

## New Frontiers in Materials Science for Art Conservation: Responsive Gels and Beyond

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### CONSPECTUS

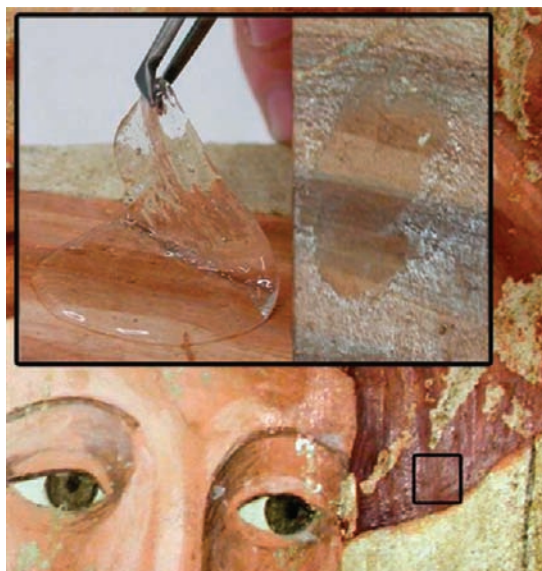
The works of art and artifacts that constitute our cultural heritage are subject to deterioration, both from internal and from external factors. Surfaces that interact with the environment are the most prone to aging and decay; accordingly, soiling is a prime factor in the degradation of surfaces and the attendant disfigurement of a piece. Coatings that were originally intended to protect or contribute aesthetically to an artwork should be removed if they begin to have a destructive impact on its appearance or surface chemistry.

Since the mid-19th century, organic solvents have been the method of choice for cleaning painted surfaces and removing degraded coatings. Care must be taken to choose a solvent mixture that minimizes swelling of or leaching from the original paint films, which would damage and compromise the physical integrity of all the layers of paint. The use of gels and poultices, first advocated in the 1980s, helps by localizing the solvent and, in some cases, by reducing solvent permeation into underlying paint layers. Unfortunately, it is not always easy to remove gels and their residues from a paint surface.

In this Account, we address the removal problem by examining the properties of three classes of innovative gels for use on artwork—rheoreversible gels, magnetic gels, and “peelable” gels. Their rheological properties and efficacies for treating the surfaces of works have been studied, demonstrating uniquely useful characteristics in each class:

- (1) Rheoreversible gels become free-flowing on application of a chemical or thermal “switch”. For art conservation, a chemical trigger is preferred. Stable gels formed by bubbling CO<sub>2</sub> through solutions of polyallylamine or polyethylenimines (thereby producing ammonium carbamates, which act as chain cross-links) can be prepared with a wide range of solvent mixtures. After solubilization of varnish and dirt, addition of a weak acid (mineral or organic) displaces the CO<sub>2</sub>, and the resulting free-flowing liquid can be removed gently.
- (2) Incorporation of magnetic, coated-ferrite nanoparticles into polyacrylamide gels adds functionality to a versatile system comprising oil-in-water microemulsions, aqueous micellar solutions, or xerogels that act as sponges. The ferrite particles allow the use of magnets both to place the gels precisely on a surface and to lift them from it after cleaning.
- (3) Novel formulations of poly(vinyl alcohol)—borate gels, which accept a range of organic cosolvents, show promise for swelling and dissolving organic coatings. This family of gels can be quite stiff but can be spread. They are non-sticky and have sufficient strength to be removed by peeling or lifting them from a sensitive surface.

These three classes of gels are potentially very important soft materials to augment and improve the range of options available for conserving cultural heritage, and their interesting chemical—physical properties open a rich area for future scientific investigation.



## 1. Introduction

Pictorial surfaces can be viewed as solid/gas interfaces where the solid phase is intrinsically microheterogeneous along the surface and in the dimension orthogonal to it. Both easel and mural paintings consist of a macroscopic support onto which a thin layer of a paint material has been applied. This pictorial layer, with or without a varnish coating, is the preferential site of degradation because it is where the artwork exchanges matter and energy with the surrounding environment (i.e., the atmosphere).<sup>1</sup> This Account highlights some new approaches to cleaning easel paintings using gels.

**1.1. A Scientific Approach to Cleaning Artwork.** A varnish coating can even the appearance of a paint surface, provide saturation of color, add gloss over a picture surface, or increase contrast in matte and glossy areas. Coatings also provide barriers to dirt and (if formulated appropriately) ultraviolet radiation; protective varnishes may be considered sacrificial. Varnishes are water-based (such as egg white,<sup>2</sup> gum, or glue) or solvent-based (such as “spirit varnishes” from tree resins or oil–resin mixtures<sup>3</sup> or synthetic organic polymers<sup>4</sup>). They deteriorate as a result of cross-linking and chain scissions, becoming brittle, yellow, and (sometimes) increasingly insoluble at rates that depend on their chemical compositions and ambient conditions.<sup>5</sup> Thus, paint surfaces can become disfigured by deteriorated coatings and other deposits such as old consolidants and overpaint.

Ideal cleaning agents selectively remove deposits, additions, and deteriorated varnish without affecting underlying paint layers and are removed completely. In practice, ideal cleaning is unattainable. The approach to ideality depends on the materials to be removed, the layers beneath, and (of course) the cleaning agent: the more similar are the properties of the materials to be removed and those to remain (the paint), the greater the challenge.

Solvent cleaning has limitations: How to remove varnishes without damaging oil-based paint films, which are sometimes compounded with resins to make “meguilps”?<sup>6</sup> Unfortunately, even contemporary materials and methods, cleaning gels, enzyme-based solutions,<sup>7</sup> and laser ablation,<sup>8</sup> present unanswered issues regarding their use.

If materials to be removed are identified, the solvent blend that maximizes selectivity of the cleaning action can be chosen from Teas plots.<sup>9</sup> These diagrams plot the bulk properties of the solvents as a function of the intensity of their intermolecular, noncovalent interactions,<sup>10</sup> hydrogen bonding, dispersion forces, and dipolar interactions. Using this or related tools, the conservator can select what should be an

appropriate solvent system to solubilize the substance(s) to be removed while avoiding swelling or solubilization of the underlying paint layer.<sup>11</sup> Removal of the polymeric substances involves the following steps:

- (1) penetration of solvent orthogonal to the exterior layer (at  $\sim 10 \mu\text{m/s}$  through a polymer network<sup>12</sup>);
- (2) swelling of the polymer layer in contact with the solvent;
- (3) transformation of the polymer layer into a gel-like fluid;
- (4) solubilization or softening of the polymer.

Concurrently, solvent can penetrate the paint layer, swelling it and altering interactions between pigments and their binders (usually an oil or protein-based material).<sup>13</sup> Consequently, the paint layers can be softened, embrittled, or leached and the pigment–medium binding can be disrupted. Additionally, the increase of volume of the paint layer (a manifestation of swelling) and subsequent decrease in volume (after solvent evaporation or leaching) can induce mechanical stresses that lead to long-term damage such as microfractures, alteration of the surface morphology with local whitening effects, and decreased structural stability of the paint layer.<sup>14,15</sup> For these reasons, total control of the cleaning action is extremely difficult.

Michalski modeled swelling in terms of Hansen parameters<sup>16</sup> using a 3D representation that includes a detailed distinction among different solvent properties to identify the one most effective in solubilizing a substance.<sup>12</sup> Leaching of small binder molecules, induced when solvent swells a paint layer, also changes the stiffness of surface materials.<sup>15</sup> Several innovative approaches that combine the properties of solvents and soft matter<sup>17</sup> will be discussed in section 3.

## 2. Gels for Cleaning Works of Art

Cleaning artwork with gels and poultices has increased enormously during the last decades. Aqueous, nonaqueous, and mixed gels have been devised to remove varnish and overpaint from paint surfaces<sup>18</sup> and to remove stains from stone<sup>19</sup> and stains and adhesives from paper.<sup>20</sup> Sequestration of solvents in gel matrices minimizes the deleterious effects of using liquids for cleaning paint surfaces and introduces several advantages:

- (1) Slow release of the active solvent across the gel/coating interface reduces the risk of swelling of the paint layers for a broad range of cleaning-action rates.
- (2) The high viscosity of the gel reduces *bulk* diffusion of solubilized molecules within the gel liquid and, consequently, slows the kinetics of solubilization. Thus, in many cases,

gelled solvents work more slowly and are more easily controlled on a paint surface than neat liquids.

- (3) The varied nature of materials to be removed, especially old varnishes, requires gels with solvents of different polarities. "Solvent gels"<sup>18</sup> and gels with poly(vinyl alcohol)–borax formulations (PVA-B) as the gellant<sup>21</sup> satisfy this exigency.
- (4) The gel-based cleaning technique accommodates different solvents<sup>22</sup> and highly selective cleaning agents such as enzymes,<sup>23</sup> chelating molecules, and microemulsions.<sup>24–26</sup> Because of their diversity, gels have been used to clean frescoes,<sup>27</sup> glasses,<sup>28</sup> metals,<sup>29</sup> and even feathers<sup>30</sup> besides paint layers on wood or canvas.
- (5) The surface area exposed to a gelled solvent corresponds much more closely to the area of application; gelled solvents spread much less than neat liquids.

Solvent gels developed by Wolbers have been the most frequently used to remove varnishes.<sup>18</sup> They employ partially deprotonated (carboxylate/carboxylic acid forms) poly(acrylic acids) (PACAs) as the gellants. Gels with polar solvents or aqueous liquids have been made also with a cellulose derivative<sup>23</sup> or agar agar as the gellant. In the presence of a weak base, usually a nonionic surfactant (Ethomeen C12 or C25), PACA chains adopt extended conformations due to electrostatic repulsion by the negatively charged carboxylate groups. Chain entanglement and other interchain interactions then establish the 3D networks that are necessary to immobilize the liquid components on a macroscopic scale; at the micro and smaller distance scales, the vast majority of liquid molecules diffuse at rates comparable to those in the neat bulk.<sup>31</sup> Solvent gels are applied onto a paint surface directly (or using a spatula or other instrument), sometimes followed by mechanical action with a swab to increase gel–paint surface contact. Transfer of the liquid component at the gel/painted interface is controlled by thermodynamics (the chemical potential of the liquid in the two layers) and kinetics (the ease with which the liquid crosses the interface).

A serious potential problem with the use of these gels as cleaning agents, even though they are often very effective, has been ensuring their complete removal (after the cleaning action) in a manner that does not damage the paint surface.<sup>32</sup> Solvents applied neat may have other problems as noted, but they can be removed with small mechanical force, and residual solvent evaporates with time. The viscoelasticity of gels requires application of some type of force to remove them from a paint surface, and some of their gellant components may stay on the surface or in cracks and fissures after removal of the bulk. Burnstock and Kieslich<sup>33</sup> demon-

strated by GC-MS and SEM analyses that residues of Ethomeen from PACA-based gels were present after a gel was removed mechanically by a swab roll and even after applying clearing solvents.

### 3. Responsive Gels for Cleaning Works of Art

Gels that react or respond to an external stimulus (especially pH, temperature, and magnetic fields discussed here) increase the options available to conservators.

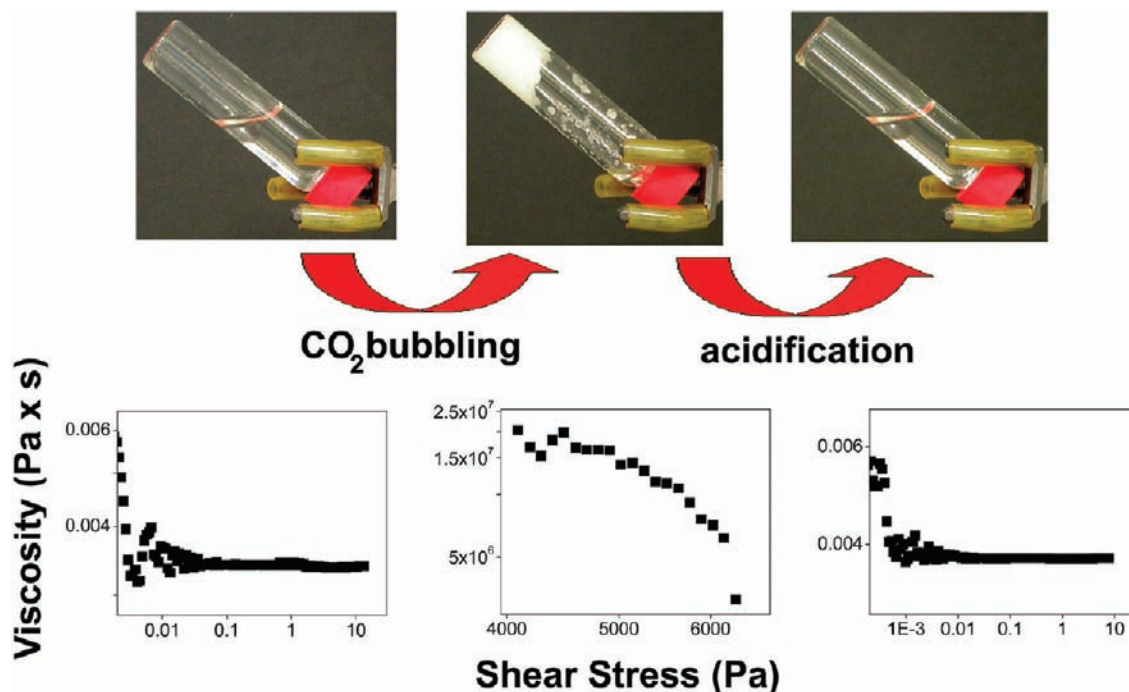
**3.1. Rheoreversible Gels.** Our efforts to clean and remove degraded varnishes from surfaces of artwork using gels began with the development of gels with low molecular-mass organogelators (LMOGs)<sup>31,34–36</sup> that can be transformed reversibly and without heating into free-flowing liquids. Carbon dioxide gas is passed through a solution of a solvent and a low concentration (<5 wt %) of an amine LMOG.<sup>37–41</sup> Gelation occurs spontaneously with the rapid uptake of CO<sub>2</sub> and formation of an ammonium carbamate (eq 1) The gels revert to their free-flowing liquid state when a displacing gas, such as N<sub>2</sub>, is passed through them at ambient or slightly elevated temperature.



In media of relatively low polarity (i.e., low dielectric constant,  $\epsilon$ ), the positive charge on the ammonium groups and negative charge on the carbamate ions ( $q_1$  and  $q_2$ ) prefer to remain very close (i.e., at an average distance  $r_{12}$ ) in order to reduce their total energy,  $q_1q_2/(\epsilon r_{12})$ . When several ion pairs aggregate, the energy can be reduced further according to the Madelung energy<sup>42</sup> if the charged centers of the ion pairs establish an alternating network and the uncharged organic tails organize around them.<sup>43,44</sup> In this way, a self-aggregated fibrillar network (SAFIN) forms and immobilizes the liquid component *macroscopically*.<sup>34</sup> Because the vast majority of the liquid molecules are able to diffuse *microscopically* as they would in the absence of the SAFIN, there is a dynamic interaction between the liquid of a gel and a surface with which it is in contact.

It was anticipated that rheoreversible gels of this type would combine the desirable properties of nonrheoreversible hydrogels<sup>18</sup> and organogels,<sup>45,46</sup> controlled positioning on the upper (varnish or overpaint) surface and slowed diffusion of the liquid into the paint layers, with the advantages of a neat liquid, a wide range of polarities, easy removal from a surface, and low levels of residue remaining after cleaning. Especially for the purposes of minimizing the amount of residue on





**FIGURE 1.** Appearances (top) and dynamic viscosities (bottom) of an aliquot of 4 wt % PAA in 1-pentanol before and after bubbling  $\text{CO}_2$  through it (to make a gel, PAA- $\text{CO}_2$ ) and after adding a few drops of 0.05 M acetic acid. Reproduced with permission from ref 51. Copyright 2004 American Chemical Society.

a surface after removal of the cleaning agent,<sup>32</sup> the LMOG was changed to a commercially available polymer (initially, polyallylamine (PAA)<sup>47,48</sup> and, later, different types of polyethyl-enimines (PEI)).<sup>49</sup> These polymers were selected because (1) they are available in large quantities and undergo the same chemistry shown in eq 1, (2) they are soluble in many of the organic liquids used commonly to clean paint surfaces, (3) they are formed easily, without need for sophisticated chemical manipulations or equipment and can be made easily by conservators in a studio, (4) whereas LMOGs, essentially “zero-dimensional objects” on a micrometer distance scale, must aggregate first into one-dimensional rod-like objects and then cross-link to make a SAFIN, the polymers have one dimension already prepared and need only to cross-link to establish a SAFIN, (5) the rate of diffusion of a polymer into a paint layer is much slower than that of an LMOG,<sup>50</sup> selective cleaning by the solvent component can occur without significant contamination, and (6) the periods of stability of PAA- and PEI-based gels far exceed the contact times employed to clean a paint surface.

Because the method in eq 1 for the rapid return of *bulk* samples of these gels to their free-flowing state is not feasible for a film that is between a few micrometers and a millimeter thick on a paint surface, and an alternative (heating the surface) could cause serious damage to the paint, its back-

ing, or to the “ground layer” between the paint and its backing, a different strategy has been adopted: addition of a small amount of a very dilute solution of aqueous acetic acid to the gel surface opposite the one in contact with the work of art.<sup>47,48</sup> Figure 1 shows the dynamic viscosities and appearances of an aliquot of 4 wt % PAA in 1-pentanol before and after bubbling  $\text{CO}_2$  through it and after adding a few drops of dilute weak acid to destroy the gel,<sup>51</sup> returning it to a free-flowing liquid. Thus, very dilute aqueous acetic acid or solutions of nonanoic acid in toluene or mineral spirits have proven equally effective at returning these gels rapidly to their free-flowing states,<sup>52</sup> and the latter do so without introducing water onto the paint surface. Protonation of the carbamate causes a very rapid loss of  $\text{CO}_2$ , as well as protonation of the newly formed amine; the polymer chains become repulsive instead of attractive (eq 2). Although this procedure does not allow the gels to be reformed as described in eq 1 in the absence of extensive chemical and physical manipulation, it does permit a nearly instantaneous transformation to a free-flowing liquid that can be removed easily using a tissue or cotton swab to absorb the solubilized varnish. In fact, reuse of the gel for the purposes of cleaning surfaces is not advisable because the material removed in a first cleaning could be deposited during a second one. What is required is easy, rapid, and complete removal of the gel on demand!



The cleaning ability of a PAA-CO<sub>2</sub> gel was tested on a 16th century wood painting with a nonoriginal superimposed layer of a naturally aged varnish (Figure 2), and PEI-CO<sub>2</sub> gels were used to clean an easel painting that was lined, varnished, and completely overpainted with brown paint (Figure 3). A gel, prepared by bubbling CO<sub>2</sub> through a solution of 3 wt % PEI (MW 25 000 Da) in 1/1 (v/v) 1-octanol/xylenes, was applied to the painting in Figure 3 while it was lying flat. After <10 min, the overpaint and underlying varnishes were solubilized. By visual analysis, the glossy overpaint and various layers of varnishes, including shellac, were gently and effectively removed. The original, cracked surface was revealed, and stereomicroscopic analysis showed that no skinning or abrasion had occurred at the crack edges. On taking up so much material, the gel lost some of its viscoelasticity. Complete free-flow was attained almost immediately by dripping a few microliters of 2% nonanoic acid in mineral spirits onto the surface. The solubilized paint and varnishes were lifted with a cotton swab, and the surface was cleared using a swab wet with mineral spirits.

**3.2. Magnetic Gels.** Magnetic chemical gels for art conservation have been described recently.<sup>53</sup> They were prepared by embedding ferrite magnetic nanoparticles (coated with a dicarboxylic derivative obtained through the esterification of poly(ethylene glycol) (PEG) with maleic anhydride) in a polyacrylamide matrix (Figure 4). The nanoparticles are attached by chemical means to the PEG through the carboxylate functional groups, while the two double bonds per molecule resulting from the esterification anchor the nanoparticles chemically within the gel matrix. Radical copolymerization of these functionalized nanoparticles with acrylamide and *N,N'*-methylene bisacrylamide produces a nanomagnetic gel where both the physicochemical properties of acrylamide-based gels and the magnetic response of ferrite nanoparticles are retained.<sup>54</sup>

The viscoelastic nature and structure of the magnetic gels (Figure 5, left) are very similar to those of conventional acrylamide gels, with nanoscaled mesh sizes, inhomogeneous domain sizes of a few tens of nanometers, and micrometric pores. The chemically anchored magnetic nanoparticles act as entanglement sites and increase the value of the elastic modulus, *G'*.

These gels behave as “containers” for aqueous droplets; they can be freeze-dried to obtain magnetic xerogels and then rehydrated like “sponges” to ca. 10× their dried weight. Even in their hydrated state, the gels can be cut with a knife to a desired shape and moved with an external magnet. The

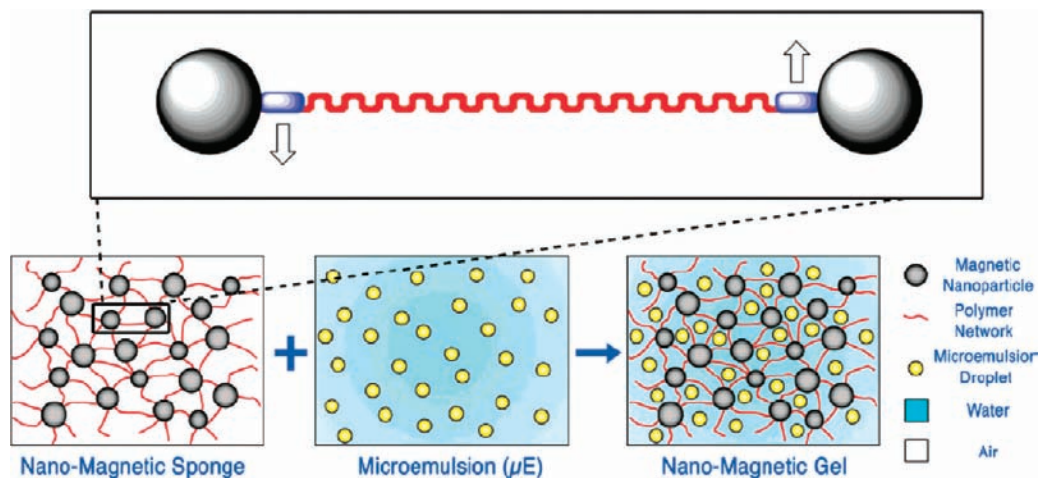


**FIGURE 2.** (A) A 16th century painting from the National Gallery in Siena, Italy. The black square defines the area where the cleaning test was conducted. (B) Grazing light image of the area treated with a 5 wt % PAA-CO<sub>2</sub>/1-pentanol gel. Reproduced with permission from ref 47. Copyright 2004 American Chemical Society.

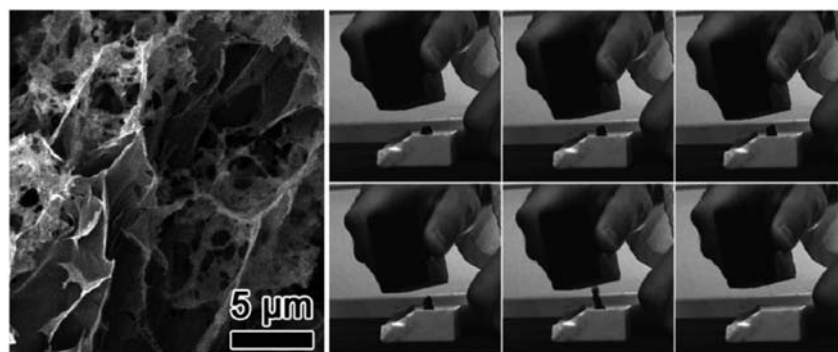


**FIGURE 3.** (A) A painting, likely dating from the late 19th century, used for testing purposes. It has been lined, varnished, overpainted, and revarnished. (B) Detail of the bottom right-hand corner after treatment (see text).

sponges have been loaded with aqueous micellar solutions and more complicated systems, such as oil-in-water micro-



**FIGURE 4.** Schematic representation of the gel with a microemulsion and ferrite magnetic nanoparticles. The inset shows cross-linked nanoparticles (black spheres) bonded to methacrylate residues (blue rectangles) and a PEG chain (red line); arrows represent the binding group to the polymer network of acrylamide and bisacrylamide. Reproduced with permission from ref 53. Copyright 2007 American Chemical Society.

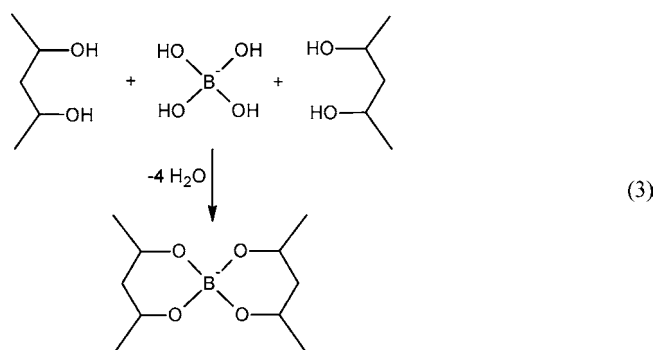


**FIGURE 5.** (left) SEM micrograph showing the microscaled pores, together with the acrylamide gel layers where the magnetic nanoparticles are copolymerized (brighter regions). Reproduced with permission from ref 54. Copyright 2008 American Chemical Society. (right) Sequence from top left to lower right illustrating the removal of a microemulsion-loaded gel from the surface of marble by an external magnet. Reproduced with permission from ref 53. Copyright 2007 American Chemical Society.

emulsions that have been used previously in the removal of Paraloid coatings from the surfaces of artwork.<sup>26</sup>

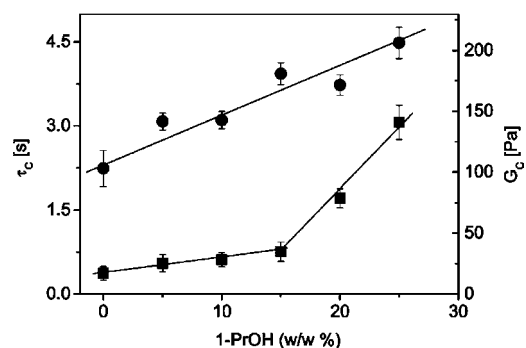
The microemulsion-loaded nanomagnetic gels have removed Paraloid from marble, fresco, and painted surfaces. They may be especially useful when there is a need for careful spatial control of the area to be treated or a triggered or tuned release or uptake of the confined material.

**3.3. “Peelable” Gels.** Hydrogels employing two component gellants, poly(vinyl alcohol)<sup>55,56</sup> and borate as a cross-linker (PVA–B) (eq 3),<sup>57</sup> have been investigated extensively. The ester cross-links are reversible, so a steady-state concentration of them is established. Initially formed gels “age”, allowing conformations of the polymer chains and locations of cross-links to change. Depending upon the length (i.e., average molecular weight) of the PVA chains, the concentrations of PVA and borate ion, temperature, and pH of the aqueous part,<sup>58–61</sup> the gels can be very stiff or quite malleable.<sup>62–64</sup>



We have investigated how these gels might be applied for cleaning surfaces of artwork, especially when the aqueous liquid is mixed with a cosolvent, 1-propanol (although propylene carbonate, 1-pentanol, cyclohexanone, and 2-butanol have been added as well).<sup>21</sup> Because of their high elasticity, these gels can be peeled from a surface in one piece without introducing a strong lateral force or adding other chemicals.





**FIGURE 6.** Crossover parameters,  $G_c$  (●) and  $\tau_c$  (■), as a function of 1-propanol (1-PrOH) content. Vertical bars are standard deviations of six measurements. Reproduced with permission from ref 21. Copyright 2009 American Chemical Society.

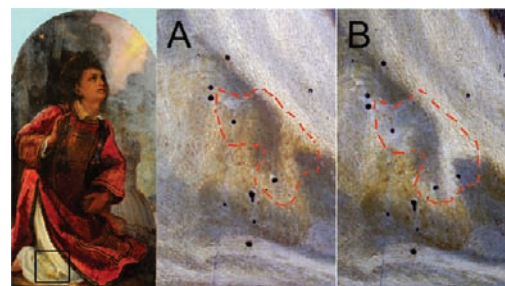
With 1-propanol as the cosolvent, the free water index (FWI), the mole fraction of water that behaves as if it were in the neat bulk,<sup>65</sup> was calculated in PVA–B gels using eq 4 (where  $\Delta H_{\text{exp}}$  is the enthalpy change of the melting water,  $\Delta H_{\text{init}}$  is the enthalpy of fusion of water in the gel assuming that all of it is frozen at 0 °C, and  $A$  is the weight fraction of water in the gel).

$$\text{FWI} = \Delta H_{\text{exp}} / (A\Delta H_{\text{init}}) \quad (4)$$

Because the FWI decreases linearly and rather precipitously with increasing 1-propanol concentration (to a value of 0.45 at 25 wt % 1-propanol, the highest concentration possible without syneresis), the alcohol exerts a cosmotropic effect (i.e., it acts as a water-structure maker, reinforcing the PVA–B SAFIN).<sup>66</sup> For some cleaning applications, a cosmotropic effect may be desirable because more water and less alcohol should reside, on average, at a gel–painting interface and swelling of underlayers is reduced.

Consistent with this effect, rheological measurements demonstrate that the gels become stronger, presumably as a result of more cross-links, with increasing 1-propanol concentration. The crossover values between the elastic and viscous moduli,  $G_c$  and the corresponding apparent relaxation times,  $\tau_c$  for PVA–B gels as a function of 1-propanol concentration were calculated from a frequency sweep test. Figure 6 shows that increasing 1-propanol content enhances the elasticity of the hydrogels over the frequency range investigated. The relaxation time of the hydrogels increased above ca. 15 wt % 1-propanol, indicating that the rate of the shear-induced rearrangement of the network is much slower than that at 0–15 wt % 1-propanol.

After we successfully removed various types of varnishes from test panels using PVA–B hydrogels containing 20 wt % 1-propanol, a piece of gel was placed on a section of a wood panel by Ludovico Cardetti detto “il Cigoli” (1559–1613, from



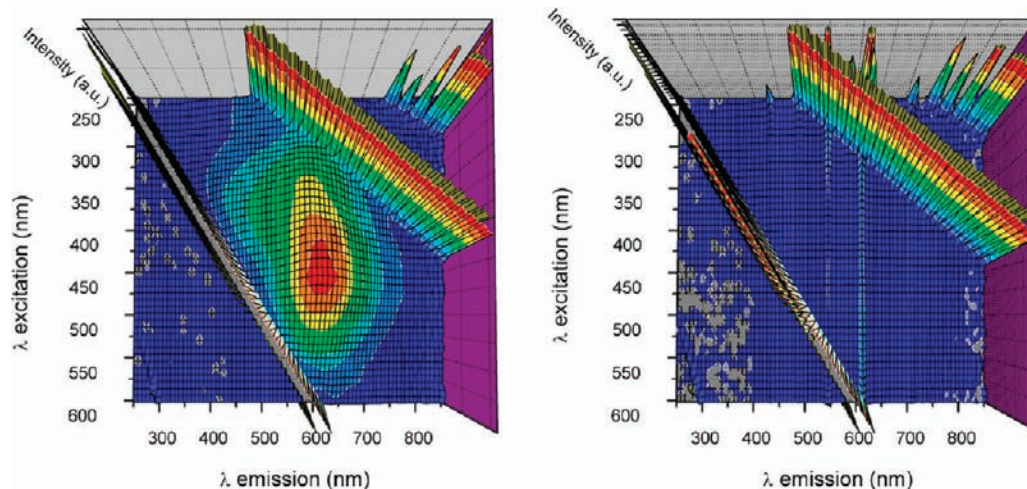
**FIGURE 7.** Wood panel by Ludovico Cardetti detto il Cigoli. Magnified views of the boxed region on the complete painting before (A) and after (B) two applications of the gel in the area delimited by the red dashed line. Reproduced with permission from ref 21. Copyright 2009 American Chemical Society.

the collection of the Curia Museum; displayed at Santo Stefano al Ponte Church, Florence) to which had been applied previously a varnish, now brown and oxidized (Figure 7). After two applications of the gel, no visible dirt or varnish remained.

Recently, we have found that the weight fraction and range of organic liquids within the aqueous liquids of borate gels can be increased significantly by employing poly(vinyl alcohol-co-vinyl acetate)s (PVAc–VA) as the cogellants.<sup>67</sup> Preliminary cleaning tests have been conducted on a fragment of a 19th century Italian wooden frame composed of a gesso underlayer as a base, a yellow bole for silver leaf, and a toning top layer of unbleached shellac. The shellac is old, and microfissures have allowed the silver to tarnish in many spots. The shellac was removed selectively and gently by applying a piece of gel (PVAc–VA (ca. 40% vinyl alcohol)–B gellant and 80/20 (w/w) ethanol/water as liquid). After 15 min, the gel was lifted with a spatula, and the surface was dabbed with a soft tissue to remove residual liquid. Fluorescence (Figure 8) and visual analyses of the surface before and after cleaning<sup>68</sup> indicate that all of the shellac was removed while the silver leaf remained intact; the fluorescence with a maximum at 625 nm under excitation between 300 and 550 nm is characteristic of unbleached shellac.<sup>69</sup> Under more drastic cleaning conditions (i.e., 30 min contact time with a gel containing PVAc–VA (ca. 73% vinyl alcohol)–B gellant and 50/50 (w/w) ethanol/water as liquid), the silver leaf was disrupted, probably due to softening of the bole and glue-based gesso under the leaf.

#### 4. Open Questions and Challenges for Future Developments

The state of the “art” of the science of conserving artwork with gels has been presented. Three types of responsive gels and examples of their application as cleaning agents have been described. The word “responsive” here signifies gels that can



**FIGURE 8.** Three-dimensional fluorescence spectra of a 4 mm diameter area of the surface of a frame with silver leaf before (left) and after (right) cleaning (see text). Only data within the central delineated regions are meaningful. Red indicates highest intensities and blue the lowest.

be easily and rapidly removed via a response to a “chemical switch” (rheoreversible gels) or an external magnet (gels with embedded magnetic nanoparticles) or by peeling (highly elastic gels).

Although these gel types offer heretofore unavailable opportunities for cleaning paint surfaces, many questions remain about the range of their applications and the long-term consequences of using them (or any other medium) as cleaning agents: How much residue is left after cleaning and what is the topology of the gel action (i.e., the depth and rate of cleaning action, especially as measured quantitatively and *in situ*)? Answers should be forthcoming from the application of modern analytical tools adapted to conservation studies.<sup>69,70</sup> Clearly, materials chemistry and, in particular, gels will be key elements to address many of the formidable challenges that have been identified in this field.

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