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A NEW METHOD FOR CLEANING MARBLE

Kory Berrett, Virginia Naude and Richard Wolbers

Abstract

This paper describes a recent treatment project that succeeds in providing deep cleaning of stained marble where traditional methods had failed. The treatment methodology builds on poulticing techniques using an aqueous cleaning system delivered with a gel-paste poultice mixture. Two materials new to conservation are introduced: a gelling agent, Vanzan NF-C, that is especially effective for aqueous media and can tolerate an unusually wide pH and ionic strength range while maintaining high viscosities; and nitrilotriacetic acid (NTA) a chelator for calcium ions able to disrupt relatively insoluble calcium salts, and staining agents formed by residues of prior treatments (detergents, soaps, coatings, etc.), without affecting the calcium carbonate itself. This new approach promises to be useful for similarly stained marble sculpture.

Background

A new method for cleaning marble was developed under the sponsorship of the Union League of Philadelphia. Located at Broad and Sansom Streets, a few blocks from Philadelphia City Hall, the Union League occupies an 1865 brownstone French Renaissance style building and a conjoined 1910 Beaux Arts building. The architectural complex houses an extensive collection of painting and sculpture as well as an important archive and library of Civil War history.

The Union League was among the first private institutions in Philadelphia to work with conservation professionals in caring for their collections. Following the establishment of programs to address the needs of the archives and the paintings collections, the sculpture collection was surveyed in the mid 1980s and treatment projects were designed to go forward annually.

This paper describes the treatment of two marble figures: the first, “America Mourning Her Fallen Brave” is a life-sized allegorical figure carved in 1867 as a response to the American Civil War by Philadelphia sculptor James Henry Haseltine. The work includes elements that symbolize both the Union and Confederate causes.

The second, “Esmeralda” is by an unknown artist. The image represents the Gypsy girl Esmeralda and her goat Dalji, characters from French novelist Victor Hugo’s famous work “The Hunchback of Notre Dame”, published in 1831.

Figure1 (left). "*America Mourning Her Fallen Brave"* by James Henry Haseltine (1833-1907), Collection of the Union League of Philadelphia 72" x 26" x 24". Photograph by Naudé.

Figure 2 (right). "*Esmeralda*" Artist unknown, Collection of the Union League of Philadelphia 42" x 25" x 26". Photograph by Naudé.

These figures were cleaned in 1988 as part of a program to improve the appearance of the five major marble sculptures in the entrance spaces. No records of past treatment were available. It seemed likely that housekeeping staff had included the objects in their routine maintenance and possible that outside advice had been solicited for occasional treatment. Virginia Naudé and a team from Norton Art Conservation Inc. removed an opaque, buff, water-soluble wash that may have been applied to disguise staining in the stone. Underneath the wash they encountered grime, passages of wax and occasionally areas of paint. The 1988 treatment consisted of an overall cleaning using deionized water and Stoddard solvent emulsion (mixed 1:1 with a Synthrapol-N non-ionic detergent serving as an emulsifier) followed by localized use of organic solvent and commercial stripers where necessary. After cleaning, a wax-resin varnish was applied consisting of 3 parts Cosmolloid 80 H microcrystalline wax and 1 part Laropal K-80 resin in Stoddard solvent. This formula was developed at the Victoria and Albert Museum (Hempel and Moncrieff

1972). The resin was added to harden the surface and make it easier to routinely water clean in galleries that have constant particulate dirt problems. It was used here to protect the marble surfaces from food and beverage spills in the Club's busy reception spaces and to enable staff to water wash any incidental markings or spatters.

Although after cleaning the marble surfaces were acceptable and the sculptures' presentation was markedly improved, there was a distinct discoloration that had failed to yield to any combination of solvents or poultices tested during treatment. It appeared that some material was lodged subsurface that did not yield to available methods and materials. Although the color was not dissimilar to the lighter orange areas in iron staining patterns on marble, the uniformity and consistency of the overall color was familiar from past experience with the effect of a treatment or coating application.

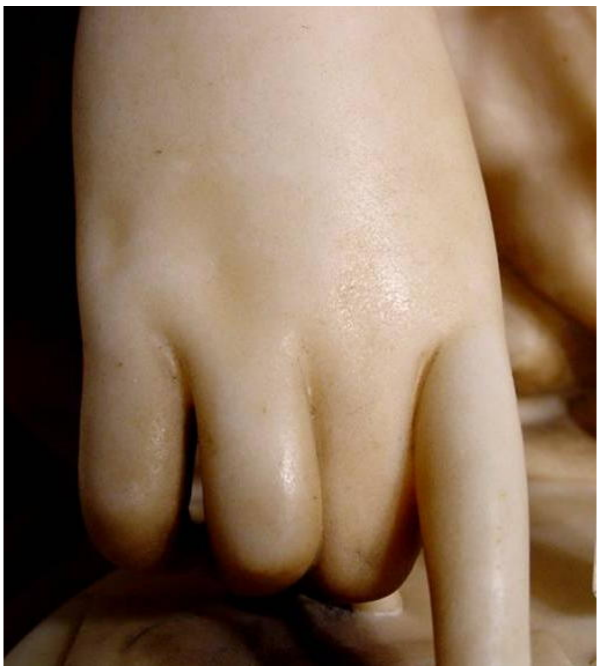


Figure 3. "*Esmeralda*" Detail of hand showing yellow discoloration. Photograph by Berrett.

Naudé returned to address this dilemma as other sculpture conservation projects went forward at the Union League, testing the discolored surfaces with non-polar solvent gels, buffered ammonium citrate solutions and proprietary paint strippers as these systems were developed and came into use by sculpture conservators. The turning point occurred during a major architectural renovation in 2004 when improving the visual appearance of the marble sculpture became a high priority. The conservator and the staff of the Union League responsible for the art collection agreed that identification of the subsurface material, and the design of a treatment targeted specifically at its removal, was the appropriate next step. The client understood that it would probably be necessary to remove a small stone sample. More importantly, they knew that the research and testing program they were asked to fund was not guaranteed to succeed. Hence, the Union League's commitment to the collection was essential to the development of this method.

Analysis

Berrett removed a small fragment (approximately 1cm^3) of the stone from a curl on the underside of the goat's tail, an unobtrusive area on the reverse of the "Esmeralda" group, using a Dremel tool. Wolbers mounted the sample in Extec polyester resin and cross-sectioned it using a disc-type sander (Sears) and an array of graded bound-abrasive cloths (Micromesh). In cross section, the staining material was yellowish in normal light, lightly auto-fluorescent under UV-blue light illumination conditions, and clearly penetrated the porous stone surface up to an average depth of 50 µm (0.05mm).

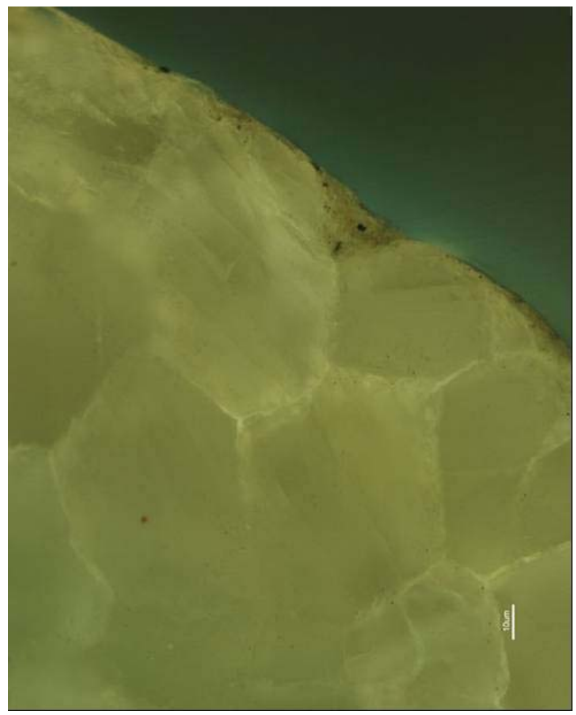
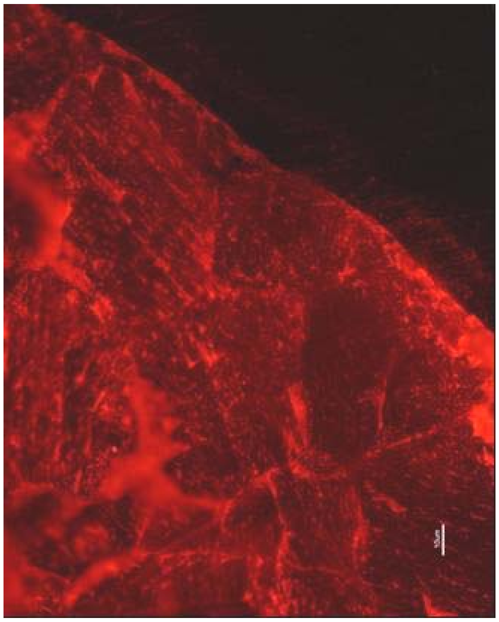


Figure 4 (left). Normal light view, Magnification 125 X Nikon Excite 120 Xenon lamp; cross-polarized. Photograph by Wolbers.

Figure 5 (right). Violet excitation, Nikon BV-2A cube; EX 400-440, BA 470nm. Photograph by Wolbers.

The staining material was a heterogeneous mixture of oily or lipid materials ranging from normal surface soil deposition material to residuals from both applied paints, and paint removal agents (positive staining with lipid soluble fluorescent dyes). As expected, the surface also appeared to contain a continuous non-fluorescent clear coating, and a second distinctly turbid non–fluorescent material applied over it, consistent with the conservation records noting that both a wax (Cosmoloid 80H) and a synthetic resin (Laropol K) had previously been applied to the surface.

The cross-sectioned sample was stained with reactive fluorescent dyes, and yielded positive results for both lipid (+Rhodamine B) and fatty acid moieties (Bromomethylmethoxycoumarin) on staining.



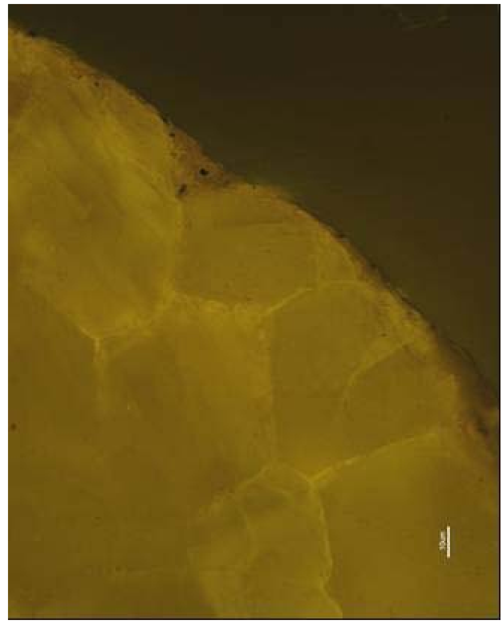


Figure 6 (left). Green excitation stained with RHOB, (.02% Rhodamine B in ethanol). Photograph by Wolbers.

Figure 7 (right). Violet light stained with BMMC (6,7 Bromomethylmethoxycoumarin .25% in acetone). Photograph by Wolbers.

This suggested that both lipid moieties were present in the sample and that in all likelihood calcium salts of these fatty materials would be present as well, given the $CaCO_3$ matrix of the stone. The presence of even weakly acidic materials like long chain fatty acids might initiate the breakdown of $CaCO_3$, and yield calcium salts of these fatty acids which are highly insoluble materials normally (Pohle 1944). It also suggested that a combination of surfactant and chelating cleaning systems might be the most effective approach to removing the soiling materials.

Testing

Reaching the deeper soiling and staining materials within the stone surface first required reducing the overall surface burden of wax-resin material (the protective coating applied in 1988). A xylene gel was chosen for this, because pure solvents that would solvate the wax and resin materials would risk driving more material into the porous stone surface at the moment of their dissolution. Solvent gels like the one used are essentially surfactant and polymer complexes carried in solvent systems (Wolbers 2000). The surfactant in this case was Ethomeen C-12 (Akzo Chemie, available through Talas, NYC) an ethoxylated cocamine derivative. As a ‘basic’ material, the Ethomeen could be bound ionically to a polyacidic material like Carbopol 954 (a polyacrylic acid material produced by B.F. Goodrich, available through Talas. NYC) to form a stable polymer/surfactant complex. The Ethomeen still retains much of its surfactant-like character, even 'bound' to the polymer. The advantage is two-fold in this arrangement: the viscosity of the gels produced from low concentrations (1-2% w/w) in solvents of surfactant-polymer complex are quite high (40-60K centipoise), limiting diffusion of materials into the stone surface. An added benefit is the relative ease in clearing these materials from even porous surfaces; the polymer-surfactant complex is so high in molecular weight that they are physically restricted from penetration and more likely to be retained at the surface.

The composition of the xylene gel used was:

100ml xylene
20ml Ethomeen C-12
2 g Carbopol 954
1ml de-ionized water

The gel was applied to the stone surface in areas 10 cm square, allowed to dwell for one minute, stirred with a soft brush, and wiped from the surface along with solubilized materials. The area thus treated was then rinsed and cleared with mineral spirits to remove the last remnants of gel.

After surface cleaning and coating removal, discoloration of the stone remained. As a second stage of cleaning, a poultice approach was chosen to allow for extended contact time, provide an absorbent matrix for retention of solubilized materials, and to effectively bring the required surface chemistry to bear on the residual staining or soiling material present both at the surface and deep within the stone.

The aqueous phase in the poultice featured a chelating material, nitrilotriacetic acid. The log dissociation constant for NTA with Ca^{+2} (7.60) favors the formation of Ca^{+2} NTA complexes in the presence of various other calcium salts, but not the dissociation of the stone substrate itself (log pK_{sp} $CaCO_3$ is 8.54). Under essentially CO_2 free conditions (e.g. under a gel or poultice) where air is restricted severely at the substrate surface or is completely unavailable, the most stable pH for a carbonate like marble is about 10.3 (Livingston 1992). At pH values this high however NTA would be of little use since, like most of the common anionic chelators, NTA works best above its highest pK_a (5.5) and below pH 9. By way of compromise, the pH of the cleaning system was elevated to about 9 using a sodium borate (pK_a 9.3) buffering system. A non-ionic surfactant (Triton XL-80N) was also included because of its general compatibility with the other ionic materials in the mixture (Triton X:-80N is an alkyloxypolyethyleneoxy-polypropyleneoxy ethanol type surfactant produced commercially by Union Carbide. As a neutral or non-ionic structure, it can be mixed with other ionic solutes without precipitating them from solution.) The HLB for Triton XL-80N is 12.5, and is just sufficient for detergency and solubilization of likely residual soiling, coating, and staining materials ('HLB' is an acronym for 'Hydrophile Lipophile Balance' number, which defines a surfactant's functionality and strength. See Wolbers for more detailed discussion of surfactants and HLB number in aqueous cleaning systems).

To summarize, the poultice contained the following aqueous solution:

100ml de-ionized water
0.5g sodium borate
0.5g NTA
6 drops Triton XL-80N

A small volume (approximately 2ml) of a dilute sodium hydroxide solution (1M NaOH, Sigma Aldrich) was added to induce rapid dissolution of the NTA and then the pH of the mixture was re-adjusted between 8.5 and 9 with a dilute HCl solution (1M HCl, Sigma Aldrich) using a calibrated standard glass electrode pH meter (Oakton, model WD-35624-22 pH Tester). Next the Triton X-L80N was added to the solution. The solution was then gelled using a xanthan gum, Vanzan-NFC (1% w/v, Vanderbilt Chemical Co).. This gelling agent is especially effective for aqueous media and can tolerate an unusually wide pH and ionic strength range and still maintain high viscosities. The gel was then further modified into a gel-paste by adding an equal volume of Whatman CF-11 cellulose fiber to create both a viscous and absorbent matrix for the poulticing effect. The texture of the gel-paste poultice can vary depending on the ratio of cellulose fiber added to the mix, from a light 'meringue'(5:5) to a consistency more like bread dough (5:7). Spot tests revealed that changes in texture affected the handling characteristics of the material without altering is effectiveness. During the treatment phase we found the dough consistency was easier to apply and to remove. Examination of the stone surface after treatment using 5X and 10X magnification revealed that the surface polish of the sculptures were undisturbed.

This two-step cleaning process was spot tested *in situ* over two days. In all, more than three dozen small cleaning tests were performed, with adjustments to working variables including changes to pH within the range of 8.0 to 10.0; and changes to dwell time between two and 20 hours, using a layer of thin polyethylene wrap to prevent evaporation. At the conclusion of the testing phase a contact time of 6 hours was established as the minimum needed for optimum performance. The final test areas were prominently located to help convince the decision makers the treatment method showed promise.

Treatment

The proposal for treatment included seven steps: 1) vacuum to remove loose dust and soil; 2) remove the old wax-resin coating and embedded soil using xylene gel; 3) clear the gel with mineral spirits using pre-cut absorbent cotton pads (Webril, Handi-Pads, available from Talas, NY) and cotton swabs; 4) apply the NTA gel paste poultice and cover with polyethylene film; allowing the mixture a minimum of 6 hours to work; 5) clear the gel paste using paper towels, Webril pads and swabs; 6) clear all residues with thorough water washing; and finally, 7) apply a protective coat of Renaissance microcrystalline wax. The wax-resin mixture previously applied has been reported to be more difficult to remove than wax alone. Since the new installation location did not require frequent washing the less complex coating was selected.

The sculpture *"America Mourning Her Fallen Brave"* was treated in the fall of 2005. Scaling up the method to a level appropriate to accomplish these treatments required an estimate of surface area for each sculpture, acquisition and preparation of materials, and relocation of the sculpture to a well-ventilated work site. The firm of George Young Company, Philadelphia, was contracted to move the sculpture and its two base elements to a work space in their warehouse. The sculpture and its base support were disassembled and moved in sections. This work space featured large doors on either side, allowing cross ventilation and diffuse ambient light from daylight. At the work area short piers of timber were erected to hold each of the elements above the floor at a reasonable working height.

The first treatment step after photographic documentation was vacuuming all surfaces to remove loose soil. Next the old coating of wax and grime was cleared using xylene gel, working from bottom to top. The xylene gel proved to be very efficient and could be cleared almost immediately using mineral spirits and cotton pads. This step required personal protective gear including respirators with organic vapor cartridges and disposable gloves rated for xylene exposure.

Once several broad passages were cleared of the old coating the gel-paste poultice was applied. The extended dwell time dictated a rhythm to the treatment's execution, with gel-paste poultice applied as the last step in the afternoon, followed by clearing of the gel-paste poultice the following morning, some 16 to 18 hours later. This working interval was a matter of convenience since no significant variation in results between the 6 hour minimum and longer exposures was noted during testing (Fig. 8).

After clearing and rinsing the previous day's poultice, the next adjacent section was cleared of wax and subsequently treated with gel paste poultice. No tide lines or visible boundary lines were observed as newly treated areas overlapped previous work (Fig. 9).

Figure 8. "*America Mourning Her Fallen Brave*". Detail; poultice has been applied over half of the face, covered in plastic wrap, and left overnight. Photograph by Berrett.

Figure 9. "*America Mourning Her Fallen Brave*". Detail; after removal of poultice and water rinsing. Photograph by Berrett.

During work it was useful to reserve an area that demonstrated this difference for a variety of visitors to the work site. Throughout the treatment process clearing the stone of both previous and current working materials was of critical concern. As work proceeded, each area was cleared of bulk material, then rinsed repeatedly with water and wiped dry (Figs. 10, 11).

Some of the deeper recesses required additional applications. In a few crevices the final cleaning was accomplished using a steam machine (Robby Steam machine VS 3000, 45-65 psi.).

When the sculptures were disassembled for movement to the work site, the base under each was found to include an internal metal armature that also required treatment. At the top of the hollowed base element there is set into the stone an iron ring with three spokes and a raised pin at its central hub. This fixed installation receives a wheel with five-spokes. Each spoke terminates with a steel roller (Fig. 12).

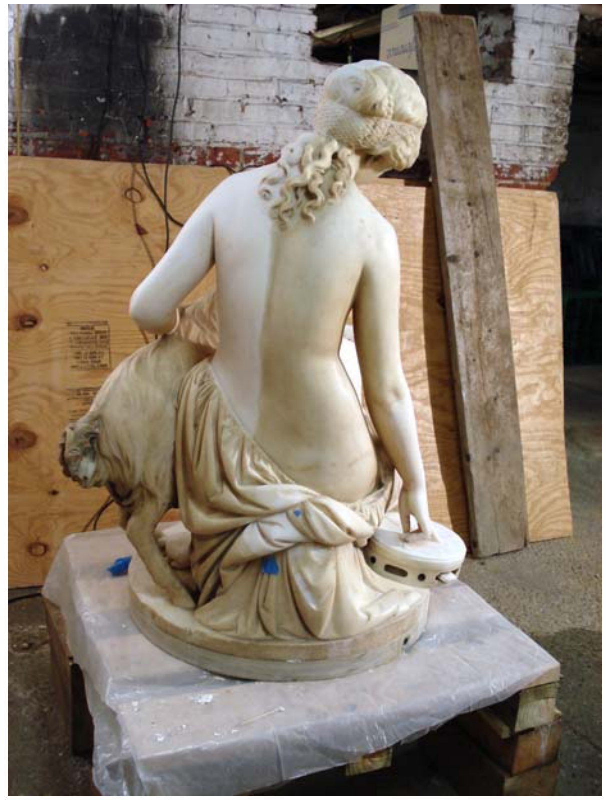


Figure 10 (left). "*Esmeralda*". Poultice applied over left arm, shoulder, and right forearm sections. Photograph by Naudé.

Figure11 (right). *"Esmeralda"*. After removal of poultice and clearing of working materials. Photograph by Naudé.

Figure12. "America Mourning Her Fallen Brave". Iron armature in upper section of base, rotating arm piece turns on central pin, after treatment. Photograph by Berrett.

The rollers move between the iron ring set in the base and a corresponding ring set into the lid, allowing the sculpture to be turned manually (Fig. 13).

Figure13. "*America Mourning Her Fallen Brave*". Iron ring mounted in underside of cover for base, before treatment. Photograph by Naudé.

It was not uncommon in the Victorian period to provide decorative handles to allow the viewer to rotate the sculpture on its base and consider the work in a different light. On both of these base units it was possible to thread decorative brass handles into steel bushings set into the stone allowing a change in orientation with very little effort. The iron elements were vacuumed and then cleaned of superficial rust using synthetic abrasive pads (3M Scotch-Brite) to loosen soils and oxidation without scratching the metal, and mineral spirits on cotton to clear surfaces. The cleaned metal was rinsed and dried with ethanol followed by acetone and then coated with microcrystalline wax applied with heat.

Small compensations to both sculptures were made using the mixture of polyvinyl acetate AYAC, ethylene acrylic acid copolymers A-C 540 and 580, and Irganox 1076 (Gänsicke and Hirx 1997). The fills were colored prior to application by adding Golden PVA paints into the melt chosen because the commercially prepared paints disperse more readily into the resin mixture than pure pigments (see Figs. 14, 15).

"Esmeralda" was treated in late January and early February of 2007 using the same materials and techniques. This project was carried out in a secure and well-ventilated area in the basement of the Union League building. The heavier soiling and deeper staining of this work resulted in even greater contrast between its 'before' and 'after' treatment, appearance (Figs. 16, 17).

Figure14. "*America Mourning Her Fallen Brave"*. Overall view, before treatment. Photograph by Berrett.

Figure15."*America Mourning Her Fallen Brave"*. Overall view, after treatment. Photograph by Berrett.

Figure16. *"Esmeralda"*. Overall view, before treatment. Photograph by Berrett.

Figure17. *"Esmeralda"*. Overall view, after treatment. Photography by Berrett.

Conclusion

In many ways this treatment is typical of the solubility problems that conservators confront routinely on these kinds of surfaces. The accumulation of coating materials, waxes, polishes, and residues from prior treatments (detergents, soaps, salts of acid and bases from cleaning, etc.) tend not only to occlude these surfaces, but present special challenges to the conservator in terms of the wide variety of materials likely to be encountered and in need of removal. One unifying feature in these cases is the inevitable presence of calcium itself from the substrate material, and concomitantly, the formation of relatively insoluble calcium salts with weakly acidic materials in these mixtures that make them so seemingly intractable. NTA as a chelator for calcium ions in particular will be a useful tool for conservators working on marble cleaning problems. NTA's ability to bind calcium is as high as practically possible without surpassing the stability of calcium carbonate itself, making it's inclusion in aqueous preparations for cleaning these types of surfaces an important new tool. The use of chelates in aqueous preparations for cleaning artifacts is not new, of course; both citrate and EDTA have found use as general chelating materials on a wide variety of artifact surfaces. But predictably, citrate would have a much weaker effect on marble cleaning problems than NTA (weaker binding to calcium, and therefore a weaker ability to dissociate other calcium salts present), and EDTA would be far too aggressive, surpassing the stability of calcium carbonate itself.

Acknowledgments

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Suppliers

Carbopol 954: Distributed by Talas, 20 W. 20th Street, 5th Floor, New York, NY 10011 www.talasonline.com

Ethomeen C-12: Distributed by Talas, New York, NY

Micromesh Abrasive Cloths: Obtained as a kit from Peachtree Woodworking Supply, 3250 Oakcliffe Ind. St., Atlanta GA (770 458 5539).

Nitrilotriacetic Acid 'NTA': Sigma cat no. N 9877, Sigma-Aldrich, 3050 Spruce St., St. Louis, MO 63103 www.sigma-aldrich.com

Vanzan NF-C: Product number 70506 XP, R.T. Vanderbilt Company, Inc. P.O. Box 8500-1361, Philadelphia, PA 19178-1361 www.rtvanderbilt.com

Whatman CF-11: Cellulose powder distributed by Bodman Indrustries, P.O. Box 2421, Aston, PA 19014

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