

Thermo-reversible rigid agar hydrogels: their properties and action in cleaning

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Abstract

Various polysaccharide-based materials, insoluble in water at room temperature, can dissolve and produce thermo-reversible hydrogels once subjected to a heating–cooling cycle. Pure water can be gelled, as well as aqueous solutions containing various ‘active agents’: buffers, surfactants, chelators and enzymes. Working concentrations of gelling polysaccharides are generally low: 2–5% by weight. Depending on the conditions of the aqueous solutions, the resulting hydrogels can be used for surface cleaning, or removal of film-forming materials, of artefacts made from different materials, delivering very limited amounts of water and not requiring extensive aqueous clearance. Agar-based thermo-reversible gels can be applied in three different ways: as pre-formed rigid gels, for almost perfectly flat surfaces; in a semi-solid state for objects; and grated to tiny particles for action on fragile surfaces. Various mechanisms contribute to the overall mode of action: water diffusion, capillarity, ion diffusion, osmosis, interfacial action and, potentially, a mild chelating action. The application of rigid hydrogels to various artefacts is discussed and analytical studies are presented. A model attempting to explain the mode of action is also proposed.

Introduction

Due to its high surface tension, water is a liquid characterized by limited wetting ability of surfaces and a high rate of vertical and capillary diffusion. Both features may represent a risk factor when using water or aqueous solutions for surface cleaning of artworks, or for more complex procedures such as the removal of film-forming materials (varnishes and coatings, and retouches and overpaints with a variety of binding media). The general risk can be described as the unwanted contact of water with water-sensitive materials or layers. Some materials may be intrinsically sensitive to water in terms of partial solubility, swelling and biodeterioration – cellulose, gelatine and plaster are probably the most representative examples. In other instances, this sensitivity may either be the result of chemical changes during ageing (mainly oxidative and hydrolytic processes occurring, for example in drying oils and natural terpenoid resins) or caused by the presence of various additives used to modify the properties of binding media such as surfactants, gelling agents and fillers – a critical issue for contemporary water-based paint media (Cooper *et al.* 2014).

One of the strategies generally adopted to overcome these limitations relies on the use of gelling agents: polymers that dissolve in an aqueous solution (e.g. cellulose ethers and xanthan gum) or that both dissolve and swell in water (e.g. polyacrylic acid derivatives) and increase its viscosity due to tight cross-linking of their macromolecules (Wolbers 2000; Cremonesi 2012). Although effective in restricting the diffusion of water, this procedure suffers from a major drawback: free water must be used for a

proper removal of residual gelling material, and in some instances this could nullify the advantage originally achieved by the choice of using a gel.

Thermo-reversible hydrogels based on agarose do not suffer from this limitation: they combine very limited adhesion to a surface and high retention of water, and one of their most interesting features is that even when tested on one of the most porous and adsorbing surfaces (a plaster cast), no residual gelling material was detectable by analysis on the surface (Anzani *et al.* 2008).

The main limitation of agar gels is their surface morphology: being rigid, the pre-formed gels can only make contact, and consequently act upon, a surface almost completely flat and planar. However, in many instances this limit can be circumvented by applying the gel not as a pre-formed solid pad, but in another form: a semi-solid, still fluid state, ready to turn solid as soon as it is applied onto the surface. In the last decade agar hydrogels have been used extensively for the treatment of artworks of varying nature: paper, textiles, wooden supports, mobile and mural paintings, plaster and stone sculptures as well as metals (Campani *et al.* 2007; Cremonesi 2008, 2013).

The structure, properties and the gelling mechanism of agar have been extensively described elsewhere (Armisen and Galatas 2000). Here it suffices to recall the fact that agar is composed of two polymers: agarose, the non-ionic gelling fraction homopolymer of galactose, and agarpectin, the non-gelling, acidic, structurally more complex fraction, containing sulphate and pyruvate ionizable functional groups.

Preparation and application of agar gels

Agar (2–4 g) is dispersed in 100 ml demineralized water, and the mixture is heated to boiling in a microwave oven, stirring occasionally, and taking care to prevent water from boiling out of the container. Boiling is continued, generally from 30 seconds to 1 minute, until solid particles are no longer detected on the walls of the container. The hot solution is then allowed to cool, and at this stage, depending on the chosen application, two different procedures can be followed:

- pour the solution into a flat container to the desired thickness, and allow to cool to room temperature;
- cool the solution until a semi-solid paste is yielded and then quickly brush onto the surface of the object to be treated.

Most common types of agar have a gelling temperature around 39–40 °C. When treating sensitive surfaces according to the second procedure listed above, a type of agar with a lower gelling temperature of 29–30 °C ([agar type E, Sigma-Aldrich](#)) should be used: the gel in its semi-solid state can then be applied at moderate temperatures of 35–40 °C, which is safe for many traditional paints. When treating highly porous materials (such as plaster) or capillary materials (e.g. paper and textiles) it is best to prepare the gel by two heating–cooling cycles to produce the optimum retention of water in the gel.

If an aqueous solution, rather than pure water, is gelled with agar, all components of the solution must be stable to temperatures of 100 °C, although for only a short time otherwise enzymes and other protein-based materials, for example, would be irreversibly denatured. A different protocol must then be adopted: 75% of the required amount of water is used to prepare the agar gel, while the remaining 25% of water is used to dissolve the sensitive material at an appropriate temperature, around 45–50 °C. Once the agar solution has cooled to 40–50 °C the two solutions can safely be mixed together. A further application has been developed which is particularly effective for treating fragile, sensitive surfaces that require mild aqueous cleaning: a pre-formed rigid gel can be grated into tiny particles, which are then worked onto the surface with a soft brush (Cremonesi 2016).

Besides the actual components of the aqueous solution gelled with agar, different factors will affect the application time: the nature of the material to be removed (i.e. soil or a film-forming material); its thickness; the porosity/capillarity of the surface and the agar concentration. A 2% w/v gel will allow more water to diffuse into the surface, whereas in a 4% w/v gel, the pores are much smaller (i.e. the right size to promote gel capillarity) so water will tend to move into the gel. Fig. 1 compares the amount of water released from agar gels of different concentrations.

{Insert Fig. 1 here }

Once the desired action is obtained, the gel is carefully lifted from the surface to avoid leaving behind residual material. The clearance process then depends on the type of action that agar has produced, which will in turn depend on the treatment:

- when removing soiling material, the particles become attached to the gel membrane and generally no other action is required: the surface simply has to dry, untouched;
- when the gel has transferred the right amount of water to swell a film-forming material, such as gelatine, requiring removal, the swollen material is collected with a dry cotton swab, thus completing the process;
- when material has migrated into the gel (tannins, coloured cellulose oxidation products from wood or paper supports), likewise a gentle superficial action with a dry cotton swab may complete the process satisfactorily.

In general, no rinsing is required. However, if there is the possibility of leaving residual components (such as buffers or chelators used in aqueous solutions in the gel), then another rigid gel may be applied, at 4 w/v% agar, made with pure water, to act as a 'rinsing gel'. Such a choice should also be carefully evaluated on fragile surfaces in terms of ion concentration, as will be explained later.

Case study treatment

Agar should be regarded as more than just a gelling material – it can be considered one of the ‘safest’ available ways for delivering water:

- to surfaces that are extremely sensitive to water, for example those with partially soluble binding media, paper and wood supports, water gilding, etc.;
- whenever it is considered appropriate, for whatever reason, to limit the amount of water in a treatment.

Mural paintings provide one of the best examples when the amount of water needs to be limited: agar gels have been tested and proved to be effective in extracting salts from mock-ups of fresco paintings, purposely saturated with salts (chlorides, nitrates and sulphates). Traditionally, this treatment has been achieved by applying poulticing materials loaded with water. Such treatments are effective, but release a large amount of water into the plaster, which maintains the mobility of the salts for a long time. As a consequence, after the initial successful extraction, salts often tend to migrate slowly back into the surface. In comparison, simple visual examination of wall paintings treated with an agar gel has shown that after several months no salts had migrated back to the surfaces.

A particularly useful application of agar gels is for the cleaning treatment of polychrome painted and sculptural elements on wooden ceilings which were traditionally painted with water-based proteinaceous media such as milk, egg and caseinates which can withstand only limited contact with water – and often no mechanical action at all. Through the centuries, damage has resulted mainly from water seeping through damaged roofs and mobilizing soiling material, tannins and glues. Frequently, whole rooms, including the decorated ceiling, have been painted over with various paints or lime (as a preventive health measure). Recovering the original polychromy is always a complex task – in many instances, safe intervention can only be carried out by mechanically removing the overpaints with a scalpel. Agar gels can provide effective alternatives to this time-consuming and sometimes risky approach.

{Insert Fig. 2 here}

An example of a useful application is shown in Fig. 2: an agar gel applied in the semi-solid state to a wooden stretcher. After a few minutes’ application the gel is lifted, and the soiling material is easily picked up from the surface with dry cotton swabs. No additional amount of water is required for completing the cleaning procedure.

With regard to the treatment of paper, the authors in collaboration with ICRCPAL (Istituto Centrale per il Restauro e la Conservazione del Patrimonio Archivistico e Librario) in Rome, Italy, focused first on agar and then considered other similar gelling materials in comparison. One type of gellan gum, Kelcogel CG-LA, was finally selected as the best-performing material for paper due to its transparency, flexibility and

chemical compatibilities (Berzioli *et al.* 2011). Fig. 3 compares the optical properties of agar with two types of gellan: Phytigel and Kelcogel CG-LA.

{Insert Fig. 3 here}

Analytical studies

The authors first became involved in the study of agar in 2004, when the Italian conservation community was introduced to the use of rigid agar gels by Richard Wolbers during a workshop in Verona. Analytical studies were then started, mainly aimed at addressing the residues issue. The decision was made to test artworks made of three of the most porous, water-sensitive materials: paper; wall paintings and plaster sculptures. Compared to these, most other artworks exhibit much less sensitivity in terms of water diffusion, water acting as a solvent and persistence of residues.

Plaster fragments from sculptures were treated with a 2.5% w/v agar gel for 3 minutes, 20 minutes and until gel dryness. Once dry, a sample (approx. 1 cm² and 0.5 g) was then taken from each treated area. Each sample was powdered and extracted in boiling distilled water. The resulting solutions were gradually dried out and each residue was analysed with Fourier transform infrared (FTIR) spectroscopy and gas chromatography–mass spectrometry (GC–MS). Galactose, the main monosaccharide constituting the gels, was detected only in trace amounts (Fig. 4), based on the area ratio of the chromatographic peak of galactose to that of the internal standard sorbitol, thus proving that a very limited amount of the gel permeated into the plaster (Anzani *et al.* 2008).

{Insert Fig. 4 here}

When applying agar gels to paper, the use of pre-formed gels is the only advisable procedure – in the semi-fluid state the gel would become too strongly adhered to the surface. In this instance, the main concern, besides the permanence of residual gel material, is an issue that is critical in the washing of cellulose-based textiles: water may wash out coloured, soluble oxidation products of cellulose and polysaccharide fragments that still contribute to the material's cohesion. The same process on paper would result in decreased mechanical strength in the treated paper. Seventeenth-century paper samples were tested for mechanical strength, both untreated and treated with a 2% w/v agar gel. The results indicated that treated paper samples do not appear weaker: on the contrary, there was an average increase in strength and in the strain to failure when compared to untreated paper. Scanning electron microscopy (SEM) observation of the treated paper did not reveal residual material on the surface. This was in contrast to an aqueous gel made from methylhydroxyethylcellulose when used as a comparison (Berzioli *et al.* 2011).

Characterization of residual gelling material was also carried out on mock-ups of fresco paintings, comparing the two main application techniques: 2 and 4% w/v pre-formed rigid and semi-solid gels. To achieve the same cleaning results, pre-formed gels had to

remain in place for up to 40 minutes, whereas a 10-minute application of semi-solid gels was sufficient. Trace amounts of residual galactose were detected only in the samples treated with pre-formed rigid gels; this can be explained as a consequence of the much longer application time (Selva Bonino 2008).

Considerations on the use of agar gels

Working with an agar rigid gel made with pure water will often give the impression that the action is greater than that expected from pure, non-gelled water. At least two different advantages to using the pure water agar gel may be evident: increased action for insoluble iron corrosion products and the ability to produce similar effects to those generally expected from aqueous solutions with an appreciable ion content. We will now examine the first of these experiences. Treating stone surfaces with agar gels at times led to an unexpected result: spots of iron corrosion products could be appreciably thinned down and in a few instances even completely removed. The surprising fact is that these gels were made with pure water alone; such an action would normally be expected only when using aqueous solutions containing chelators such as citrates, polyphosphates, ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA).

No specific reference has been found on the ability of agar to act as a chelator for bi- and tri-valent metal ions. However, on a theoretical level the poly-hydroxylated structure of agarose would be compatible with chelation: it can act as a poly-dentate chelator, mostly a mild chelator considering that the molecules bear no charges, due to its non-ionic structure. 'Agar influences the bio-availability of metals by binding to them' is a statement often encountered when searching through biological sources related to the preparation of culture media based on agar. With phenol groups, which are ionizable in alkaline medium, a stronger chelating action might reasonably be expected. However with non-phenolic hydroxyl groups this milder complexing action, independent of pH, is probably more likely.

Another similarity could be hypothesized with adsorptive resins, gel types and microporous resins made of functionalized polymers and capable of exerting chelating activity on metal ions (Sud 2012; Wheaton and Lefevre 2000). These resins generally have an ionizable structure of the amino-carboxylic acid type such as EDTA, and this is the feature missing in agarose. However, another important parameter in the action of these resins is the porous matrix and its ability to retain ions, a feature that agarose possesses. Lastly, agaropectin (the ionic part of agar), has a structure which could be compatible with a chelate-like action towards Fe^{3+} ions: a cation-exchange reaction, performed by the sulphate and pyruvate acidic functional groups. One of these mechanisms – or more likely a contributing factor from each of them – could explain the experimental findings. Specific studies should be devised to clarify this interesting aspect.

Regarding the second type of action that agar displays when it is loaded with pure water – that of more closely resembling the activity of an aqueous solution with some ionic content – a more straightforward explanation can probably be extrapolated from the experimental findings. Unlike pure agarose, agar is an ionic gelling material. Even when loaded with pure distilled or deionized water, an agar rigid gel will have some ionic content, as recent analysis of current commercial products has revealed.¹ The conductivities measured for agar gels of different concentration are: 440 $\mu\text{S}/\text{cm}$ for a 2% gel, 540 $\mu\text{S}/\text{cm}$ for a 3% and 630 $\mu\text{S}/\text{cm}$ for a 4% w/v. When a rigid gel is in contact with a porous surface, it will allow diffusion of a certain amount of water, depending on its concentration and the time of contact. At this point, the system of the rigid gel and wet porous layers will aim to reach equilibrium between the concentrations of ionic species.

Two different processes can theoretically be considered: ion diffusion and osmosis. Ion diffusion occurs when there is an ion concentration gradient. The intrinsic characteristics of the surface itself (porosity and pore size) determine which ions preferentially migrate across the interface between the gel and the surface. Through the painted surface of a painting on canvas, based on organic binding media, simple, small ‘mineral’ ions rather than ionized macromolecules (e.g. proteins) would be more likely to migrate. Conversely, in an osmotic process, water molecules would migrate against the concentration gradient, trying to dilute the more concentrated side of the system.

However, there is a strict requirement for an osmotic process to occur: in the general description of osmosis, the presence of a semi-permeable membrane separating the solutions, i.e. a membrane allowing only water molecules (and at most, some smaller ions) to move across. In our specific context, this would be an organic film-forming material, separating the ‘true solution’ – the gelled water – from the layers once wet. Without this specific feature, no osmotic processes can be expected, but instead just water and ion diffusion. The lipid bilayer surrounding the cells in living organisms is an example of such a membrane of natural origin.

{Insert Fig. 5 here}

Is it reasonable to hypothesize the existence of anything similar on the surface of a work of art? The authors have devised a simple but effective test in an attempt to answer this crucial question. It originates from a simple operation: sprinkling salt on cut vegetables before grilling. This draws the water out from the vegetables, by osmotic movement, making them crispy once baked. This is how the ‘zucchini test’ was adapted to our area of interest (Fig. 5a). A small jar is filled with demineralized water to the very top. Next, a disc of filter paper, on which a film-forming material has previously been painted, is placed on top of the jar, making contact with the water underneath. Rock salt is then sprinkled on the surface of the coated paper disc. If after some time droplets of water seep through and surround the salt grains, this movement can be taken as an indication of the ‘painted paper’ acting as a semi-permeable membrane. A control paper disc, similarly painted but with no salt applied, did not allow water to penetrate under the

same experimental conditions. The polymer that was painted on (in this case, gelatine) therefore has some ability to promote osmosis.

The tests show that all water-soluble natural polymers tested (gelatine, albumen, caseinate, polysaccharide gums and cellulose itself) behave like semi-permeable membranes. In contrast, negative results were obtained from linseed oil and natural terpenoid resins. Fig. 5 compares the result obtained from gelatine (Fig. 5a), after 10 minutes with that obtained from dammar in turpentine after as long as 40 minutes: one month after application to the paper (Fig. 5b) and after three years of aging in a domestic environment. A small amount of water only permeated the layer in the last sample. This result can be explained by considering the chemistry of terpenoid natural resins (van der Doelen 1999). When applied as a varnish onto a painted surface they are prevalently low molecular weight molecules. Their rather low polarity imparts a definite hydrophobic character to the coating, generally not likely to promote osmosis. As the resinous material ages, a higher molecular weight fraction is formed through oxidation and crosslinking, which is more polar and more hydrophilic in character. In this way, an aged, oxidized natural resin coating may become somewhat more similar to a polymeric, hydrophilic coating, making it more susceptible to osmotic processes. Likewise a young oil film possesses a definite hydrophobic (water-repelling) character. In addition, being unpigmented, this coating can hardly be representative of a true oil-based paint layer.

From a practical point of view, this latter finding may have important consequences – the presence of a natural resin varnish on a painting on canvas/panel, aged but still fairly even, unbroken and compact – would probably represent a ‘barrier’ to osmotic water movements rather than a semi-permeable membrane. Could this be taken as an indication that there should be less concern with the ion concentration in the cleaning solution when treating a painting coated with a natural resin varnish with aqueous media? Another critical factor should also be considered when evaluating the likelihood of osmosis: the length of the contact time of water with the surface which is required to produce osmotic movements. Does the actual ‘cleaning time’ match this length? Furthermore, the same could be said about the more recently introduced ‘low-molecular weight resins’ of synthetic origin, namely aliphatic hydrocarbon and urea-aldehyde resins, which are capable of mimicking in many ways the behaviour of the natural terpenoid resins. These remain open questions until further investigation is carried out.

If the surface of the artwork to be cleaned with an aqueous medium is capable of promoting osmosis, then the ion concentration of the aqueous solution itself becomes an important parameter. More specifically, a concentration imbalance between the ion concentration of the cleaning solution and the ion concentration that water will encounter once applied to the artwork may promote the movement of water. If the osmotic pressure associated with these movements is too high, it could be damaging to the surface. Both sides of the imbalance are potentially damaging (Fig. 6), for example:

- if the ion concentration of the cleaning solution is lower than that of the artwork (hypotonic conditions) – as occurs in general when using demineralized water – water may diffuse into the layers;
- conversely, if the solution has higher concentration than the layers (hypertonic conditions), water that initially wet the layers by diffusion or capillarity will tend to migrate out. In itself, this is a positive effect as it means shorter permanence of water inside the layers. However, if this outbound movement is too intense, the associated pressure could open cracks on the surface.

{Insert Fig. 6 here}

Ideally, isotonic conditions, namely a similar ion concentration both in the cleaning solution and in the wet layers, would be the most appropriate, allowing free and stress-free water movements in and out of the layers. An even wiser choice would be a ‘slightly hypertonic’ condition to ensure that water moves out and the layers dry faster.

Based on these considerations we can now return to the discussion on how rigid agar gels behave on different surfaces. First, by severely restricting water diffusion into the surface, these gels may ‘mitigate’ the potential effects of water, including osmosis: the higher the agar concentration, the more restricted the diffusion. As was shown in Fig. 1, the contact time of the gel with the surface will also affect this.

The second most important factor is the ion concentration of the aqueous phase of the gel, bearing in mind that agar itself contributes to the overall ion content. When a rigid agar gel is applied to an inorganic/mineral surface, such as a plaster sculpture, it may be reasonable to rule out the likelihood of osmotic diffusion of water: the porosity is much too high and, more importantly, there is no film-forming material capable of acting as a semi-permeable membrane. There is also a balance between the capillary forces of the plaster and those of the agar pores. The practical response appears to confirm this mechanism: an outbound flow or force seems to detach the soiling material from the surface and move it towards the gel. As a practical example, the conductivity measured on a plaster fragment (wetting and inserting into it the metal electrodes of a conductivity meter) was *c.* 0 $\mu\text{S}/\text{cm}$, and that of a 2% w/v rigid agar gel about 450 $\mu\text{S}/\text{cm}$; the gel would then be hypertonic versus the plaster fragment (Stavroutis and Doherty 2013), and the movement of water driven by osmosis out of the fragment could promote the surface cleaning action. Naturally, this takes for granted the presence of a proper semi-permeable membrane.

{Insert Fig. 7 here}

The simple test described above could provide an explanation of this controversial issue: when a rigid agar gel was tested under the same conditions, water was found to seep out of the gel and wet the salt grains within less than 10 minutes (Fig. 7). Agar itself (i.e. the gel matrix) is acting as a semi-permeable membrane.

In view of these findings the overall picture changes quite significantly: any time water or an aqueous solution is delivered in the form of a rigid agar gel to a surface for cleaning or different purposes, osmotic processes should be expected, independently of the material type of the artwork whether varnished or unvarnished paintings, paper, textiles, wooden, gypsum or stone objects. A critical factor in formulating the cleaning solution will then be its ion concentration. After measuring the conductivity of the surface to be treated in the most accurate way, the conductivity of the cleaning solution should be adjusted according to the measured surface value. In general, hypotonic conditions are considered the most dangerous and should always be avoided: they drive water into the layers and may cause swelling and potential disruption. Isotonic, or better still, moderately hypertonic conditions, are safer under most circumstances. The conductivity of the solution can be lowered as necessary by diluting with water or raised by adding neutral salts such as sodium or potassium chloride.²

Conclusion

It is interesting that some of the most innovative cleaning treatments have been made possible by agar, one of the oldest known gelling materials, used for centuries at least by eastern civilizations (Armisen and Galatas 1987). From the start agar looked to be an interesting material for producing aqueous gels suitable for cleaning treatments of various works of art and its effectiveness became immediately obvious. Furthermore, 'structural' interventions, and not just true cleaning procedures, could be carried out with safety margins unattainable with other techniques: for example, removal of residual animal glues from water-sensitive surfaces. It only remains to characterize the residue issue which a number of analytical studies have started to address.

Thanks to the positive results obtained, the use of agar gels on a variety of works of art can be regarded as 'safe', and it has become a standard strategy for applying an aqueous medium to highly sensitive surfaces. The authors remain firmly convinced that, at least on works of art based on organic materials, agar should be used as a gelling material for aqueous media only, in preference to recent recommendations that propose the combination of water and polar organic solvents miscible with water, such as acetone and ethanol. Polar solvents by themselves possess a broad spectrum of actions on fresh and aged film-forming materials; if the ionization/dissociating ability typical of water is also added, effectiveness definitely increases but at the expense of selectivity.

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Materials and supplier

- 05040 agar, gelling temperature 39 °C; A4675 agar type E, gelling temperature 26–28 °C: Sigma-Aldrich Co, St. Louis MO, <http://www.sigmaaldrich.com>

Notes

1. Moira Bertasa, Oscar Chiantore, Tommaso Poli, Chiara Riedo, Valeria di Tullio, Carmen Canevali, Antonio Sansonetti and Dominique Scalarone, ‘A study of commercial agar gels as cleaning materials’, in this volume.
2. A final remark on agar gels: the ionic character of agar may modify the parameters of the aqueous solutions that are being turned into rigid gels. Table 1 compares the conductivities of agar gels prepared from pure water and various aqueous solutions. For the measurements of pH and conductivity, small discs (respectively 10 and 3 mm in diameter) cut with plastic cylinders from the cast rigid gels were placed in contact with the flat electrode of a Hanna Instruments Skincheck pH meter and the measuring cell of a Horiba LAQUAtwin B771 conductivity meter. In general, buffers seem able to maintain the original pH of the solutions, even in the moderate concentration used (25 mM). DTPA buffered to pH 8 is the most striking exception: the pH of the gel is considerably lower than that of the parent solution. No satisfactory explanation can yet be offered. For conductivity it is also difficult to explain the unexpected finding that the conductivity of the agar gels is lower than that of the parent-free solutions. It may be linked with the restricted mobility of some ions inside the gel matrix or it may simply reflect the experimental difference between the two measurements: one in solution, the other on the rigid gel surface. It is rather difficult to make predictions: it is safer always to re-measure the pH once the rigid gel has been prepared.

References

- Anzani, M., Berzioli, M., Cagna, M., Campani, E., Casoli, A., Cremonesi, P., Fratelli, M., Rabbolini, A. and Raggiardi, D. 2008. ‘Gel rigidi di agar per il trattamento di pulitura di manufatti in gesso’, *Quaderni CESMAR* 7 6. Padua: Il Prato.
- Armisen, R. and Galatas, F. 1987. ‘Chapter 1. Production, properties and uses of agar’, in D.J. McHugh (ed.), *Production and Utilization of Products from Commercial Seaweeds*, Rome: Food and Agriculture Organization of the United Nations. Available at: <http://www.fao.org/docrep/x5822e/x5822e03.htm> (accessed 20 March 2017).
- Armisen, R. and Galatas, F. 2000. ‘Agar’, in G.O. Phillips and P.A. Williams (eds), *Handbook of Hydrocolloids*. Boca Raton, FL: CRC Press, 22–40.
- Berzioli, M., Botti, L., Casoli, A., Corazza, A., Cremonesi, P., Iannuccelli, S., Isca, C., Placido, M., Residori, L., Ruggiero, D., Sotgiu, S. and Tireni, L. 2011. ‘Evaluation of cleaning and chemical stabilization of paper treated with a rigid hydrogel of gellan gum

by means of chemical and physical analyses’, in J. Bridgland (ed.), *Preprints of the ICOM-CC 16th Triennial Congress*. Paris: ICOM, paper 0602. [CD only]

Campani, E., Casoli, A., Cremonesi, P., Saccani, I. and Signorini, E. 2007. ‘L’uso di agarosio e agar per la preparazione di “Gel Rigidi”’, in D. Kunzelman (tr.), *Quaderni CESMAR7*, 4. Padua: Il Prato.

Cooper, A., Burnstock, A., van den Berg, K. H. and Ormsby, B. 2014. ‘Water sensitive oil paints in the 20th century: a study of the distribution of water-soluble degradation products in Winsor & Newton Artists’ oil colour paint swatches, with case studies from Tate’s collection’, in A. Burnstock, M. de Keijzer, J. Krueger, T. Learner, A. de Tagle and G. Heydenreich (eds), *Issues in Contemporary Oil Paint*. Cham: Springer, 295–310.

Cremonesi, P. 2008. ‘Applicazione di metodologie di intervento più recenti per la pulitura del materiale cartaceo’, in M. Fratelli and E. Signorini (eds), *Problemi conservativi dei manufatti dell’Ottocento. I dipinti, la carta, i gessi*. Padua: Il Prato, 41–8.

Cremonesi, P. 2012. *L’ambiente acquoso per il trattamento di opere policrome*, I Talenti – Metodologie, tecniche e formazione nel mondo del restauro 20. Padua: Il Prato.

Cremonesi, P. 2013. ‘Rigid gels and enzyme cleaning’, in M.F. Mecklenburg, A.E. Charola and R.J. Koestler (eds), *Cleaning 2010: New Insights into the Cleaning of Paintings*. Washington, DC: Smithsonian Institution Scholarly Press, 179–84.

Cremonesi, P. 2016. ‘Surface cleaning? Yes, freshly grated agar gel, please’, *Studies in Conservation* 61(6): 362–7.

Sansonetti, A., Casati, M., Striova, J., Carnevali, C., Anzani, M. and Rabbolini, A. 2012. ‘A cleaning method based on the use of agar gels: new tests and perspectives’, paper present at the *12th International Congress on the Deterioration and Conservation of Stone*. New York: Columbia University.

Selva Bonino, V.E. 2008. *Studio preliminare di gel rigidi a base di agarosio per il trattamento conservativo di pitture murali*, unpublished Master’s dissertation, Department of Chemistry, Università degli Studi di Parma.

Stavroudis, C. and Doherty, T. 2013. ‘The modular cleaning program in practice: application to acrylic paintings’, in M.F. Mecklenburg, A.E. Charola and R.J. Koestler (eds), *Cleaning 2010: New Insights into the Cleaning of Paintings*. Washington, DC: Smithsonian Institution Scholarly Press, 139–45.

Sud, D. 2012. 'Chelating ion exchangers: theory and applications', in A.A.K. Inamuddin and M. Luqman (eds), *Ion Exchange Technology I: Theory and Materials*. New York: Springer Science and Business Media, 372–402.

van der Doelen, G.A. 1999. *Molecular Studies of Fresh and Aged Triterpenoid Varnishes*. Amsterdam: FOM-MOLART.

Wheaton, R.M. and Lefevre, L.J. 2000. *Dowex Ion Exchange Resins: Fundamentals of Ion Exchange*, Midland, MI: The Dow Chemical Company. Available at: http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0032/0901b803800326ca.pdf (accessed 21 March 2017).

Wolbers, R. 2000. *Cleaning Painted Surfaces: Aqueous Methods*. London: Archetype Publications.

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