addition to being visually distracting, the deterioration of the adhesive had made the writing on the document more difficult to read.

The residues on the surface of the paper were first removed mechanically using a scalpel. To reduce the stain in the paper, many options were available, though the sensitivity of the ink and the presence of a wax seal reduced the treatment options. As a result, a localized treatment was required.

Nanorestore Gel© in ethanol proved capable of removing a significant amount of adhesive staining from this document. In this instance, the gel allowed the document to be treated locally, without leaving a residue on the paper or the creation of a tide-line.

After several tests, the more absorbent gel was selected(the Max dry© formulation). The initial duration of the application began at four minutes and was slowly increased to twenty minutes, until no further visible change was observable in the document or in the gel. The first few applications of the gel

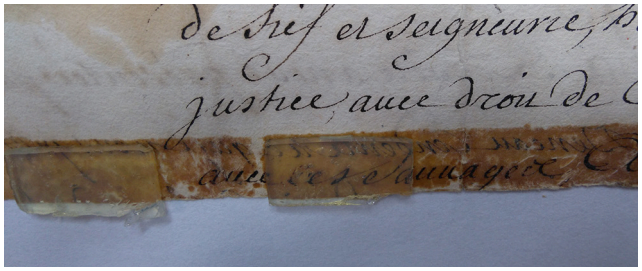

Fig. 1. Pressure sensitive adhesive stain before treatment.

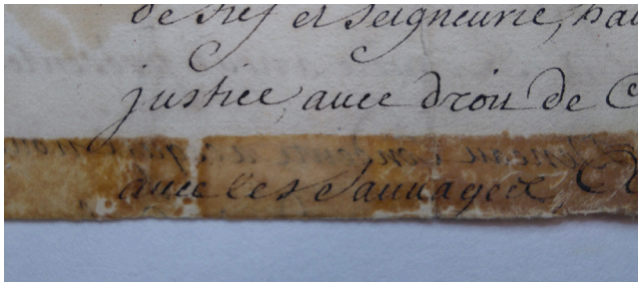

Fig. 2. Pressure sensitive adhesive stain after application of the gel.

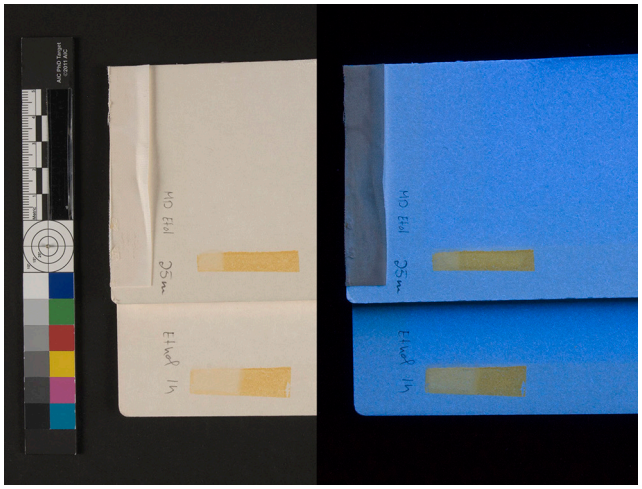

Fig. 3. Adhesive stain on mat-board sample treated with Nanorestore Gel@ in ethanol for 25 minutes and 60 minutes respectively, under natural light and UV light.

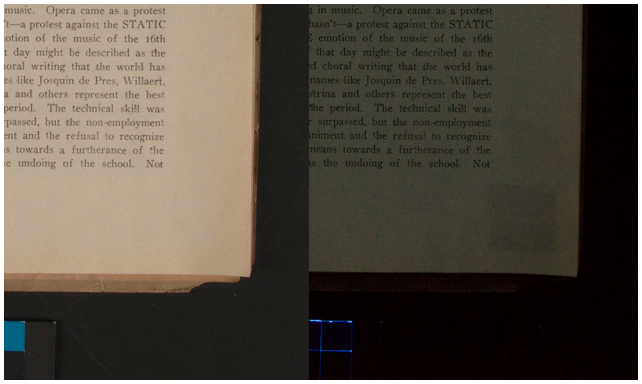

Fig. 4. No tide-line is visible under natural light or UV light after the application of Nanorestore Gel© on a 20th century paper.

Table 1. Comparison of Gellan gum and Nanorestore Gel©

Gel	Solvent compatibility	Retention	Utilization	Accessibility	Reusable	Cost price
Gellan gum	Water	High	Small to large surface	Good	No	Medium
Nanorestore Gel©	Water, polar organic solvents	Very high to excellent	Small surface, local treatment	Difficult	Yes (same solvent)	High

Table 1. Comparison table of the main characteristics of Gellan gum and Nanorestore Gel©.

were made on the recto, followed by applications alternating between the recto and the verso of the document. Between each application, the gel was re-immersed in clean solvent for 12 hours. The gel has the ability to be re-used many times, but with a decrease in absorption capacity. We can see in figure 1 and figure 2 which show the adhesive stains before and after treatment, that the discoloration of the stain is reduced and the opacity of the paper is increased, allowing the document to be read more easily and improved in its general appearance.

The very high absorption ability of the Nanorestore Gel© allows the local treatment of paper without the creation of a tide-line. The sample in figure 3 is a thick mat-board with pressure-sensitive adhesive tape residues. A square of the Nanorestore Gel© in ethanol, has been applied on the surface for 25 minutes and 1 hour respectively. Under natural light and UV light, we can see that the visual impact of the adhesive residues has been reduced. The solubilized products have not spread in the matboard and no tide line is visible.

Nanorestore Gel© also works with water. A square of Nanorestore Gel© loaded with water, was placed onto a 20th century paper for a few minutes, as illustrated in figure 4. While very little change was detected in normal light, the square piece of gel had removed some soluble components from the paper without creating a tide-line. Under UV light, the shape and placement of the gel is easily visible.

ANALYSIS

Table 1 compares some of the principal characteristics of the two gels. First, the Nanorestore Gel© is compatible with aqueous and polar organic solvents, allowing its use on some hydrophobic products. The exceptional retention ability of this gel allows it to be used for localized treatments and reduces the risk of creating a tide-line.

Gellan gum is however, more suitable for the treatment of medium to large surfaces, since the size and shape of the sheet can be produced to specification by the conservator, Nanorestore Gel© is only sold in limited sized sheets. The accessibility of the Nanorestore Gel© is still limited, and current research indicates that it's only available from the producer CSGI, based in Italy. Considering the cost of the gel and the shipping fees, it's a much more expensive option than Gellan Gum.

CONCLUSION

Gels are precious tools for conservation treatments, and are the subject of many current research projects and papers, as demonstrated by an upcoming conference on Gels in Conservation, to be held at the Tate in London in 2017.

We are continuously learning more and more about the properties and advantages of Gellan gum for the conservation of paper artifacts. With a more in-depth comprehension of the gel, methodologies are refined to be more stable and efficient. Nanorestore Gel©, on the other hand, is a new product on the market that still has to demonstrate its potential. Though this gel has been developed specifically for the cleaning of painted surfaces, the results obtained from the treatment of paper samples show a possibility of it being used as a complement to gellan gum treatments.

While compatible with polar solvents, the use of apolar solvents, such as xylene and acetone, is not recommended with the Nanorestore Gel©. Looking toward the future, we hope for the development of a similar gel that will be compatible with a wider range of polar and apolar organic solvents, allowing it to work more efficiently, for example, with aged adhesive stains on paper.

NOTES

1. Iannuccelli, S., and S. Sotgiu. 2010. Wet Treatment of Works of Art on Paper with Rigid Gellan Gels. *The Book and Paper Group Annual* 29 : 25-39.

2.Baglioni, P., D. Chelazzi and R. Giorgi. 2015. *Nanotechnologies in the Conservation of Cultural Heritage*. Dordrecht, Springer Science.

3. Bonelli, R., and P. Baglioni. 2013. Chemical Semi-Ipn Hydrogels for the Removal of Adhesives from Canvas Paintings. *Applied Physics* A 114(3): 705-710

FURTHER READING

Mazzuca, C., L. Micheli, M. Carbone, F. Basoli, E. Cervelli, S. Iannuccelli, S. Sotgiu and A. Palleschi.(2013). Gellan hydrogel as a powerful tool in paper cleaning process; A detailed study. *Journal of Colloid and Interface Science* 416 (2014): 205-211.

Iannuccelli, S. and S. Sotgiu.(2010). A new methodology for wet conservation treatments of graphic art on paper with a rigid polysaccharide gel of gellan gum. *Graphic Documents Working Group Interim Meeting Icom-CC* 6-8 oct. 2010

Botti, L., A. Corazza, S. Iannucelli, M. Placido, L. Residore, D. Ruggiero, S. Sotgiu, L. Tireni, M. Berzioli, A. Casoli, C. Isca and P. Cremonesi.(2011). Evaluation of cleaning and chemical stabilization of paper treated with a rigid hydrogel of gellan gum by means of chemical and physical analyses. *ICOM-CC 16yh triennial conference, Lisbon.*

Pizzorusso, G., E. Fratini, J. Eiblmeier, R. Giorgi, D. Chelazzi, A. Chevalier and P. Baglioni.(2012). Physicochemical characterization of acrylamide/Bisacrylamide hydrogels and their application for the conservation of Easel Paintings. *Langmuir* 28: 3955-3961.

Domingues, J., N. Bonelli, R. Giorgi, E. Fratini and P. Baglioni.(2013). Innovative method for the cleaning of water-sensitive artifacts: synthesis and application of highly retentive chemical hydrogels. *Internal journal of conservation science* 4: 715-722

Domingues, J. A. L., N. Bonelli, R. Giorgi, E. Fratini, F. Gorel and P. Baglioni.(2013). Innovative hydrogels based on semi-interpenetrating p(HEMA)/PVP networks for the cleaning of water-sensitive cultural heritage artifacts. *Langmuir* 29: 2746-2755.

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