



Introduction

Walter De Maria's Pair of Small White Paintings – an Extraordinary Cleaning Challenge

Unvarnished paintings can prove difficult to clean if potentially water-sensitive materials are involved, and even more so if the paint is matte and monochrome white. A small-scale pair of paintings at The Menil Collection in Houston, Texas, by Walter De Maria (1935-2013) entitled "A Walk to Sign B" "B Walk to Sign A", 1961, 12 x 10 in. (30.6 x 25.4 cm), falls into this category. The works consist of white polyvinyl acetate paint on canvas with black plastic applications. Improper handling previous to the Menil's acquisition of the paintings, and a long period of storage in the artist's New York studio, including prolonged water exposure, led to a disfiguring soiling layer, darkened fingerprints, scuff marks and foxing-like spots.

The nature of the paint required a cleaning method with minimal mechanical impact, water release to surface, and risk of residues.*



Before treatment. Photo: Adam Neese

Paint Layer

Visual and analytical examination (XRF, FTIR and Raman) indicate the presence of two thin layers of paint containing differing amounts of titanium white pigment, calcium carbonate and silicates in a polyvinyl acetate (PVAc) binder. PVAc emulsion paints became available in the early 1950s as house paints, before acrylic paints made their appearance, and despite the development of PVAc artists' paints their use was fairly limited compared to other synthetic polymer paints [1]. PVAc emulsion paints contain the same types of additives typically found in acrylic emulsion paints, rendering them equally sensitive to aqueous and solvent cleaning methods.

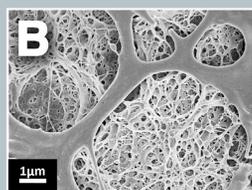
Nanorestore Gels®

The Nanorestore Gels® are novel hydrogels for cleaning artworks, developed at the Center for Colloid and Surface Science (CSGI) in Florence for the NANORESTART project (2015-2018). The Nanorestore Gels® Dry are based on a poly(2-hydroxyethylmethacrylate) and polyvinylpyrrolidone (pHEMA/PVP) semi-interpenetrated network, transparent and provide very high water retention.

Four different types of Nanorestore Gels® with water retention capacities decreasing from left to right.



The Nanorestore Gels® Peggy are based on polyvinyl alcohol (PVA) and polyvinyl alcohol/polyvinylpyrrolidone (PVA/PVP), opalescent and possess lower water retention abilities than the Nanorestore Gels® Dry. The gels come in standard-sized sheets of 5.9 x 3.9 in. (15 x 10 cm) of 2 mm thickness, or can be ordered custom-sized directly from the manufacturer (<http://www.csgi.unifi.it/products/gel.html>).



Gel matrix of a PVA/PVP gel. Image courtesy of Bonelli et al. 2019, p. 344

The idea behind the use of "rigid" hydrogels for cleaning is to confine cleaning fluids within a gel matrix that releases them in a controlled way onto the surface [2-4]. The Nanorestore Gels® combine high water retention with great flexibility, while allowing for a residue-free application.

Pioneering studies on their applicability and safety for artworks have been done in recent years at Tate and Los Angeles County Museum of Art (LACMA) [5-7].

References

- [1] Crook, J., Learner, T. 2000. *Modern Paints, The Impact of Modern Paints*, 21-24. New York: Watson-Guption Publications.
- [2] Baglioni, P., Chelazzi, D. (ed.) 2013. *Nanoscience for the Conservation of Works of Art*, RSC Nanoscience & Nanotechnology No. 28. Cambridge: RSC Publishing.
- [3] Baglioni, P., Chelazzi, D., Giorgi, R. 2015. *Nanotechnologies in the Conservation of Cultural Heritage – A compendium of materials and techniques*. Dordrecht: Springer.
- [4] Bonelli, N., Poggi, G., Chelazzi, D., Giorgi, R., Baglioni, P. 2019. Poly(vinyl alcohol)/Poly(vinyl pyrrolidone) hydrogels for the cleaning of art, *Journal of Colloid and Interface Science* 536 (2019) 339-348. <https://doi.org/10.1016/j.jcis.2018.10.025>.
- [5] Bartolotti A., Barker, R., Chelazzi, D., Bonelli, N., Baglioni, P., Lee, J., Angelova, L. V., Ormsby, B. 2020. Reviving WHAAMI! A comparative evaluation of cleaning systems for the conservation of Roy Lichtenstein's iconic painting, *Heritage Science* (2020) 8:35. <https://doi.org/10.1186/s40494-020-0350-2>.
- [6] Bartolotti, A., Maor, T., Chelazzi, D., Bonelli, N., Baglioni, P., Angelova, L. V., Ormsby, B. 2020. Facilitating the Conservation treatment of Eva Hesse's *Addendum* through practice-based research, including a comparative evaluation of novel cleaning systems, *Heritage Science* (2020) 8:35. <https://doi.org/10.1186/s40494-020-00378-z>.
- [7] Hoover, C., Maccarelli, L. 2020. *Nanogels. An Investigation into Nanotechnologies for the Cleaning of a Painting by Ernst Ludwig Kirchner*. Oral presentation at: 48th American Institute for Conservation (AIC) Virtual Annual Meeting, July 2, 2020.

Preliminary Tests

Materials Tested

- Dry cleaning materials: sponges, erasers (proved unsuitable)
- Aqueous solutions with buffered or adjusted pH (5.7, 6.0, 7.0, 7.5) and conductivity (1000-1800 $\mu\text{S}/\text{cm}$), with and without low amounts of nonionic surfactants and chelating agent (citrate)
- Delivery systems: Rigid gels agarose (3.5, 4 and 4.5%) and Nanorestore Gels® Extra Dry (now MVWR = medium water retention), Peggy 5 and Peggy 6, and non-woven tissues Evolon® CR and Paraprint OL 60



Left: Agarose and Nanorestore Gel® plugs on mockup (scale: metric)
 Right: Water release of the gels on blotter after approx. 1 min

Surface Measurements

For the purpose of establishing suitable cleaning solution parameters, pH and conductivity measurements were taken on soiled and unsoiled areas of the paint surface with 4% agarose plugs. After 5 minutes on the surface, they were placed into the sensor units of pH and a conductivity meters (Horiba LAQUAtwin series). Based on the results, a solution pH of 6.0 and conductivity of 1000 $\mu\text{S}/\text{cm}$ was considered a good starting point.

Methodology

A first test series was done with cotton swabs loaded with the different solutions. After selecting an efficient solution, delivery systems were tested in a second test series. The gels were prepared by cutting out small 3 x 3 mm plugs with a plastic brush cover, and loading the plugs with the solutions by immersion over 24 hours. The gels were blotted on paper before use. Tissues were placed on the surface dry and wetted with loaded cotton swabs.

The visual assessment for the swab tests was done in situ and on photomicrographs after:

- 8 swab rolls (1 swab roll = back and forth)
- 50 swab rolls or until clean.

For the delivery systems (gels and tissues) after:

- 10 min,
- 20 min,
- 30 min exposure (under Dartek® cover, acrylic sheet and light weight).

The level of cleaning was evaluated on a scale 1-10 (1 = unchanged, 10 = clean), and potential undesired changes described.



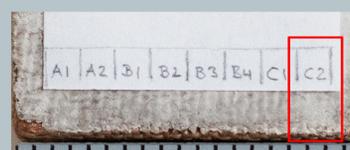
Test setup with gel plugs

Test Results

Small test fields

A buffer solution containing 0.1% (w/v) citrate and 0.2% (w/v) ECOSURF™ EH-9 at pH 6.0 and 1800 $\mu\text{S}/\text{cm}$ (C2) showed the best cleaning results (rated 8) of all solutions in the swab tests, while no adverse changes of the surface were observed. The surfactant and citrate test fields were rinsed with acetic acid/ammonium hydroxide buffer at pH 5.7 and 1000 $\mu\text{S}/\text{cm}$.

The delivery system that produced the best results in terms of cleaning efficacy and preservation of the surface quality were 4% agarose and both Peggy gels. The most significant cleaning effect was observed within



Swab test fields with buffer (A), buffered surfactant (B) and mixed surfactant and citrate (C) solutions (scale: imperial)

Larger test fields

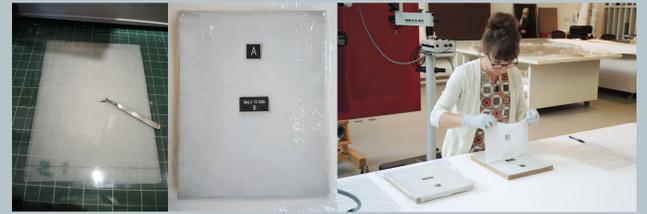
In areas measuring approx. 30 x 30 mm, sheets of 4% agarose and Peggy 5 were placed on the surface for 30 min under light weight. While agarose produced an insufficiently and unevenly cleaned surface due to its lack of conformity to the surface, the area cleaned with Peggy 5 was visibly lighter. Remaining dark scuff marks were reduced with swabs.



Before treatment Peggy 5 on surface After gel cleaning After treatment

Cleaning Treatment

Treatment Steps



Left: Cutting "windows" into the gels. Center: Peggy 5 gel on the painting with Dartek® cover during treatment. Right: Peeling off the gels after treatment

- 1 Nanorestore Gels® Peggy 5 sheets ordered custom-sized, slightly larger the dimensions of the paintings
- 2 Soaked in deionized water for 4 days (water exchanged daily) and cut to shape with openings for the plastic applications
- 3 Soaked in cleaning and rinsing solutions for 24 hours
- 4 Cleaning gels removed from container and blotted on both sides
- 5 Gels placed on the painting, covered with Dartek® and pressed gently to ensure close conformity with the surface
- 6 Cleaning gels removed from paint surface after 30 minutes
- 7 Rinsing gels removed from container and blotted on both sides
- 8 Gels placed on the painting, covered with Dartek® and pressed gently to ensure close conformity with the surface
- 9 Rinsing gels removed from paint surface after 15 minutes
- 10 All used gels placed in fresh deionized water for storage and future re-use
- 11 Treatment repeated once more with fresh gels



Cleaning gel before (left) and after use (right), visibly darkened by the absorbed grime and dirt

Treatment Results

The gel treatment resulted in a visibly brighter appearance of the paint and fainter stains and scuff marks, while retaining the particular, "imperfect" character of the paintings shaped by their life in the artist's studio. Because further cleaning with swabs resulted in enhanced gloss, remaining pronounced dark marks were instead addressed by retouching.



After gel cleaning treatment. Photo: Adam Neese

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