
Wolber's World:

A Review of a Textile Wet-Cleaning Workshop Held in Oaxaca, Mexico

Richard Wolbers, Associate Professor and Coordinator of Science and Adjunct Paintings Conservator at the University of Delaware, offered a wet-cleaning workshop during the 8th bi-annual North American Textile Conservation Conference held in Oaxaca, Mexico, November 8-11, 2011.

The two-day instruction covered what he normally teaches during one week, so needless to say we all left with plenty of food for thought. Wolbers divided his lectures in four parts: Part I covered basic wet cleaning methods, Part II described macro and microemulsions (which Chris Stavroudis outlined at the last WAAC conference in Austin, Texas), Part III discussed enzyme applications, and Part IV introduced biphasic gels, in which aqueous and non-aqueous solvents join forces. I hope to provide a general overview and highlight important tools and/or materials and their applications. To try to include all the information he covered would take a book, which I'm far from qualified to write.

In Part I, Wolbers proposed a list of aqueous cleaning "tools" in order of importance: 1-Water and its conductivity; 2- pH; 3-Ionic Species; 4-Chelators, 5-Surfactants, and 6- Viscosity. That surfactants are almost at the bottom of the list surprised many of us who have traditionally paid most attention to the various properties surfactants have to offer when developing our wet-cleaning protocols.

Conductivity

Knowing the conductivity of the textile to be wet-cleaned and that of the water to be used is essential when determining the osmotic effect, or in other words the rate at which the fibers will swell. Conductivity is the ability of a material to conduct an electrical current. The most gentle but least effective cleaning would occur under conditions in which the conductivity levels of both textile and water are exactly the same, resulting in no net exchange of solutes in or out of the textile.

If a textile with a relatively high conductivity is placed in non or low conductive water, such as pure distilled or deionized water, the fibers will swell very quickly, and could, at a microscopic level, literally burst (Wolbers pointed out that this phenomenon is capitalized upon in the manufacturing of commercial detergents). On the other hand, if the conductivity of the textile is much lower than that of the bath, the textile can lose water very quickly, causing it to shrink.

Wolbers noted that the general rule of thumb when determining the appropriate conductivity of a solution is to not exceed or go below ten times the conductivity of the textile to be wet-cleaned, with the least aggressive levels ranging between one and two times that of the textile.

Wolbers has an ingenious way of measuring the conductivity of the textile using a gel block and a conductivity meter with a measurement well (the Horiba B-173 Micro Conductivity Meter). A tiny (1 mm diameter) circular block of gel punched out with a leather hole punch is placed on the textile and left to sit and absorb the salts on the textile for approximately five minutes. The gel is then transferred to the

conductivity meter well, making sure that the gel is in full contact with the two electrodes in order to get an accurate reading. This system leaves no mark on the textile, and the gel sample can be saved for further analyses if desired.

Those familiar with Wolbers' publications and cleaning methods already know he has been working with gels bulked with various materials for a number of years now. He chose agarose, a single polysaccharide derived from seaweed, as his bulking agent for the gel block for several reasons: it has a relatively neutral pH, the gel can contain up to 95% water, it gels above room temperature, and it's readily available. Agarose can be purchased in various levels of purity (a food grade version is used as a vegetarian alternative to gelatin in cooking and in Japanese desserts, and is readily available in health food stores).

While Wolbers used a very pure version distributed by Sigma Aldrich for the workshop (product number A0701), other less expensive versions are acceptable (such as those sold on goldbio.com and universalmedicalinc.com). This system for measuring conductivity can be used for other materials as well, such as archaeological ceramics as one of the workshop participants, Nancy Odegaard, pointed out.

pH and Buffers

Textile conservators have often measured the pH of a textile by wetting out an area and placing a pH paper strip on the surface. This can be both impractical, since wetting out an area can form tide lines on the textile, and inaccurate, since pH papers offer only a range and have a finite shelf life. Luckily, Horiba has also developed a pH meter with a measurement well (Horiba Twin Micro pH Meter), and the same little gel sample used to measure the conductivity of the textile can be used to measure the pH.

Wolbers pointed out that since the pH meter contains salts, it is best to measure the conductivity first and then transfer the gel sample to the pH meter. It should be noted here that both meters can be dipped in aqueous solvents as well and are very user friendly, offering a little smiley face when the readings are complete. Like all meters, however, calibration is required. And ease of use does take some practice. Tests conducted post-workshop revealed that weighting the gel sample on the textile surface to ensure full contact provides more consistent results, due to the three dimensional nature of the woven surface.

In order to maintain a working pH when wet-cleaning, buffers are often added to the bath solution. Wolbers noted that the two most advantageous buffers for our textile wet-cleaning needs are citrate, that holds the pH within 2.2 and 6.5 and triethanolamine (TEA), holding the pH within 7.0 and 8.3.

Ionic species and Chelators

Different salts containing various ionic species dissociate in water into different concentrations of ions. Adding specific salts to the bath water will effect the conductivity as well

as the ability to dissolve salts in the textile that would otherwise remain insoluble. The salt additives that assist with disalutation are known as chelators, and are usually complex, multi-valent compounds (meaning having multiple charges) containing at least three organic functional groups that interact with metal ions through dipolar, hydrogen, or ionic forces.

Wolbers offered two examples of weak chelating materials to dissolve calcium deposits bound to residual soaps often present in textiles: Citric acid and Nitrilotriacetic acid (NTA). Chelators are also used to dissolve rust stains, although the most effective one used up until now, Ethylenediamine-tetraacetic disodium salt (EDTA), dissociates at a relatively low pH and is therefore rarely used on textiles. Wolbers introduced a new chelator on the scene which appears to be just as effective in removing iron and works under neutral conditions: N,N'-di-(2-hydroxybenzoyl)-ethylenediamine-N, N'-diacetic acid (HBED). This chelator may be beneficial in general wet-cleaning as well, since many soils contain iron salts.

Surfactants

Surfactants are basically compounds with a hydrophilic (water loving) end and a hydrophobic (water repelling) end. They may be ionic, anionic, or non-ionic. The hydrophobic ends are attracted to each other and to the organic soils in the textile. Surfactants have various properties that are taken into account when determining which to use when, and Chris Stavroudis did an excellent job in explaining these in his January 2009 article "Sorting Out Surfactants" (WAAC Newsletter Vol. 31, No.1). Please refer to his article for detailed information on the critical micelle concentration (CMC) and the "Hydrophile-Lipophile Balance" (HLB). Suspension aids, such as carboxy methyl cellulose, are also sometimes added to aid in holding the surfactant(s) in solution.

Viscosity

By bulking up solutions and increasing viscosity one can increase the time the textile is in contact with the solution in a defined area during wet-cleaning. In some cases these gel solutions can include organic solvent(s), surfactants, and enzymes to aid with stain removal. The two bulking agents applied to test samples during the workshop were a xanthan gum (Vanzan NFC) and Noveon/Lubrizon's Pemulen TR-2.

The former is a naturally occurring polysaccharide used in food processing, while the latter is a synthetically produced block polymer of polyacrylic acid and a C₁₀₋₃₀ polyacrylate polyester. Polyacrylic acid compounds are used in various cosmetics and are primary ingredients in hair gels. Both are gel forming materials in aqueous systems. Xanthan gums are much more resistant to high ionic conditions, and tolerate a much wider pH range than the synthetic Pemulen materials. Noveon's Pemulen TR-2 and other polyacrylic acids are highly viscous within a pH range of 6-10, but thin at pH's above or below this range. They also do not remain

rigid in high ionic strength preparations or on salt-laden substrate surfaces (such as on a salt infused archaeological textile, weighted silk, a gypsum wall, or archaeological ceramic artifact).

Other bulking agents used to form rigid gel materials noted by Wolbers include various new forms of methyl cellulose and hydroxypropylmethyl cellulose block polymers, and less complex polysaccharides that are less sensitive to both ionic conditions and temperature. The simplest of all polysaccharides, Agarose, has already been mentioned above when discussing the measurements of pH and conductivity.

Emulsions and Biphasic Gels

Organic solvents can be added to water-based solutions to form emulsions, in which "roughly spherical droplets of one phase are dispersed into another." Emulsions are effective in dissolving what Wolbers defines as "intermixes" of materials, or "material arrangements that involve both water soluble and solvent soluble materials mixed together" such as oils and proteins, waxes and salts, proteins and carbohydrates, etc. Which, in effect, are the types of stains textile conservators most commonly confront.

Emulsions are divided into two categories: Macro and micro, dependent on particle or droplet size, which in turn effects various solvent properties. Macroemulsion particles are between 200 and 1000 nanometers in diameter, while microemulsion particles are 100 nanometers and under. The smaller particles offer larger surface areas, are optically clear rather than opaque due to the lower refractive index (their particle diameter is less than a ¼ of the wavelength of light, so they scatter little light), and have higher solubilizing capabilities.

Microemulsions are also thermodynamically more stable. In other words, macroemulsions require to be shaken before using if they have been sitting on a shelf, while microemulsions will stay emulsified indefinitely if stored under appropriate environmental conditions.

When making emulsions, surfactants are usually needed in order to form an interfacial film between the hydrophilic phase (i.e. water) and the hydrophobic phase (i.e. organic solvent or oil). The surfactants are carefully chosen "so that an ultra low interfacial tension can be attained at the oil/water interface which is a prime requirement to produce micro-emulsions."

Surfactants with high HLBs are needed to prepare emulsions with a higher concentration of water, while those with low HLBs are required to produce an emulsion with a higher concentration of oil. Bicontinuous micro-emulsions (those with equal parts water and organic solvent) require a surfactant with an intermediate HLB. Alcohol co-surfactants are also added to the water/organic solvent mix to provide the most stable of micro-emulsions. An emulsion can be bulked up to form a highly viscous, or gel-like, material to be applied locally as described above.

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Emulsions can also be made without surfactants. Pemulen TR-2 and xanthan gum, the materials used to form gels during the workshop, can readily form emulsions as well as act as bulking agents. These gelling materials now allow us to form emulsions without the addition of a surfactant.

A relatively new player in the world of bi-phasic gels, which may be useful for cleaning of water-sensitive material, is silicone-based. Velvesil Plus (Momentive Products) is a commercially available silicone block polymer that works much like the Pemulen TR-2 or xanthan gum materials do in water, forming stable water-in-solvent emulsions without the use of surfactants.

Enzymes

Enzymes are sometimes used in conservation to help break down and remove adhesives and residues. Those most often found in the conservation field are three hydrolases (enzymes that catalyze the break-down of bonds, or hydrolysis). These three include lipases, proteases, and amylases. Lipases catalyze the break down of oil-based polymers, proteases help break down protein-based polymers (such as animal glue), and amylases help break down cellulosic polymers (such as wheat starch paste). Enzymes are site-specific, so one can fine tune their selection to prevent a chemical reaction from occurring on a specific material (e.g. wheat starch paste on a paper substrate or animal glue on a silk fabric). Certain metal ions are sometimes needed in order for the desired reaction to occur.

Naturally occurring enzymes require body temperature to activate, and will de-nature above a certain temperature. There are synthetically derived enzymes now available, however, that can work across a wider temperature range (including room temperature!). Wolbers showed us the BRENDA (Braunschweig Enzyme Data Base) available online that is an excellent tool to help determine which enzyme to use for each specific material and condition.

However, a general knowledge of the Enzyme Commission code system is necessary in order to understand the information provided. There are four numbers in the code. The first defines the class of enzyme, such as hydrolase. The second defines the subclass by the type of substrate or bond cleaved. The third defines the subclass by the electron acceptor or the type of functional group removed. The fourth is a classification based on the reaction mechanism that occurs. Descriptions and definitions of all four are available on BRENDA.

Concluding Thoughts

Wolbers, coming from the painted-surfaces end of the spectrum, offered textile conservators a wide range of tools to tweak and adjust to our needs and our discretion. Each participant left the workshop with his or her own questions to ponder. I, for one, rarely wet clean, since more often than not the textile in question may contain multiple types of materials that react differently when wet. The dyes may be fugitive, and/or the fibers may be so aged and degraded that

exposure to water could do more harm than good. When I do wet clean, I test all factors as much as possible before committing to this irreversible technique. I also think long and hard about whether what I take out is doing more damage than what I might leave behind.

Which leads me to my main concern about using gels on textiles: Do the gelling agents discussed here *really* rinse out completely? One of the posters at the conference helped answer this to a degree: Maria Stavropoulou and Stavroula Rapti at the Department of Conservation of Antiques and Works of Art, Technological Educational Institute in Athens, Greece, conducted SEM analysis on new and aged samples of cotton fabric that had been cleaned with three different solvent combinations, two bulked with hydroxypropyl methyl cellulose and one with hydroxypropylcellulose (Klucel G®).

They found that the residues remained on all the fabric samples to various degrees, *with the aged samples containing the highest level* (my emphasis). Residue levels were also dependent on the type of gel applied, the number of times the gel was applied, and how it was removed. They noted that further research is needed, and that it is “paramount to examine the possible substrate alteration and the long term effects the residues may have on the textile substrate.” I agree.

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