Workshop Review: Nanotechnologies for Conservation of Cultural Heritage

Nano-lime, Emulsions, Gels, and Nanostructured Materials

In February 2018 Pratt Institute, Brooklyn, NY held its second workshop on Nanotechnologies for Cultural Heritage Preservation. The workshop was led by Professors Piero Baglioni and Rodorico Giorgi from the CSGI -- Center for Colloidal and Surface Science (Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase) based in Florence, Italy.

The workshop was organized by Cindie Kehlet, Sarah Nunberg, and Soraya Alcalá. Before going into the details of the workshop, it must be said that Cindie, Sarah, and Soraya put an enormous amount of work into the preparations for the workshop. They prepared and artificially aged mockup sets of tiles coated with resins and paints; stones covered with spray paint; and canvas covered with animal glue, alkyd, and latex paints. They also divided up gels and emulsions to make kits for each participant to take home. All this in addition to the normal tasks associated with hosting a workshop with two instructors and 23 participants.

Drs. Baglioni and Giorgi were amazing – charming, direct, and to the point, and so willing to share information. The workshop was accessible to all the participants necessitating that some of the more complicated details be simplified. However, when they were asked a technical question, the full depth of their knowledge and experience became obvious and was freely shared.

CSGI is a research entity. They spend about 10% of their time on conservation issues. They are also the supplier for the products discussed in the workshop. So, while it is easy to say that the workshop is just a come-on for the product line, this does the workshop no justice. While to some extent underplayed, many of the concepts and products represent anything from a leap forward in materials to a paradigm shift in approaches to cleaning.

Their research focuses on physical aspects of chemistry, offering the conservation community new tools for cleaning works of art based on selectively removing unwanted varnish, dirt, or overpaint while avoiding penetration into, and interaction with, the original layers below. The materials they have developed have low toxicity and, compared with neat solvents, generally have a lower environmental impact. As Professor Baglioni says, “only thinking out of the TEAS triangle will we be able to reduce the use of solvents, toxicity, and interaction with the original.” Meaning we need to start exploring different ways to clean and not to focus on solubilization of the material to be removed.

To put the workshop and methods into context, one must understand that development started with questions and problems relating to fresco paintings – consolidation and removing incompatible treatment materials like Paraloid B-72 and wax from the surface of a fresco (Baglioni et al. 2012). This research was developed as part of the EU NANOFORART project. Since then their methods (and products) have been extended to modern and contemporary surfaces (Chelazzi et al. 2017) as part of the ongoing EU project called NANORESTART.

Nano-lime (sold as Nanorestore Plus®)

One of the vexing problems with treating lime-based plasters is consolidation. Ideally one would use materials of similar mechanical and chemical properties. And, this is indeed the trend for filling voids and large-scale delaminations. Since the setting and cohesive strength of lime plaster is from the reaction of calcium hydroxide with carbon dioxide to form calcium carbonate, an ideal consolidant would be calcium hydroxide in water, or lime water.

However the problem with this is that calcium hydroxide is not very soluble in water so it is nearly impossible to get sufficient carbonation to occur in the matrix to strengthen a friable substrate. Flooding the surface and substrate with the water necessary to carry the calcium hydroxide solution opens other avenues of decay as it can mobilize soluble and semi-soluble salts.

An ideal consolidant would deliver higher concentrations of calcium hydroxide into the substrate where it could react with water and carbon dioxide to form fresh cementitious networks to strengthen the weakened original plaster network. The strengthened network would still be able to breathe and have the same mechanical properties.

Here enters nano-lime, calcium hydroxide crystals formed on a nanoscale. The 50 to 200 nanometer particles are suspended in an alcohol, either ethyl or isopropyl, and are at concentrations of 5 or 10 grams/liter, or higher. Due to the size of the particles and the interaction between the hydroxide bonds on the nano particles with the –OH groups on the alcohol, the particles don’t agglomerate. A quick shake and the lime is dispersed in the solvent carrier (Baglioni et al. 2015).

In practice, the nano-lime is allowed to soak into the surface by brushing through tissue. The solution consists of particles that are as small as possible and, consequently, has a greater number of particles and much greater surface area per given amount of calcium hydroxide. This results in a solution with higher reactivity and greater penetration. The reaction with the substrate is faster and more efficient requiring fewer applications than other consolidants (Baglioni et al. 2015).

It is important to test the solution to determine the proper concentration before large-scale application. The nano-lime dispersion can be diluted with the same solvent it is delivered in (ethanol or isopropanol) but anhydrous solvents must be used to avoid trace water reacting with the calcium hydroxide.

If the surface has low porosity or the nano-lime concentration is too high a white haze may form. If that happens, the haze can be removed using water. After the application of the solution, first you wash the surface with solvent and then apply humid cellulose pulp. The pulp should remain on the surface treated until the pulp is dry.

by Chris Stavroudis and Soraya Alcalá

A review of the CSGI workshop at Pratt Institute 12-16 February 2018

Microemulsions (sold as Nanorestore Cleaning®)

We've been hearing about microemulsions for the last few years and, at least in the US, we have thought about them in terms of solubilization. There are two ways to make use of a microemulsion.

A microemulsion allows the solubilization of both materials more or less simultaneously. This solves problems like removing intermixes of materials such as glue/wax or varnish/glue mixtures.

The other, perhaps more common, use of a microemulsion system is to suspend an active dispersed phase into an inert continuous phase. Here, we think of microemulsions that disperse a polar phase into mineral spirits or solvent into an aqueous phase. But again we normally think of the dispersed phase in terms of solubilization.

The cleaning systems developed by CSGI are designed to exploit two different physico-chemical mechanisms to remove unwanted materials. Depending on the nature of the materials to be removed, i.e. low molecular weight substances can be removed by solubilization, while polymers with high molecular weight can be de-wetted.

Dewetting is a difficult concept to describe. It can be thought of as gently encouraging the substance-to-be-removed to cohere to itself rather than adhere to the surface.

Using the example of removing Paraloid B-72 from a surface, the dispersed phase, the solvent(s) in the microemulsion, swells the polymer coating. This raises the B-72's glass transition temperature (Tg) changing the film from the durable, glassy state to a soft rubbery state.

As the B-72 swells, the polymer molecules slip over one another forming a soft blob. The surface energy of the blob will want to be at a minimum and form a spherical blob. The presence of the continuous phase of the microemulsion, the water, will further encourage the formation of the spherical blob and also tend to repel the blob from the surface – hence "dewetting" the surface (Baglioni et al. 2017).

Dewetting is the opposite of wetting a surface. If we want to apply a coating to a surface, we want the coating (and solvent) to wet well onto that surface so a continuous film is deposited without alligatoring or orange peeling. If we apply an aqueous coating to silicone Mylar®, we know that the opposite of wetting will occur – it will bead up and, on drying, will leave a film that is not at all adhered to the silicone surface.

In dewetting, we have the soft blob of B-72 repelled by the more polar surface of the artwork, assisted by the water in the continuous phase of the microemulsion. It is repelled and trying to get off the surface – all without solubilizing the B-72. And most unconventionally, the dewetted coating is removed mechanically, and dry. The coating is simply pushed off of the surface with a dry swab or stick, rolling-up the swollen blobs of B-72. Using a dampened swab inhibits the rolling up of the coating – it's a process that is counterintuitive and takes some getting used to.

A typical microemulsion developed for removal of PVAc or B-72 (Giorgi et al. 2010) is:

73.3	water (% w/w)
3.7	SDS (sodium dodecyl (lauryl) sulfate), surfactant
7	1-pentanol, cosurfactants
8	propylene carbonate
8	ethyl acetate

Note how low the percentage of surfactant is.

The commercially available microemulsions sold by CSGI are called Nanorestore Cleaning® Polar Coating S; Polar Coating B; Aploar Coating; and Wax. Polar Coating S and B are for removing acrylic and vinylic synthetic polymers as well as aged natural resin varnishes. Apolar Coating has been formulated for mildly polar synthetic and natural polymeric coatings. The Wax microemulsion is formulated for removing wax and oily soils. Full descriptions of the products can be found on the CSGI website: http://www.csgi.unifi.it/products/orders.html under the "Products" drop-down menu. Not yet on the website, but of interest is Polar Coating G which is designed for dewetting acrylic coatings (like graffiti).

Gels: Dry; Extra Dry; Max Dry; PG5 and PG6 (sold as Nanorestore Gel®)

CSGI has created a group of gels that will act as carriers for aqueous (or predominantly aqueous) cleaning solutions and leave no residue of the gel behind. The gels conform to a surface but because of how closely the cleaning solution is held in the gel, only the surface of the object is wet, not the substrate (Baglioni et al. 2014). During the workshop they presented chemical hydrogels Nanorestore gel®, chemical organogels, and physical PG gels.

Gels are defined by their rheological properties and are considered in contrast to a viscoid liquid. Many of the so-called gels in conservation are actually viscous liquids (e.g. "solvent gels," xanthan and Pemulen "gels") although agarose and gellan gum gels are true gels. Defining a true gel is a difficult prospect, best summed up: "a gel is a gel as long as one cannot prove it's not a gel" – a slippery proposition indeed.

Gels can be divided into two "big families": physical gels and chemical gels.

Physical gels are characterized by their dynamic crosslinking easily changing between solid and liquid and are based on interactions between secondary bonds such as dispersion forces, hydrogen bonds, electrostatic or hydrophobic interactions (Baglioni et al. 2014). Agarose and gellan gum are two examples of physical gels widely used in conservation. Both are derived from naturally occurring polysaccharides.

Agarose is gelled via intermolecular hydrogen bonding – weak bonds that are prone to change physical condition with any change of temperature or pH. Gellan gum is gelled both by hydrogen bonding and more strongly by the addition of cross-linking calcium ions.

Agarose's and gellan's hydrogen bonded gelled structure can be useful for some aspects in conservation such as their thermo-reversibility. For example we can use it in transition between liquid solution and solid gel, but this can also be an issue in terms of residues left on the surface.

A chemical gel is made by reactions between polymers that create covalent bonds between the molecules. This cross-linking between polymer chains creates a stable, thermal resistant gel that cannot leave any residue on a surface. Chemical gels can be selectively altered to create structures with a wide variety of physical and chemical properties including porosity and flexibility.

The Nanorestore Gels® Dry, Extra Dry, and Max Dry are chemical hydrogels that are flexible sheets, similar to, but much thicker than, soft contact lenses. They can be cut into different shapes, manipulated and removed easily from the surface of an artwork without the possibility of leaving a residue.

The Nanorestore Gels are made of crosslinked chains of poly(2-hydroxyethyl methacrylate) (p(HEMA)) interpenetrated with chains of poly(vinyl pyrrolidone) (PVP) (Domingues et al. 2013). This means that the HEMA monomer is loaded with already polymerized chains of the PVP before the HEMA is polymerized and crosslinked. The PVP chains are mechanically held in place by the network of the p(HEMA) – hence interpenetrated. The PVP is the hydrophilic component that holds water in the gel structure.

The different Nanorestore Gels when saturated for use are usually between 50% and 65% water but are nonetheless cohesive, solid structures. The gels are transparent, cast into 2 mm thick sheets with flat surfaces and are flexible to a degree. They conform to large textural features, e.g. undulations in paper, but are not soft enough to conform to the irregularities of, say, canvas texture. The also have a tendency to break during extended handling.

Different proportions of p(HEMA) to PVP give different pore sizes within the gel and therefore different degrees of holding water or a cleaning system in the gel.

Nanorestore Gel® Dry has the largest pores and is comparatively less water retentive, Extra Dry with medium pores, and Max Dry is the most retentive and has the smallest pore size.

The Nanorestore Gels, as well as the Peggy gels, to be discussed shortly, are delivered loaded with (and stored in) water. The water in the gel is exchanged by simple diffusion with a cleaning system by soaking the gel in the desired cleaning solution.

The gels can be rinsed for reuse by soaking in fresh distilled/deionized water. Note that dilution effects should be considered in the case of soaking a larger gel in a small volume of cleaning solution. [For example, a standard 15 cm x 15 cm sheet of gel holds a volume of roughly 25mL of water. If the gel is soaked in 50mL of cleaning solution, the final concentration of the cleaning solution in the gel would only be 66% of the concentration of the cleaning solution's starting concentration. Using larger volumes of cleaning solution to condition the gel minimizes this effect.]

In use, the gel is blotted on both sides to remove excess liquid. This blotting step is critical to controlling the amount of water brought to the surface of the artwork, and some experimentation is often necessary to match the degree of blotting of the gel to obtain the desired wetting of the surface. It is useful to use two gels in a treatment, one holding the cleaning solution and the other carrying the rinse system. By controlling the degree of blotting of the cleaning gel and the rinsing gel, application and clearance of the cleaning solution can be optimized.

The gels can also be loaded with polar solvents mixed with water. The family of Dry gels can hold up to 90% ethanol while the Peggy gels can hold only 40-50% alcohol in water. (Note that the gels should not be stored loaded with polar solvents as they will irreversibly dehydrate. Always rinse and load with fresh water after using a gel with solvents.)

The "Peggy" gels are literally the most flexible of the gel systems. They were formulated for the treatment of a Jackson Pollock at the Peggy Guggenheim Museum in Venice, hence the name "Peggy" and the designation "PG." The gels are currently under development but should be commercially available by the time you read this. If they are not listed on the CSGI website, email and ask for them by name.

The "Peggy" gels are interpenetrated physical gels based on poly(vinyl alcohol) (PVA). Being physical gels they are distinct from the chemical gels discussed above. Despite this difference they behave like the chemical gels in that they are manufactured into cohesive sheets (as well as pyramids, trapezoids, or sticks which can be used with a blotting action) that cannot leave a residue. Rather than being formed by crosslinking, weaker intermolecular bonds between the PVA molecules give the gels their physical structure. Undisclosed black magic involving freezing and thawing create the weaker-than-chemical crosslinking.

As with the "Dry" gels, the PG gels are interpenetrated with hydrophilic polymers. PG5 is interpenetrated with PVP and PG6 or "Peggy 6" with PVA. (And here's the real black magic: in the Peggy 6 gel, the PVA is physically crosslinked but there are also free, uncrosslinked polymers held within the crosslinked gel structure.)

The PG5 and PG6 gels are more elastic than Nanorestore® gels and they adapt very well to contoured or uneven surfaces. They retain a lot of the liquid that is loaded inside the structure and function to swell and solubilize the target material, pulling the grime, swelled varnish, or overpaint into the gel.

Organogels

Chemical organogels are based on cross-linking methyl methacrylate (PMMA) and ethylmethy methacrylate (PEMA), within a liquid phase composed of organic solvents. They are the only gels of the Nanorestore products that are designed to carry organic solvents. The organogels are complimentary to the hydrogels described above and expand the range of "tools" for cleaning, thinning, or removal of natural or synthetic varnishes, coatings, and adhesives (Baglioni et al. 2015).

These gels function in a similar manner to the pHEMA gels. They retain the solvent inside the gel system, allowing for controlled swelling of the target area and migration of the wetted surface into the gel. The organogels are used specifically to remove acrylic paints and adhesive tape on paper, and present many other possibilities.

A solvent not commonly used (or even heard of) in conservation, diethyl carbonate, is the solvent in the organogel that is very efficient at removing tape residue from works on paper. (We did have some problems using the gel for tape removal. It was excellent at removing the carrier from the adhesive but we didn't work with it enough to feel comfortable using it to remove the adhesive layer from the paper itself.)

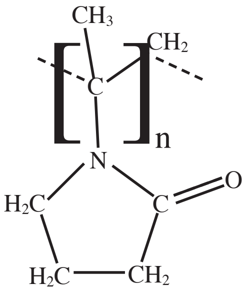
Nano-lime for cellulose based artifacts (sold as Nanorestore Paper®)

Another application of calcium hydroxide nanoparticles presented by Drs. Baglioni and Giorgi during the workshop was for the deacidification (or pH adjustment) of cellulose-based artworks (like paper, wood, or canvas). When cellulose ages, the fibers depolymerize, a process which is typically catalyzed by low pH. The calcium hydroxide particles of the nano-lime when applied onto paper's cellulose fibers react with carbon dioxide from the air, deacidifying and forming a calcium carbonate reservoir on the paper fibers.

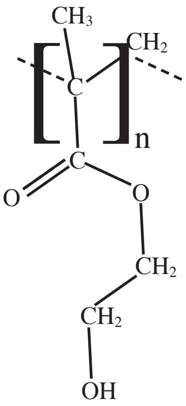
Traditionally, aqueous solutions of calcium hydroxide have been widely used for deacidification. However, this treatment can lead to hydrolysis of the cellulose, mainly because of the strong alkaline conditions of the solution and the hygroscopic characteristic of the support. To overcome this reaction CSGI formulated nano-lime into non-aqueous solutions based on short chain alcohols.

These dispersions of nano-calcium hydroxide particles in alcohol are kinetically stable so the particles don't agglomerate. The dispersed nano calcium hydroxide is sold in 5% and 10% concentrations in either ethanol or isopropanol. The nano particles of calcium hydroxide are carried into the porous paper and as the alcohol evaporates, there is rapid neutralization of the pH and the formation of a calcium carbonate alkaline reserve.

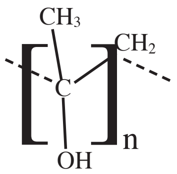
The polymers used in the gels



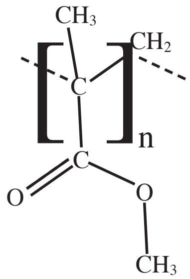
PVP- poly(vinyl pyrrolidone)



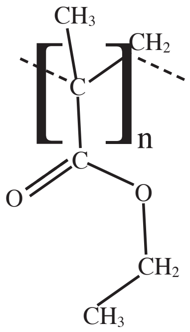
P(HEMA) - poly(2-hydroxyethyl methacrylate)



PVA - poly(vinyl alcohol) [This is a nomenclature problem for conservators as we have traditionally referred to poly(vinyl acetate) as PVA while in the polymer world it is referred to as PVAc]



PMMA - poly(methyl methacrylate)



PEMA - poly(ethyl methacrylate)

Nano-lime, Emulsions, Gels, and Nanostructured Materials, continued

Conclusion

All in all, the workshop was well organized, fun, and extremely informative. New materials and new concepts are always difficult to take in and internalize. Conservators can be hesitant to use new materials and processes, and this is a healthy trait. The hydrogels can be appreciated and used by even the most skeptical among our ranks.

Nano-lime for the consolidation of calcium carbonate-based materials is well established although conservators might have to acquaint themselves with its use and properties, as is the case with any consolidant. Paper conservators will have to play with the Nanorestore Paper and, as a group, probably revisit the whole concept of deacidification and alkaline reserves.

The microemulsions, however, represent a revolution in cleaning systems. It will take some experimentation to adapt them into our practice. Not only do these microemulsions make for a shiny new tool for our tool belt, but they represent a whole new mental model of the cleaning process.

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These are approximate prices from the website, which include the 22% VAT tax.

Nanorestore Plus® $50 to $70 / L, depending on the formulation

Nanorestore Cleaning® all formulations $70 / L

test kit $56

Nanorestore Gel® $20
Each package contains a water-loaded sheet (approx. 150 cm^2 - 2 mm thick), which can be reused up to 4-5 times, depending on the specific case.

test kit $28

Nanorestore Paper® $110 to $140 /L, depending on the formulation

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Chris Stavroudis membership secretary

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