Nanotechnology & Materials Testing:

Using Nanoparticles to Tag Consolidants to Determine Depth of Penetration

Organization: New York State Office of State Parks, Recreation & Historic Preservation
Principal Investigator: Joyce Zucker
Team: Seyfollah Maleki, Professor of Physics, Union College, Schenectady, NY;
Mary Betlejeski & Erin Moroney, Conservators, New York State Office of Parks, Recreation & Historic Preservation

National Center for Preservation Technology and Training
Technology Serving the Future of America's Heritage
www.ncptt.nps.gov/products
© 2008 NCPTT

Nanotechnology & Materials Testing:
Using Nanoparticles to Tag Consolidants to Determine Depth of Penetration

Grant No. MT-2210-10-NC-03
Organization: New York State Office of Parks, Recreation & Historic Preservation
Principal Investigator: Joyce Zucker
Team: Seyfollah Maleki, Professor of Physics, Union College, Schenectady, NY
Mary Betlejeski & Erin Moroney Conservators, New York State Office of Parks, Recreation & Historic Preservation
Contact: Joyce Zucker. joysof@verizon.net
Date: June 30, 2011

2. Table of Contents ii

3. Executive Summary iii

4. Introduction 1

5. Methods & Materials
- **Identification of Materials** 2
- **Solvent-Nanoparticle Compatibility Test 1** 6
- **Nanoparticle-Matrix Compatibility Test 2** 10
- **Nanoparticle–Consolidant Test 3** 15
- **Nanoparticle/Consolidant-Matrix Compatibility Test 4** 17
- **Pilot Project** 26

6. Results & Discussion 33

7. Conclusion 34

8. Acknowledgments 35

9. Bibliography 36

3. Executive Summary

A research team including conservators from the New York State Bureau of Historic Sites, scientists with the Physics Department of Union College, Schenectady, NY, and scientists from the nanotechnology industry began experimenting with nanoparticles to advance conservation treatments in the field of historic preservation. This collaboration was prompted by a challenging mural conservation project. The mural suffered from decades of deterioration and multiple failed conservation treatments making the need for a new approach apparent.

Before undertaking yet another conservation campaign, the structure and materials of the mural were thoroughly analyzed and a range of consolidation treatments were considered. As part of this investigation a variety of consolidants were tested and evaluated on mockups of the mural's structure.

A critical factor in evaluating the consolidant's effectiveness was to measure it's depth of penetration through the mockups. Various techniques exist to determine depth of penetration but research has found that these techniques are unreliable. Advancements in nanotechnology have offered an alterative to these traditional methods.

We theorized that nanoparticles could be used as an effective tagging material to determine depth of penetration. While nanoparticles exhibit a wide range of characteristics, we only focused on nanoparticles that fluoresced under ultraviolet light. The technique involved adding a small amount of nanoparticles in solution to a liquid consolidant. The tagged consolidant was then applied to the surface of a sample. The nanoparticles served to tag the consolidant, enabling the normally invisible consolidant to be seen under UV light. This technique was tested on a representative range of consolidants and matrices.

Unfortunately, compatibility problems were soon encountered. One of the problems was a complete immiscibility between the nanoparticles and alcohols. The second incompatibility problem encountered was between nanoparticles and select matrices. Electrostatic forces within some matrices repelled the nanoparticles thus preventing their penetration through the matrix.

Successful results were achieved with adobe, mortar, limestone and marble. This technique was also very successful with materials commonly used for wall painting and ornamental plaster. The technique was applied to small samples of the mural that inspired the project. The nanoparticles revealed that the consolidants had completely failed to penetrate beyond the paint layers. This explained why all previous consolidation treatments were unsuccessful, and will help to develop an effective conservation treatment.

We were disappointed to discover the techniques limitations, but we feel as the field of nanotechnology grows so to will its practical use within the field of historic preservation.

4. Introduction

Building and objects are in a constant state of deterioration and as a result require consolidation treatments. Our ability to determine the potential success of a treatment is undermined by our inability to accurately determine the depth of penetration of the consolidant. The need for a reliable technique was apparent while examining an mural that has continued to deteriorate since it's execution in the 1920's.

The mural, painted by Robert Withrop Chanler at Coe Hall, Planting Fields State Park, began flaking soon after its completion. The whimsical mural depicts a Wyoming landscape with bison, elk and Native Americans on horseback. Chanler's use of materials and technique combined with dramatic changes in environmental conditions led to chromic flaking, spalling and loss. Over decades multiple attempts have been made to stabilize the mural, with limited success.

Various techniques exist to determine depth of penetration but research has found that these techniques may impede penetration, require subjective observations, or result in imprecise measurements. To effectively track depth of penetration, the tagging material must be stable, inert, compatible, visible and not impede penetration. Advancements in nanotechnology may have provided a solution.

Nanoparticles are microscopic particles with a least one dimension less than 100nanometers. A nanometer is equal to one billionth of a meter. Working with scientists with the Physics Department of Union College, Schenectady, NY, and scientists from the nanotechnology industry, conservators from New York State Bureau of Historic Sites began experimenting with nanoparticles to determine depth of penetration.

The technique involves adding a small amount of nanoparticles in solution to a liquid consolidant.[1] The nanoparticles should serve to tag the consolidant, enabling the normally invisible consolidant to be seen under UV light. Standard consolidants used in historic preservation and conservation will be tested.

The nanoparticles selected for testing were not only stable and inert, but also displayed an intense visible fluorescence under ultraviolet (UV) light. The research began with Quantum Dots, a specific class of nanoparticle, but was later expanded to include a wider range of fluorescing nanoparticles. The Quantum Dot's immiscibility with alcohols prompted the investigation.

A series of tests will be performed to determine compatibility between:

- Solvent and nanoparticle
- Nanoparticle and consolidant
- Nanoparticle and matrix
- Nanoparticle/consolidant and matrix

The results will then be confirmed using basic laboratory tests and advanced analytical tests. If these tests prove that the nanoparticle successfully traveled with the consolidant through the matrix, the technique will be applied to mock ups of the Coe Hall mural. Finally, the technique will be tested on small samples of the mural to develop a successful consolidation treatment.

[1] This technique was developed for testing purposes only. It is not recommended that nanoparticles be used in conservation treatment.

5. Methods and Materials

Identification of Materials

The first step in the project was the identification of materials including a list of consolidants, material matrixes and nanoparticles.

Consolidants
A range of consolidants commonly used in the conservation field were identified. This selection included consolidants from both fine art conservation and architectural conservation disciplines. The following consolidants were identified to be included in the research project:

Chart 1

#	Name	Base	Type
1	Paraloid B-72	methyl acrylate and ethyl methacrylate	synthetic resin
2	Lascaux P550	butyl methacrylate	synthetic resin
3	PVA-AYAA	polyvinyl acetate	synthetic resin
4	Isinglass	water soluble fish glue	collegen
5	Ethulose	Ethyl hydroxyethyl cellulose	cellulose
6	Prosoco OH100	Silicic ethyl esters	Ethyl silicate
7	Prosoco H100	Silicic ethyl esters	Ethyl silicate
8	Cyclododecane	cyclic alkane	cyclic alkane

Matrix Materials
In addition to the mock-up of Planting Fields mural a range of building materials were also tested. All of the materials tested were artificially aged to replicated the compromised condition of materials that are generally consolidated.

Chart 2

#	Material	Base Composition
1	Mortar Cube	Calcium hydroxide, silica
2	19th c. plaster	Calcium hydroxide, silica, animal hair
3	Brick	Silica, clays, calcium hydroxide, iron oxide, manganese
4	Marble	Calcium carbonate
5	Limestone	Calcium carbonate
6	Sandstone	Calcium carbonate, silica, iron oxide, clays
7	Adobe	Silica, clays
8	Gesso	Calcium sulphate
9	Sugar Cube	Sucrose
10	Planting Field's mural mock-up	Plaster, gesso & paint layer Calcium hydroxide, silica, calcium sulphate, pigment

Nanoparticles

A range of nanoparticle that fluoresce under ultraviolet light were selected. Initially the research was limited to Quantum Dots. After solubility issues were discovered a wider range of nanoparticles were explored. These included phosphor dots, silica nanoparticles and polystyrene nanoparticles.

Chart 3
Nanoparticle Identification

#	Class	Emission λ	Manufacturer Name	Type
1	Quantum Dots	520nm	Evident T2 Evi Dot™ Adirondack Green	Semiconductor crystals
2	Quantum Dots	520nm	Evident T1 Evi Dot™ Adirondack Green	Semiconductor crystals
3	Quantum Dots	540nm	Evident T2 Evi Dot™ Catskill Green	Semiconductor crystals
4	Quantum Dots	560nm	Evident T2 Evi Dot™ Hops Yellow	Semiconductor crystals
5	Quantum Dots	580nm	Evident T2 Evi Dot™ Birch Yellow	Semiconductor crystals
6	Quantum Dots	600nm	Evident T2 Evi Dot™ Fort Orange	Semiconductor crystals
7	Quantum Dots	620nm	Evident T2 Evi Dot™ Maple Red-Orange	Semiconductor crystals
8	Quantum Dots	625nm	eBioscience eFluor™ eFluor™ 625	Semiconductor crystals
9	Quantum Dots	650nm	eBioscience eFluor™ eFluor™ 650	Semiconductor crystals
10	Phosphor Dots	617nm	Sun Innovations™ YVE1005	Yttrium vanadium oxide
11	Phosphor Dots	620nm	Sun Innovations™ YVE1101	Yttrium vanadium oxide
12	Polystyrene Nanoparticles	620nm	Corpuscular™ Nile Red (Plain)	Polystyrene rhodium B
13	Polystyrene Nanoparticles	620nm	Corpuscular™ Nile Red (Carboxylated)	Polystyrene rhodium B
14	Silica Nanoparticles	620nm	Corpuscular™ Red SiO2 Silica (Plain)	SiO2

Quantum Dots
The Quantum Dots used for this project are nanosized semiconductor crystals composed of Cadmium Slenide/Zinc Sulfide (CdSe/ZnS). The structure of the quantum dot nanocrystal consists of a core particle of cadmium selnide (CdSe) surrounded by a outer shell of zinc sulfide (ZnS). Quantum Dots exhibit intense, stable and long lasting fluorscent brightness and posess narrow emission spectrum. Quantum Dots are avaible in a range of fluorecent wavelengths ranging from 420nm to 680nm. The emission wavelenth of the quantum dot is defined by the particle size; smaller particles emit in the blue spectrum while large particles emit in the red shifted specturm. Quantum Dots fluorsce at a wide spectrum (300-400nm) but the intensity of the fluorences peaks around 400nm.

Evident T1 EviTags™
- Are coated with a sythetic coating to make them water stablized
- T1 EviTags™ are packaged in water.
- Available emissions 520nm—620nm
- The T1 EviTags™ were selected for their possible use with water based consolidants.

Evident T2 EviTag™
- The natural ligand surface of the T2 EviTags™ is uncoated and therefore not water stabalized.
- T2 EviTags™ are packaged in tolune.
- Available emissions 520nm—620nm
- The T2 EviTags™ were selected for their possible use with aromatic solvents.

eBioscience eFluor™ Nanocrystals
- The natural ligand surface of the quantum dot is uncoated and therefore not water stabalized.
- eFluor nanocrystals are packaged in tolune.
- eFluor nanocrystals were selected for their possible use with aromatic solvents.
- Available emission 490nm—700nm.
- The eBioscience eFluor™ Nanocrystals were selected for their possible use with aromatic solvents.

Phosphor Dots
Phosphor Dots are nanosized particles of natually fluorscent rare earth elements. Rare earth elements or rare earth metals are a specific list of chemical elements (metals) from the periodic table. Unlike Quantum Dots, the emission wavelegth of phosphor dots are not dependant on particle size. Phosphor dots require a narrow band uv absorption they peak at 325nm.

Phosphor Dots
- They are prepared in an aqueous solution.
- Specific emission wavelenth based on chemical composition.
- Carboxyl functionalized variety may be compatable with alcohols.
- Phosphor Dots were selected for their possible use with water based consolidants and alcohols.

Polystryene Nanoparticles
Polystryene nanoparticles are produced via emulsion and dispersion polymerizations; some of them are surface functionalized with carboxyl groups for covalent conjugation.[1] Polystryrene nanoparticles are composed of linear polystryene without any cross-linking agent.

[1]. Phosphorex, Inc. "Plain Polymer Microsphers & Nanospheres" Phsophorex, http://www.phosphorex.com.

Polystryrene Nanoparticles (Plain)
- Are prepared in an aqueous solution and they can not tolerate organic solvents.
- Are 'promoted' as stable in some water miscible solvents such as alcohols.
- Available in a range of emission wavelengths 400-650nm
- Polystryrene Nanoparticles (Plain) were selected for their possible use with alcohols.

Polystryrene Nanoparticles (Carboxylated)
- Are prepared in an aqueous solution and they can not tolerate organic solvents.
- Are 'promoted' as stable in some water miscible solvents such as alcohols.
- Available in a range of emission wavelengths 400-650nm
- Polystryrene Nanoparticles (Carboxylated) were selected for their possible use with alcohols.

Silica Nanoparticles
Core shell silica nanopartilces are fluorscent particles based on organic dyes covalently incorporated into a silica matrix.

Silica Nanoparticles
- They are prepared in an aqueous solution.
- Are an orgianic dye encapsulated in a silica core.
- Available in a red, yellow and green emisssion wavelengths.
- Silica nanoparticles were selected for their possible use with water based consolidants and alcohols.

Solvent—Nanoparticle Compatibility Tests 1

In order to determine if the nanoparticles were compatible with each consolidant a number of experiments were performed. Initial tests were performed based on manufacture's product description regarding chemical compatibility. The solvent for each of the selected consolidants was tested for solubility with nanoparticles. The solvents tested were aromatics, alcohols, ketones and water.

Test 1.1—Test Tube

The quantum, dots were sonified[1] for 5 minutes according to manufactures instructions (the aqueous nanoparticles do not require sonification). Using a micropipettor, .1µL of nanoparticles were added to 1 ml of each solvent. The solutions were then shaken and then sonified for an additional 5 minutes. The test tubes were then examined under ultraviolet light at 325nm and 350nm.

Chart 5

Nanoparticle	Toluene	Xylene	Ethanol	Acetone	Water
Evident T2 Evi Dot™ Adirondack Green	Soluble	Soluble	Slightly soluble	NA	NA
Evident T1 Evi Dot™ Adirondack Green	NA	NA	Insoluble	Slightly soluble	Soluble
Evident T2 Evi Dot™ Catskill Green	Soluble	Soluble	Slightly soluble	NA	NA
Evident T2 Evi Dot™ Hops Yellow	Soluble	Soluble	Slightly soluble	NA	NA
Evident T2 Evi Dot™ Birch Yellow	Soluble	Soluble	Slightly soluble	NA	NA
Evident T2 Evi Dot™ Fort Orange	Soluble	Soluble	Slightly soluble	NA	NA
Evident T2 Evi Dot™ Maple Red-Orange	Soluble	Soluble	Slightly soluble	NA	NA
eBioscience eFluor™ 625	Soluble	Soluble	Slightly soluble	Slightly soluble	NA
eBioscience eFluor™ 650	Soluble	Soluble	Slightly soluble	NA	NA
Sun Innovations™ YVE1005 (Plain)	NA	NA	Insoluble	NA	Soluble
Sun Innovations™ YVE1101 (Carboxylated)	NA	NA	Insoluble	NA	Soluble
Corpuscular™ Nile Red (Plain)	NA	NA	Insoluble	NA	Soluble
Corpuscular™ Nile Red (Carboxylated)	NA	NA	Insoluble	Slightly soluble	Soluble
Corpuscular™ Red SiO2 Silica (Plain)	NA	NA	Insoluble	NA	Soluble

Solvent—Nanoparticle Compatibility Chart

Based on the above test only the nanoparticles that were completely soluble or slightly soluble in the solvent were selected for further testing. It was determined that solubility was dependant on the class of nanoparticle.

- Quantum Dots (w/ out water stabilization) are completely soluble in aromatics.
- Quantum Dots (water stabilized) are completely soluble in water.
- Phosphor Dots are completely soluble in water.
- Plain Polystyrene nanoparticles are completely soluble in water.
- Carboxylated Polystyrene nanoparticles are completely soluble in water and slightly soluble in acetone.
- Silica nanoparticles are completely soluble in water.

[1]A 3/4 Gallon Cole Palmer Ultrasonic Cleaner.

Test 1.2—Fluorescent Intensity Test

The intensity of the visible fluorescence was also noted. Certain solvent-nanoparticle combinations can result in quenching. Quenching occurs when the nanoparticle surface is degraded, diminishing of visible fluorescence of the nanoparticle under ultraviolet light. Nanoparticle quenching can result from a chemical reaction with the solvent, exposure to temperature extremes or long term light exposure.

Chart 6
Solvent/Nanoparticle Fluorescence Intensity

Nanoparticle	Toluene	Xylene	Ethanol	Acetone	Water
Evident T2 Evi Dot™ Adirondack Green	Weak fl.	Weak fl.	Weak fl.	NA	NA
Evident T1 Evi Dot™ Adirondack Green	NA	NA	Weak fl.	Weak fl.	Weak fl.
Evident T2 Evi Dot™ Catskill Green	Weak fl.	Weak fl.	Weak fl.	NA	NA
Evident T2 Evi Dot™ Hops Yellow	Moderate fl.	Moderate fl.	Weak fl.	NA	NA
Evident T2 Evi Dot™ Birch Yellow	Moderate fl.	Moderate fl.	Weak fl.	NA	NA
Evident T2 Evi Dot™ Fort Orange	Strong fl.	Strong fl.	Weak fl.	NA	NA
Evident T2 Evi Dot™ Maple Red-Orange	Strong fl.	Strong fl.	Weak fl.	NA	NA
eBioscience eFluor™ eFluor™ 625	Strong fl.	Strong fl.	Weak fl.	Moderate fl.	NA
eBioscience eFluor™ eFluor™ 650	Strong fl.	Strong fl.	Weak fl.	NA	NA
Sun Innovations™ YVE1005	NA	NA	Weak fl.	NA	Strong fl.
Sun Innovations™ YVE1101	NA	NA	Weak fl.	NA	Strong fl.
Corpuscular™ Nile Red (Plain)	NA	NA	Weak fl.	NA	Strong fl.
Corpuscular™ Nile Red (Carboxylated)	NA	NA	Weak fl.	Weak fl.	Strong fl.
Corpuscular™ Red SiO2 Silica (Plain)	NA	NA	Weak fl.	NA	Strong fl.

Based on the above test only the nanoparticles that displayed a strong fluorescence in the solvent were selected for further testing. It was determined that nanoparticles with an emission wavelength of 560nm or greater were most practical for using as a visible marker.

Image 1. Solvent—Nanoparticle Compatibility Test

A range of quantum dots in xylene.
0.1µL of quantum dot in 1ml of xylene.

1: Evident T2 Evi Dot™ - Hops Yellow
2: Evident T2 Evi Dot™ - Birch Yellow
3: Evident T2 Evi Dot™ - Adirondack Green
4: Evident T2 Evi Dot™ - Maple Red Orange
5: Evident T2 Evi Dot™ - Fort Orange
6: Evident T2 Evi Dot™ - Catskill Green

Test 1.3—Capillary Tube Test

Additional miscibility tests were preformed on the solvent/nanoparticle solutions to confirm the results from Test 1.

Each of the solvent/nanoparticle solutions was drawn up in a capillary tube. The solution was drawn up approximately 2cm. The outer edge of the tube was cleaned and the tubes were mounted in putty. The capillary tubes were then observed under ultraviolet light.

The capillary tube test is more refined test than the initial test tube test. The capillary action that draws the solution into the tube separates insoluble materials from one another.

Test 1.3 confirmed the initial test results.

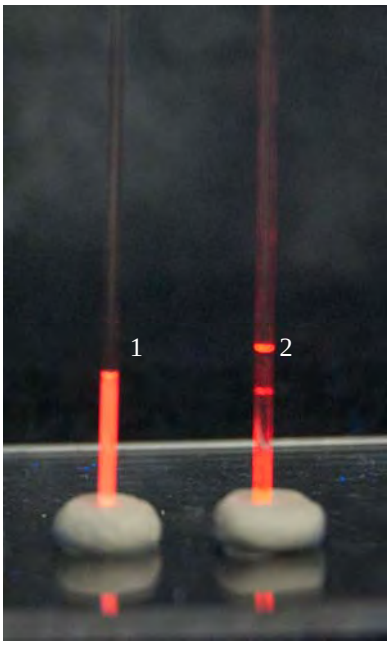


Image 2. Solvent—Nanoparticle Compatibility Test 1.3
eBioscience eFluor™ 625 in
1. xylene, 2. water
350nm UV light

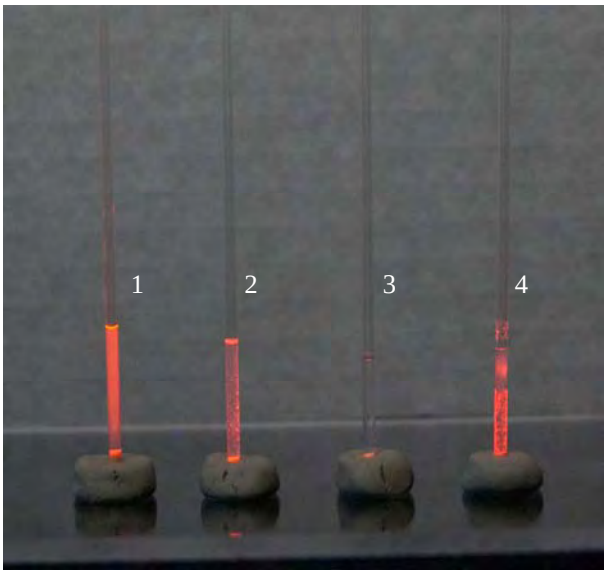


Image 3.
Solvent—Nanoparticle Compatibility Test 1.3
Evident T2 Evi Dot™ Maple Red-Orange in
1. xylene, 2. ethanol, 3. acetone, 4. water
350nm UV light

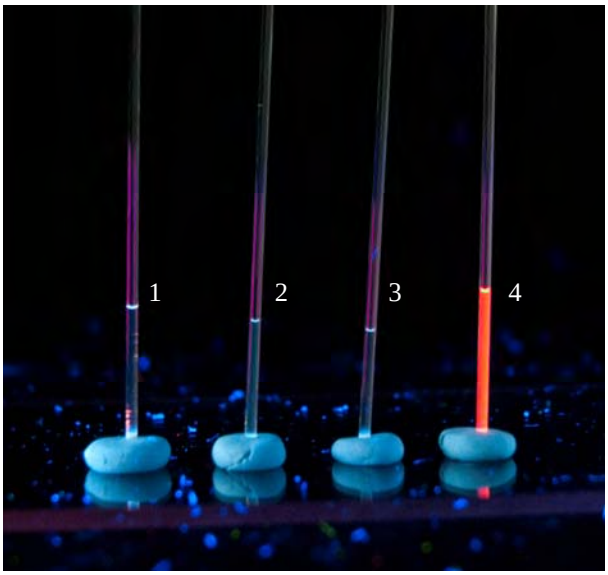


Image 4.
Solvent—Nanoparticle Compatibility Test 1.3
Sun Innovations™ YVE1005 in
1. xylene, 2. ethanol, 3. acetone, 4. water
325nm UV light

Test 1.4—Filter Paper Test

Paper chromatography was preformed on the solvent-nanoparticle solutions to further confirm that the nanoparticle would travel with the solvent and not separate out of the solution.

Each of the "slightly soluble" and "soluble" solvent-nanoparticle solutions were applied drop wise by pipette to the center of a piece of Whatman #4 Filter Paper. The dispersion pattern was outlined and the paper was allowed to dry. The filter paper was examined under ultraviolet light and in all cases the visibly fluorescing nanoparticle had traveled with the solvent.

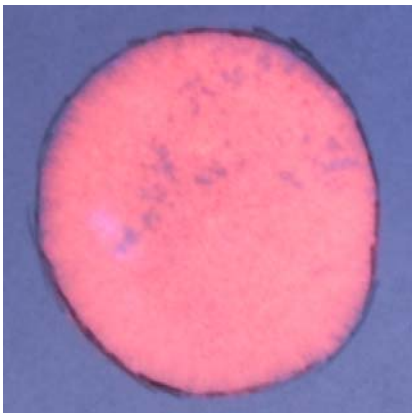


Image 5.
Solvent—Nanoparticle Compatibility
Test 1.4
Evident T2 Evi Dot™
Maple Red-Orange in xylene
350nm UV light

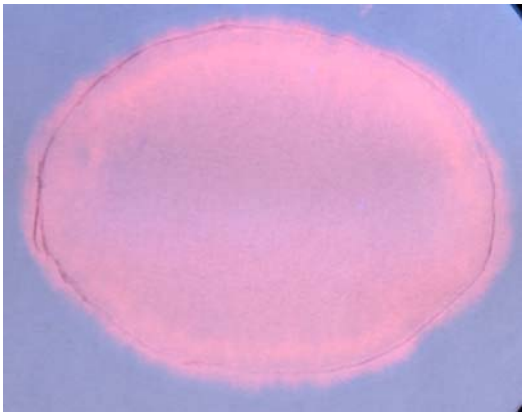


Image 6.
Solvent—Nanoparticle Compatibility
Test 1.4
Sun Innovations™
YVE1005 in water
325nm UV light

Test 1. Results
Solvent—Nanoparticle Compatibility
All of the test results produced consistent solvent-nanoparticle pairings. Subsequent testing will be conducted using the solvent—nanoparticle combinations identified in Chart 6.

Chart 6
Miscible Solvent—Nanoparticle Pairings

Solvent	Nanoparticles
Aromatics	Evident T2 Evi Dot™ , eFluor™,
Alcohols	Evident T2 Evi Dot™
Ketones	Evident T1 Evi Dot™, Sun Innovations eFluor™, Corpuscular Polystyrene Nanoparticles (Carboxylated)
Water	Evident T1 Evi Dot™, Sun Innovations Phosphor Dots™ ,Corpuscular Polystyrene Nanoparticles, Corpuscular Silica Nanoparticles

Nanoparticle—Matrix Compatibility Test 2

The purpose of this test was to determine if the solvent-nanoparticle solutions are compatible with each of the matrixes. It is crucial that the nanoparticle travel with the solvent through the matrix and not separate out of solution.

Test 2.1—Crossection Analysis
The nanoparticles were sonified for 5 minutes according to manufacturer's instructions. Using a micropipettor, .1µls of nanoparticles were added to 1ml of each solvent. The solutions were shaken and then sonified for an additional 5 minutes. The nanoparticle– solvent solution was then applied by pipette to the selected matrix. The intent was to only saturate one half of the sample. The sample was allowed to dry, and then cut to reveal the crossection. The crossection was examined under UV light. Each step was photo documented under both halogen and UV light.

As observed under UV light, the nanoparticle—matrix compatibility was determined by the even penetration of the nanoparticles through the matrix. A concentration of nanoparticles on the surface with limited penetration indicated incompatibility between the nanoparticle and matrix.

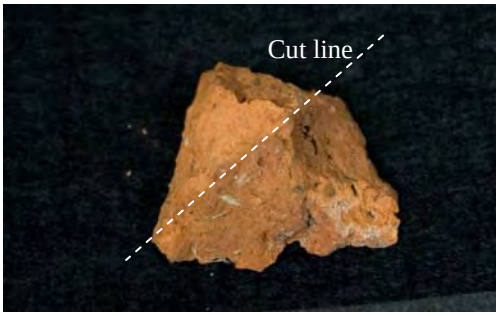


Image 7. Nanoparticle-Matrix Compatibility Test
Evident T2 EviDot™ Maple Red-Orange applied to brick sample under halogen light.

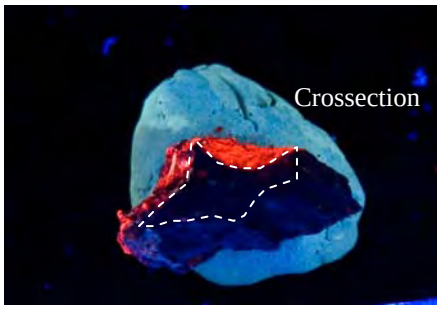


Image 8. Nanoparticle-Matrix Compatibility Test Crossection
Evident T2 EviDot™ Maple Red-Orange applied to brick sample under ultraviolet light. The fluorescing nanoparticles did not penetrate through the sample indicating a lack of compatibility with the matrix.

Image 9. Nanoparticle-Matrix Compatibility Test
Evident T2 EviDot™ Maple Red-Orange applied to mortar sample under halogen light.

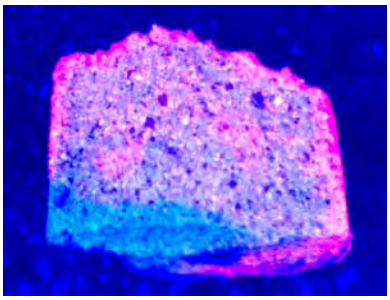


Image 10. Nanoparticle-Matrix Compatibility Test Crossection
Evident T2 EviDot™ Maple Red-Orange applied to mortar sample under ultraviolet light. Fluorescing nanoparticles throughout indicate a compatibility with the mortar.

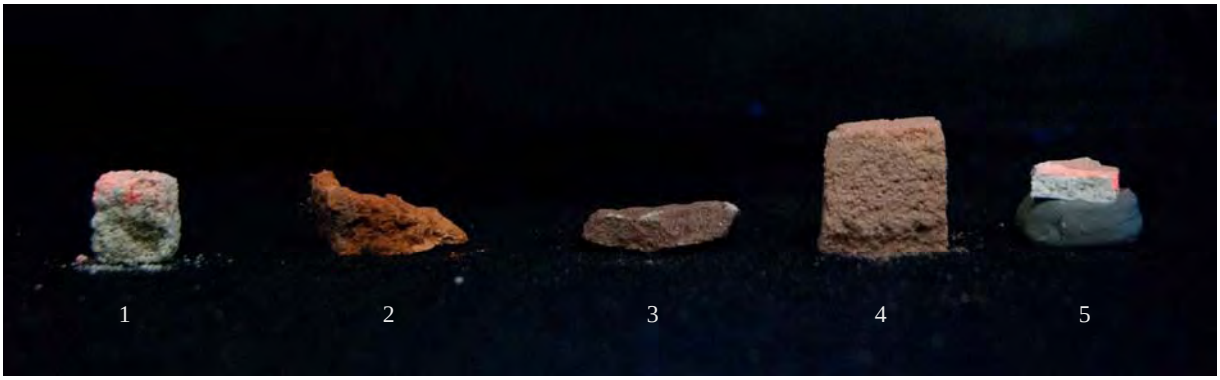


Image 11.
Nanoparticle– Matrix Compatibility Test 2.1
eBioscience eFluor™625 in xylene
under uv (350nm) & halogen light
1.Mortar, 2.brick, 3.sandstone, 4.adobe, 5.gesso

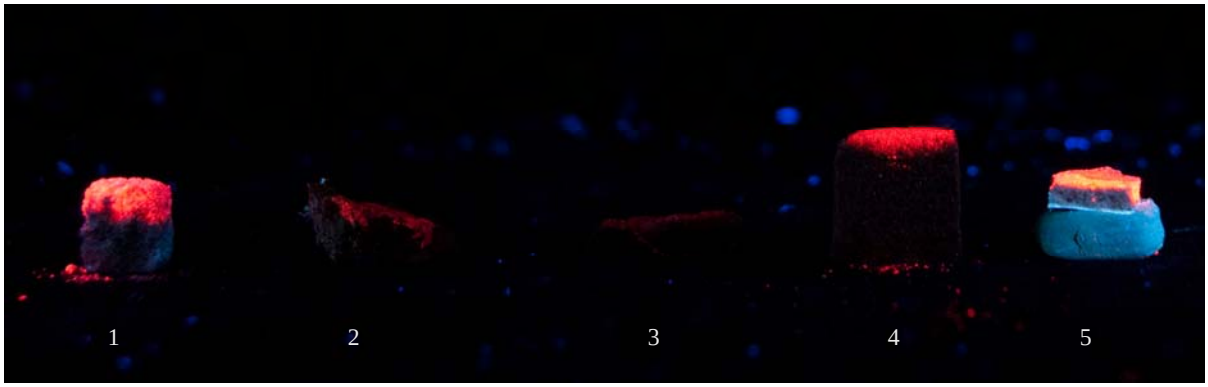


Image 12.
Nanoparticle– Matrix Compatibility Test 2.1
eBioscience eFluor™625 in xylene
under uv (350nm)
1.Mortar, 2.brick, 3.sandstone, 4.adobe, 5.gesso

In the test above the nanoparticles were not compatible with samples 2 and 3. The nanoparticles appear compatible with samples 1,4 and 5.

[2]It was theorized that the outer shell of the nanoparticle was effected by the electrostatic forces of the matrix. An attempt was made to remove the outer shell of the nanoparticle to reduce the electrostatic forces. However, this process quenched the nanoparticles.

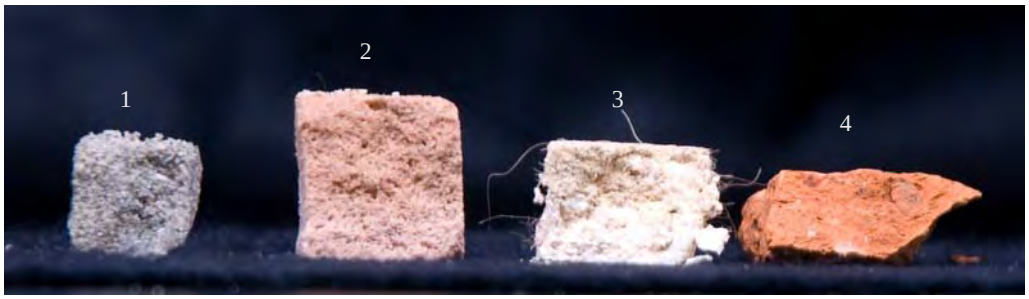


Image 12.
Nanoparticle– Matrix Compatibility Test 2.1
Sun Innovations™ YVE1005 in water
under halogen light
1.mortar, 2.adobe, 3. plaster 4.brick

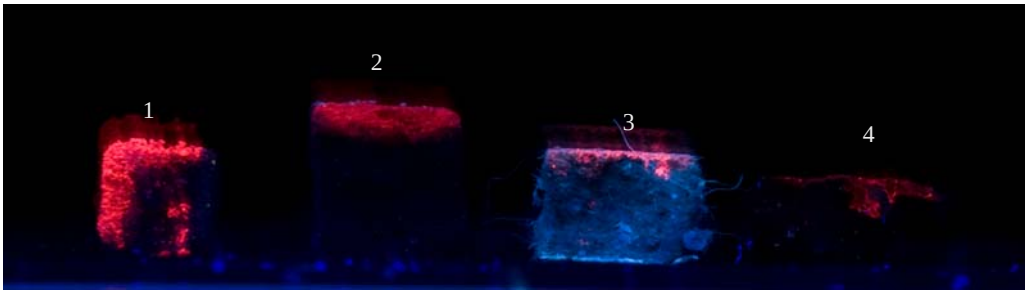


Image 13.
Nanoparticle– Matrix Compatibility Test 2.1
Sun Innovations™ YVE1005 in water
under UV light
1.mortar, 2.adobe, 3. plaster 4.brick
In the test above the nanoparticles were not compatible with samples 4, brick. The nanoparticles appear compatible with samples 1,2 and 3.

2.1 Results

The nanoparticle-matrix compatibility tests revealed a fundamental problem. The nanoparticles successfully traveled with the solvent through some but not all of the matrices. After consultations with the nanoparticle manufacturers and other scientists regarding this problem, the general consensus was that electrostatic forces inhibit the nanoparticles progress through some types of matrices. This results in the nanoparticles separating out of the solvent and failing to penetrate the matrix.[2] The matrices with strong polar forces, such as brick and sandstone, appear to exhibit this phenomenon. The degree of electrostatic interference depends on the inherent characteristics (pigment, minerals, etc.) of the matrix material. This may account for the inconstant test results. Based on this inherent problem with brick and sandstone, these materials were eliminated from the testing schedule.

Chart 7
Nanoparticle—Matrix Compatibility Test 2.1 Results

	Solvent—Nanoparticle	Mortar Cube	19th c. plaster	Brick	Marble	Lime-stone	Sand-stone	Adobe	Gesso	Sugar Cube	mural mock-up
Aromatics	Evident T2 Evi Dots™	√	√	☸	√	☸	☸	√	√	√	√
	eBioscience eFluor™	√	√	☸	√	☸	☸	√	√	√	√
Alcohol	Evident T2 Evi Dots™	X	X	X	X	X	X	X	X	X	X
	Evident T1 Evi Dot™	X	X	X	X	X	X	X	X	X	X
	eBioscience eFluor™	☸	☸	☸	X	X	X	☸	X	☸	X
	Corpuscular™ Nile Red (Carboxylated)	X	X	X	X	X	X	X	X	X	X
Water	Evident T1 Evi Dot™ Adirondack Green	√	√	X	√	X	X	√	√	√	√
	Sun Innovations™ YVE1005	√	√	X	X	X	√	√	√	X	√
	Sun Innovations™ YVE1101	√	√	X	X	X	√	√	√	X	√
	Corpuscular™ Nile Red (Plain)	X	X	X	X	X	X	X	X	X	X
	Corpuscular™ Nile Red (Carboxylated)	X	X	X	X	X	X	X	X	X	X
	Corpuscular™ Red SiO2 Silica (Plain)	X	X	X	X	X	X	X	X	X	X

Key:

√ - Nanoparticle traveled with solvent.

X - Nanoparticle separated from solvent.

☸ - Test results were inconsistant. This may have been do to inherent difference in the matrix.

Nanoparticle Visible Fluorescence Test 2.2

This test was designed to determine the most visible nanoparticle-matrix combination. The nanoparticles were sonified for 5 minutes according to manufacturer's instructions. Using a micropipettor, .1µls of nanoparticles were added to 1ml of each solvent. The solutions were shaken and then sonified for an additional 5 minutes. The nanoparticle– solvent solution was then applied by pipette to the selected matrix. The intent was to only saturate one half of the sample. The sample was allowed to dry, and then cut to reveal the crossection. The crossection was examined under UV light. Each step was photodocumented under both halogen and UV light.

The Evident T2 Evi Dots™ and the eBioscience eFluor™ nanoparticle behave in a similar manner. The only diffence is the color and intensity of the visual fluorscence. For future testing the field of Quantum Dots was therefore narrowed down to the nanoparticle with the highest intensity of visual fluorscence, this appears to be EviDot 620nm.

Of the water soluble nanoparticles, Evident T1 EviDot™ Adirondack Green, displayed a weak visible fluorescence, and was elimated for testing purposes.

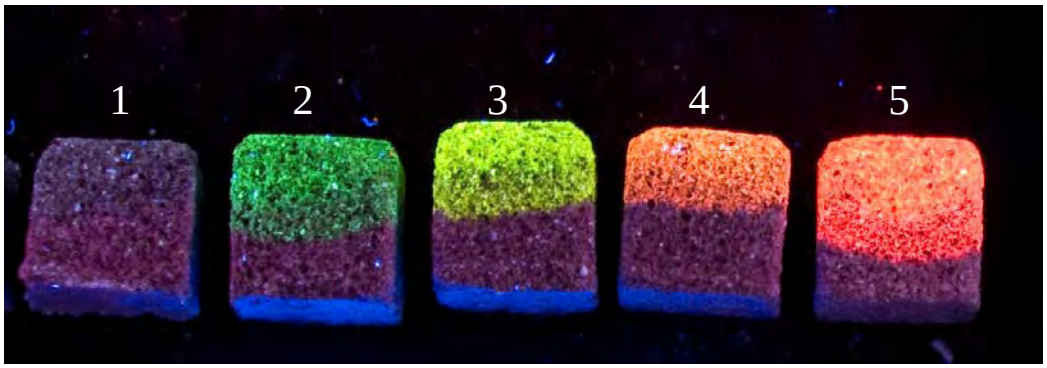


Image 9.
Nanoparticle Visible Fluorescence Test 2.2
Evident T2 Evi Dots™ in xylene applied to mortar cube observed under UV (350nm)
1. EviDot™ 540nm, 2 EviDot™ 560nm, 3. EviDot™ 580nm, 4. EviDot™ 600nm, 5. EviDot™ 620nm.

Test 2.2 Results
Nanoparticle-Matrix Compatibility
Based on the above information only nanoparticles-matrix combinations that are compatible and display a strong visual fluorescence were used for further testing.

- The Corpuscular™ nanoparticles were incompatible with all of the matrices.
- The Sun Innovations Phosphor Dots™ will be used to test the aqueous solutions.
- Brick and sandstone were eliminated for their incompatibility with nanoparticles.
- Evident T2 Evi Dot™ Maple Red-Orange will be used to test the non aqueous solutions. The eBioscience eFluor™ Quantum Dots displayed an equal fluorescence to the Maple Red-Orange, but practically there was a small quantity of eBioscience eFluor™ nanoparticles donated to the project.
- Evident T1 EviDot™ Adirondack Green was eliminated for weak fluorescence.

Nanoparticle-Consolidant Compatibility Test 3

A number of experiments were conducted to determine if the nanoparticles were compatible with the consolidants. The solvent-nanoparticle pairings already established were tested with the consolidants listed in Chart 1.

Test 3.1 – Test Tube
The nanoparticles were sonified for 5 minutes according to manufacturer's instructions. Using a micro-pipettor, 1µl of nanoparticles were added to 1ml of each consolidant. The solutions were shaken and sonified for an additional 5 minutes. The test tubes were then examined under ultraviolet light at 325nm and 350nm.

Chart 8
Nanoparticle-Consolidant Compatibility Chart

Consolidant/Solvent	**Evident T2 EviDot™ Maple Red Orange**	**Sun Innovations YVE1005**
Paraloid B-72 (10% in xylene w/v)	Soluble	NA
Lascaux P500 (10% in xylene w/v)	Soluble	NA
AYAA (10% in xylene w/v)	Soluble	NA
Cyclododecane	Soluble	NA
Prosoco OH100	Slightly Soluble	NA
Prosoco H100	Slightly Soluble	NA
Isinglass (10% in water w/v)	NA	Soluble
Ethulose (5% in water w/v)	NA	Soluble

As anticipated the Evident T2 EviDots™ were soluble in the aromatic soluble consolidants and slightly soluble in the alcohol soluble consolidants. The Sun Innovations YVE1005 nanoparticles were soluble in the water soluble consolidants.

Test 3.2 – Filter Paper Test

Paper chromatography was performed on the consolidant nanoparticle solutions to confirm that the nanoparticle could travel with the solvent and not separate out of the solution.

Each of the "slightly soluble" and "soluble" consolidant-nanoparticle solutions were applied drop wise by pipette to the center of a piece of Whatman #4 filter paper. The dispersion pattern was outlined and the paper allowed to dry. The filter paper was examined under ultraviolet light to determine if the fluorescing nanoparticles had traveled with the consolidant to the outline.

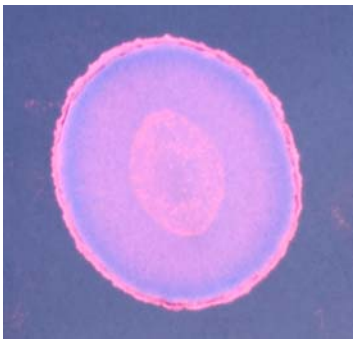


Image 9. Nanoparticle-Consolidant Compatibility –Filter Paper Test
Sun Innovations YVE1005™ & Isinglass applied to filter paper under ultraviolet light (325nm).

Image 11. Nanoparticle-Consolidant Compatibility –Filter Paper Test
Evident T2 EviDot™ Maple Red-Orange & Paraloid B72 applied to filter paper under ultraviolet light (350nm).

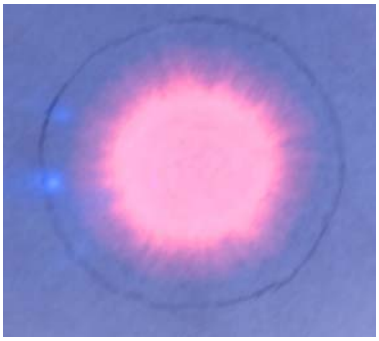


Image 10. Nanoparticle-Consolidant Compatibility –Filter Paper Test
Evident T2 EviDot™ Maple Red-Orange in Prosoco OH100 applied to filter paper under ultraviolet light (350nm).

Test 3. Results
Nanoparticle-Consolidant Compatibility

Based on the above information the nanoparticles appear compatible with the aqueous and aromatic consolidants, the filter paper did not separate the nanoparticles from these consolidant. The "slightly soluble" pairing of the quantum dots and alcohols was unsuccessful. The quantum dots did not travel as far as the consolidant, they were separated out of solution.

- The Sun Innovations Phosphor Dots™ were successful with the aqueous consolidants.
- Evident T2 Evi Dot™ Maple Red-Orange was successful with the aromatic consolidants.
- Evident T2 Evi Dot™ Maple Red-Orange was not successful with the alcohol consolidants.

\Nanoparticle/Consolidant-Matrix Compatibility Test 4

Test 4

The purpose of this test was to determine if the nanoparticle-consolidant solutions are compatible with each of the matrices. It is crucial that the nanoparticles travel with the consolidant through the matrix and not separate out of solution.

Test 4.1—Crossection Analysis

The nanoparticles were sonified for 5 minutes according to manufacturer's instructions. Using a micropipettor, 1µl of nanoparticles were added to 1ml of each consolidant. The solutions were shaken and then sonified for an additional 5 minutes. The nanoparticle– consolidant solution was then applied by pipette to the selected matrix. The intent was to only saturate one half of the sample. The sample was allowed to dry, and then cut to reveal the crossection. The crossection was examined under UV light. Each step was photodocumented under both halogen and UV light.

Chart 9
The nanoparticle/consolidant-matrix compatibility test

Nanoparticle/ Consolidant	**Mortar**	**Plaster**	**Marble**	**Limestone**	**Adobe**	**Gesso**	**Sugar Cube**
Evident T2 Evi Dots™ Paraloid B72 (10% in xylene)	√	√	√	√	√	√	√
Evident T2 Evi Dots™ Lascaux P550 (10% in xylene)	√	√	√	√	√	√	√
Evident T2 Evi Dots™ PVA-AYAA (10% in xylene)	√	√	√	√	√	√	√
Evident T2 Evi Dots™ Cyclododecane	√	√	√	√	√	√	√
Evident T2 Evi Dots™ Prosoco OH100 (undiluted)	**X**	**X**	**X**	**X**	**X**	**X**	NA
Evident T2 Evi Dots™ Prosoco H100 (undiluted)	**X**	**X**	**X**	**X**	**X**	**X**	NA
Sun Innovations™ YVE1005 Isinglass (10% in water)	√	√	√	√	√	√	NA
Sun Innovations™ YVE1005 Ethulose (5% in water)	√	√	√	√	√	√	NA

Key:

√ - Nanoparticle traveled with solvent.

X - Nanoparticle separated from solvent.

❁ – Test results were inconsistant. This may have been do to inherent difference in the matrix.

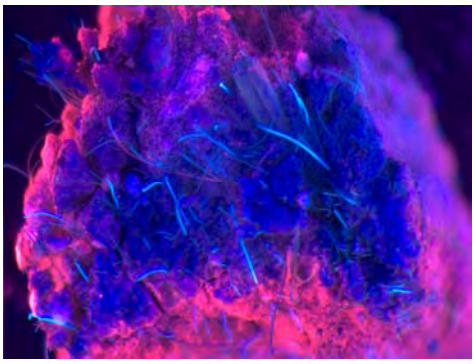


Image 11.
Nanoparticle/Consolidant–
Matrix Compatibility Test
Evident T2 EviDot™ Maple Red-Orange & Paraloid B72 applied to a plasters ample under ultraviolet light (350nm).

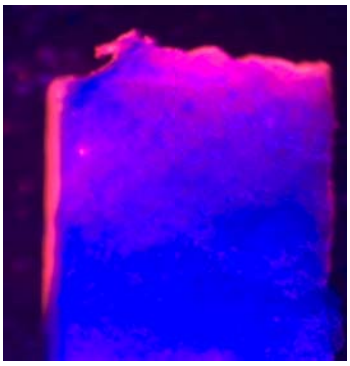


Image 12.
Nanoparticle/Consolidant–
Matrix Compatibility Test
Evident T2 EviDot™ Maple Red-Orange & Paraloid B72 applied to a marble sample under ultraviolet light (350nm).

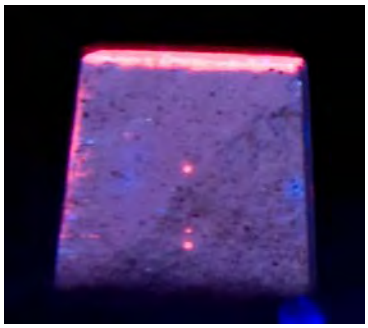


Image 13.
Nanoparticle/Consolidant– Matrix Compatibility Test
Evident T2 EviDot™ Maple Red-Orange & Prosoco OH100applied to a mortar cube under ultraviolet light (350nm).

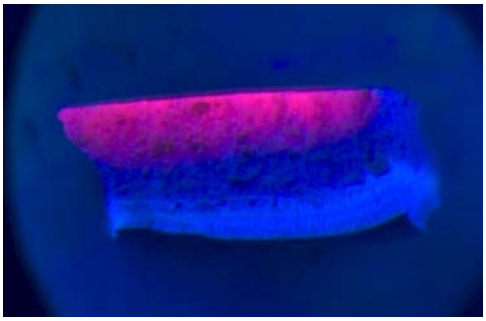


Image 14.
Nanoparticle/Consolidant– Matrix Compatibility Test
Sun Innovations™ YVE1005 & Isinglass applied to a gesso sample under ultraviolet light (325nm).

Test 4.1 Results

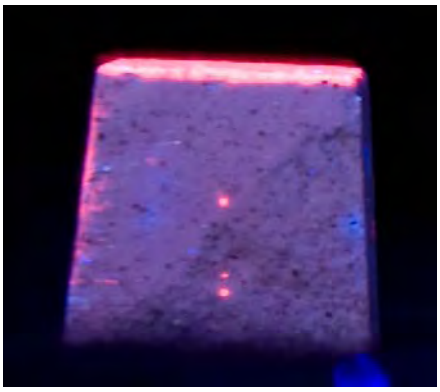
- The Evident T2 EviDot™ Maple Red-Orange & Paraloid B72 successfully penetrated all of the selected matrices without separating out of solution. The nanoparticles traveled with the Paraloid B72. This was also observed with Lascaux P550, PVA- AYAA and cyclododecane.

- The Sun Innovations™ YVE1005 and Isinglass successfully penetrated all of the selected matrices, except sugar cubes, without separating out of solution. The nanoparticles traveled with the isinglass. The was also observed with dilute solutions of Ethulose. Sugar cubes were not tested with aqueous consolidants.

- The Evident T2 EviDot™ Maple Red-Orange in OH100 and H100 appeared to separate out of solution. The nanoparticles did not appear to travel with the consolidant. The previously detected nanoparticle-alcohol miscibility issue (only 'slightly soluble') appears to inhibit the nanoparticles penetration through the matrix. These results were confirmed with Dithizone Reagent Test (Test 4.2).

Test 4.2—Dithizone Reagent Test

The purpose of this test was to confirm that the alcohol based consolidant traveled further through the matrix than the nanoparticles. Previous tests had indicated that the nanoparticles were separating out of the alcohol consolidant solutions. The Prosoco OH100 (alcohol) based consolidant contains organic tin compounds that can be detected with the reagent, dithizone. Dithizone reacts with the organic tin compounds turning the sample pink/orange.

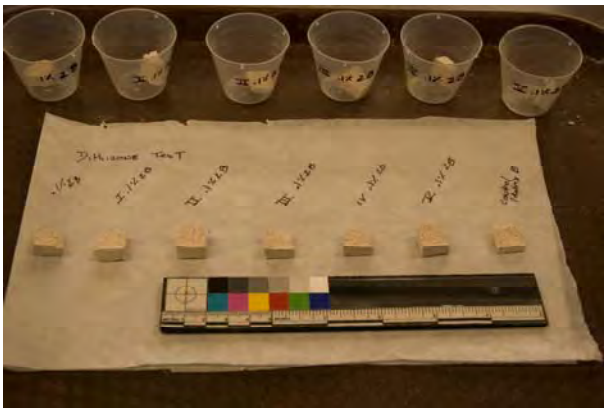


Images 26.
Nanoparticle/Consolidant– Matrix Compatibility Test
Evident T2 Evi Dot™ Maple Red-Orange & Prosoco OH100 applied to a mortar cube under UV light. The nanoparticles remained on the surface.

Dithizone Reagent Test

Weakly bound mortar cubes were treated with nanoparticle tagged Prosoco OH100. The entire sample was saturated with the solution. Once the sample had dried the sample was cut to reveal the cross section and examined under UV light. The UV examination revealed that the nanoparticles failed to penetrate the sample collecting on the surface of the sample. (Note in the sample shown to the right—the isolated nanoparticles in the center of the cube were a result of transfer during crossectioning).

The samples were then treated with Dithizone Reagent. The reagent identified the presence of organic tin compounds throughout the sample indicating the consolidant did penetrate the sample.



Images 27.
Before Dithizone Reagent Test
Evident T2 Evi Dot™ Maple Red-Orange & Prosoco OH100 applied to a mortar cube. The samples were cut to reveal the crossection. The control sample on the far right was not treated with OH100.

Images 28.
After Dithizone Reagent Test
The Dithizone Reagent turned the samples pink/orange indicting the presence of organic tin compounds. This confirms the presence of the Prosoco OH100 consolidant within the cube.

Test 4.3—Water Solubility Test
The purpose of this test was to confirm that the nanoparticles traveled with the consolidant through the matrix. It is crucial that the nanoparticles travel with the consolidant through the matrix and not separate out of solution.

Sugar Cubes
Sugar Cubes are an ideal matrix for proving that the nanoparticles successfully tagged the consolidant. Once the tagged consolidant has been applied to the sugar cube the unconsolidated portion of the sugar cube can easily be dissolved with water. The water can then be tested for the presence of nanoparticles and the consolidated sugar should fluoresce completely.

The nanoparticles were sonified for 5 minutes according to manufacturer's instructions. Using a micropipettor, 1µl of nanoparticles were added to 1ml of each consolidant. The solutions were shaken and then sonified for an additional 5 minutes. The nanoparticle–consolidant solution was then applied by pipette to the sugar cube. The intent was to only saturate a portion of the sample. The sample was allowed to dry and photodocumented under both halogen and UV light.

The treated sample was immersed in distilled water. The consolidated portion of the sugar cube was then removed and allowed to dry. The water was retained and examined under UV light. No nanoparticles were detected in the water. The dry sample was then examined and photographed under UV light. The entire consolidated sample fluoresced indicating the presence of nanoparticle.

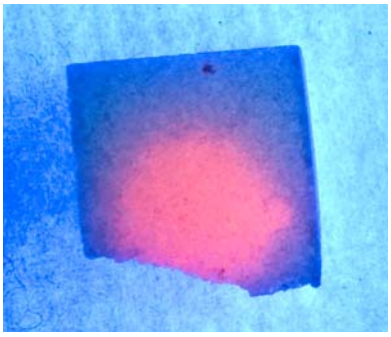


Image 15.
Nanoparticle/Consolidant–Matrix Compatibility Test
Evident T2 EviDot™ Maple Red-Orange & Paraloid B72 applied to a sugar cube under ultraviolet light.

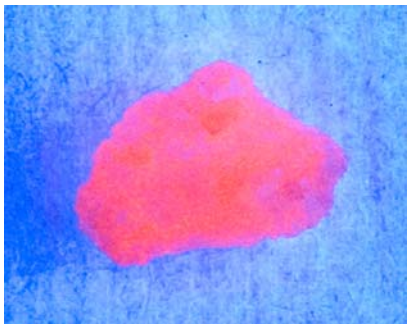


Image 16.
Nanoparticle/Consolidant–Matrix Compatibility Test
Evident T2 EviDot™ Maple Red-Orange & Paraloid B72 applied to a sugar cube under ultraviolet light. Unconsolidated material has been removed. Entire sample fluoresces.

Test 4.4—Mechanical Abrasion
The purpose of this test was to confirm that the nanoparticles traveled with the consolidant through the matrix. It is crucial that the nanoparticles travel with the consolidant through the matrix and not separate out of solution.

Mechanical Abrasion
Weakly bound mortar cubes were treated with nanoparticle tagged consolidant. Only a portion of the sample was consolidated. Once the sample had dried the unconsolidated material was mechanically removed with dental tools. The consolidated and unconsolidated materials were then examined under UV light.

The nanoparticles were sonified for 5 minutes according to manufacturer's instructions. Using a micropipettor, 1µl of Evident T2 EviDot™ Maple Red-Orange was added to 1ml of each consolidant. The solutions were shaken and then sonified for an additional 5 minutes. The nanoparticle–consolidant solution was then applied by pipette to the weakly bound mortar cube. The intent was to only saturate a portion of the sample. The sample was allowed to dry and photodocumented under both halogen and UV light.

The tagged sample was then mechanically abraded to remove all of the unconsolidated material. The unconsolidated material that was removed was examined under UV light. No nanoparticles were detected. The entire consolidated sample fluoresced indicating the presence of nanoparticle throughout the entire sample.

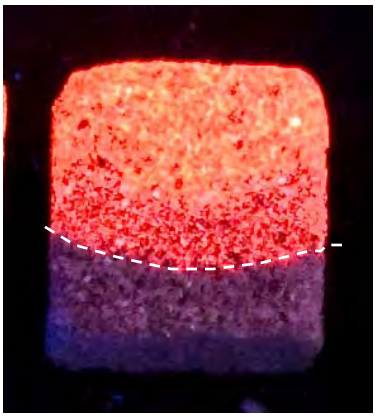


Image 17.
Nanoparticle/Consolidant–Matrix Compatibility Test
Side view—Before
Evident T2 EviDot™ Maple Red-Orange & Paraloid B72 applied to a mortar cube under ultraviolet light. The unconsolidated material is below the dashed line.

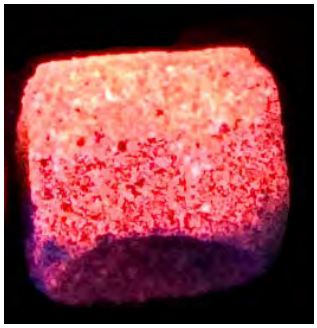


Image 18.
Nanoparticle/Consolidant–Matrix Compatibility Test
Side view—After mechanical abrasion
Evident T2 EviDot™ Maple Red-Orange & Paraloid B72 applied to a mortar cube under ultraviolet light. The unconsolidated material has been removed creating a hollowed out pocket at the bottom of the sample.

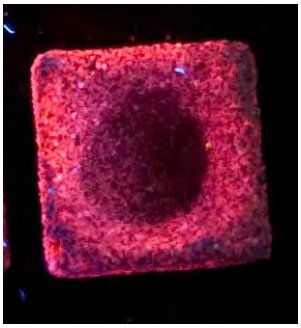


Image 19.
Nanoparticle/Consolidant–Matrix Compatibility Test
Bottom View—After mechanical abrasion
Evident T2 EviDot™ Maple Red-Orange & Paraloid B72 applied to a mortar cube under ultraviolet light. The unconsolidated material has been removed creating a hollowed out pocket at the bottom of the sample.

Test 4.5—Acid Digestion
The purpose of this test was to confirm that the nanoparticles traveled with the consolidant through the matrix. It is crucial that the nanoparticles travel with the consolidant through the matrix and not separate out of solution.

Acid Digestion
Weakly bound mortar cubes, adobe, plaster, and marble were treated with nanoparticle tagged consolidant. Only a portion of the sample was consolidated. Once the sample had dried the unconsolidated material was removed by acid digestion. The consolidated and unconsolidated materials were then examined under UV light.

The nanoparticles were sonified for 5 minutes according to manufacturer's instructions. Using a micropipettor, 1µl of Evident T2 EviDot™ Maple Red-Orange was added to 1ml of each consolidant. The solutions were shaken and then sonified for an additional 5 minutes. The nanoparticle–consolidant solution was then applied by pipette to the selected matrices. The intent was to only saturate a portion of the sample. The sample was allowed to dry and photodocumented under both halogen and UV light.

Image 18. Acid Digestion Set Up

The tagged sample was then placed on a wire mesh screen set over filter paper in a funnel. The bottom of the funnel was plugged. The funnel was then filled with a mild acetic acid solution. The unconsolidated material was dissolved by the acid falling through the wire screen to be trapped by the filter paper. The funnel was unplugged allowing the acetic acid to drain. The consolidated sample and the 'fines' (retained unconsolidated material) were allowed to dry and examined under UV light.

No nanoparticles were detected in the fines. The entire consolidated sample fluoresced indicating the presence of nanoparticles throughout the entire sample.

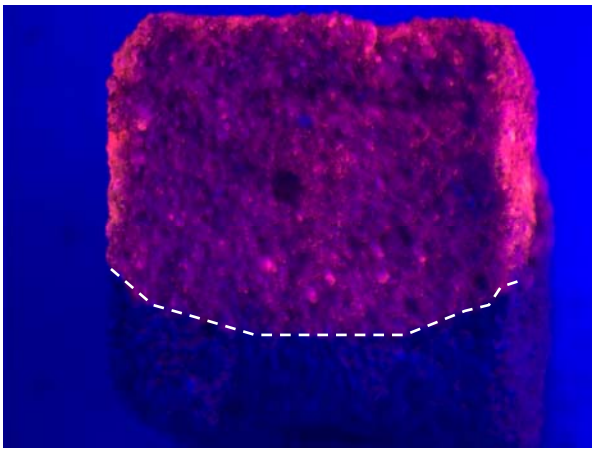


Image 19. Nanoparticle/Consolidant–Matrix Compatibility Test
Evident T2 EviDot™ Maple Red-Orange & Paraloid B72 applied to a mortar cube under ultraviolet light. The unconsolidated material is below the dashed line.

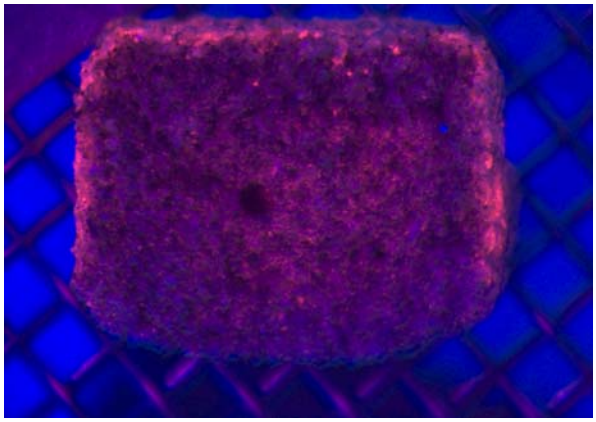


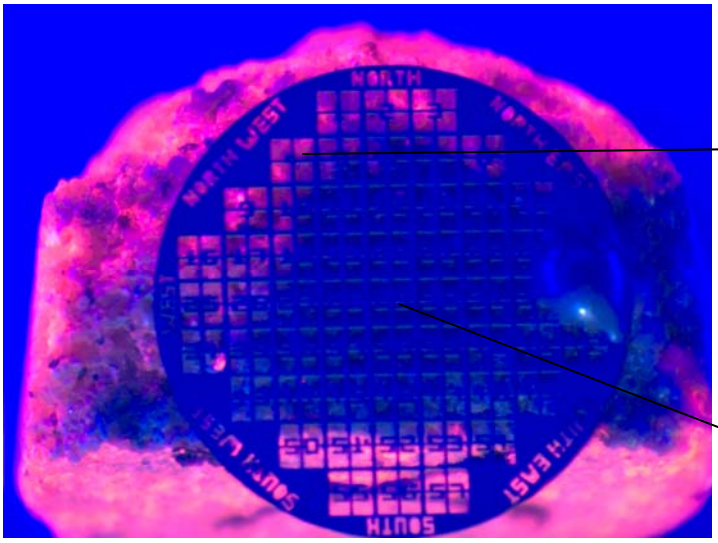
Image 20. Nanoparticle/Consolidant–Matrix Compatibility Test
Evident T2 EviDot™ Maple Red-Orange & Paraloid B72 applied to a mortar cube under ultraviolet light. The unconsolidated material has been removed by acid digestion.

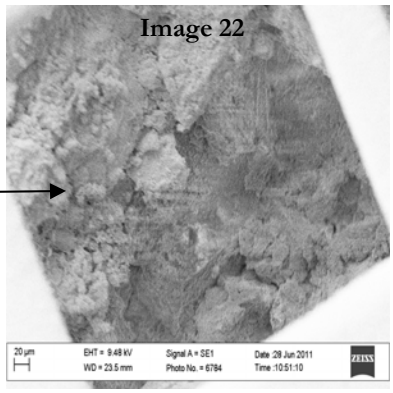
Test 4.6—Scanning Electron Microscope (SEM)
The purpose of this test was to confirm that the nanoparticles traveled with the consolidant through the matrix. It is crucial that the nanoparticles travel with the consolidant through the matrix and not separate out of solution. The previous tests could not be used to confirm the presence of isinglass so advanced analytic testing was necessary.

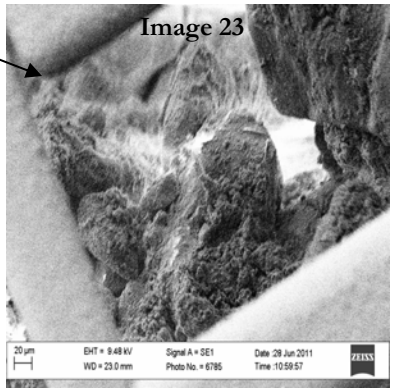
Scanning Electron Microscope (SEM) was performed to confirm the presence of isinglass on the samples. Weakly bound mortar cubes and gesso were treated with nanoparticle tagged consolidants. Only a portion of the sample was consolidated. Once the sample had dried, the sample was taken to Union College for SEM analysis. The SEM is a Zeiss EVO-50 with a Bruker axs.

The nanoparticles were sonified for 5 minutes according to manufacturer's instructions. Using a micropipettor, 1µl of Sun Innovation™ YVE1005 was added to 1ml of consolidant. The solutions were shaken and then sonified for an additional 5 minutes. The nanoparticle–consolidant solution was then applied by pipette to the selected matrices. The intent was to only saturate a portion of the sample. The sample was allowed to dry and photodocumented under both halogen and UV light. A "SEM F3-N Finder Grid Number 2 Nickel" was oriented over a cross section of the sample. This grid helps to identify sample locations under SEM. The sample with grid was photographed under halogen and UV light. Two coordinate were identified, one with fluorescing nanoparticle and one without. SEM was then conducted over those coordinates to confirm the presence of isinglass in the fluorescing area and its absence in the non-fluorescing area.

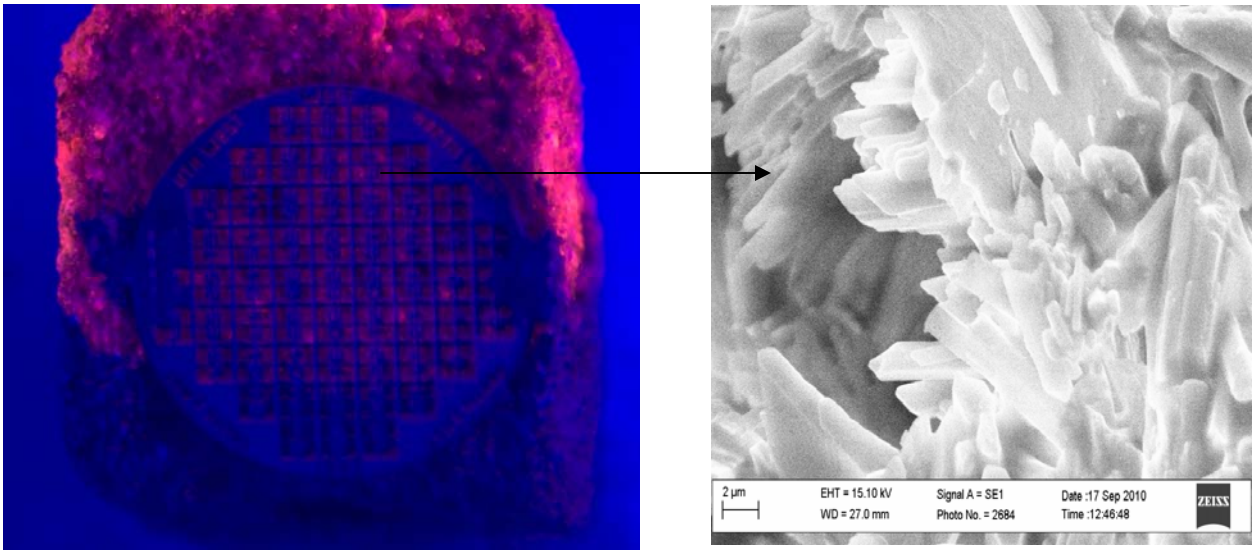
Isinglass was detected in the fluorescing coordinates but not in the other coordinates.







Images 21, 22 & 23.
Nanoparticle/Consolidant– Matrix Compatibility Test SEM
Sun Innovation™YVE1005 & Isinglass applied to a mortar cube with SEM grid under ultraviolet light. Image 21: SEM grid location NW4. Note fine cross-hatched fibrils of isinglass. Image 22: SEM grid location 29 no isinglass detected.



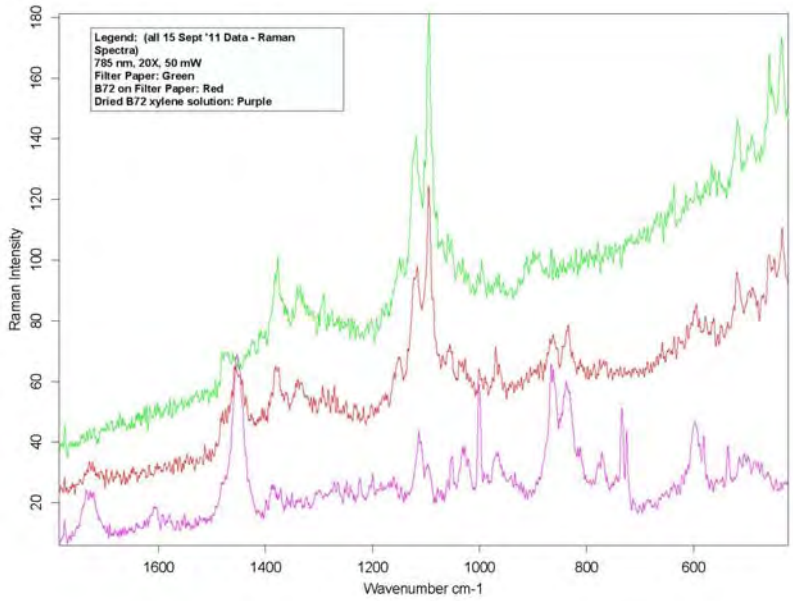
Images 24 & 25.
Nanoparticle/Consolidant– Matrix Compatibility Test SEM

Evident T2 Evi Dot™ Maple Red-Orange & Paraloid B72 applied to a mortar cube with SEM grid under ultraviolet light. Image 23: SEM grid location NW7. Image 24: SEM grid location NW7 positive identification of the presence of Paraloid B72.

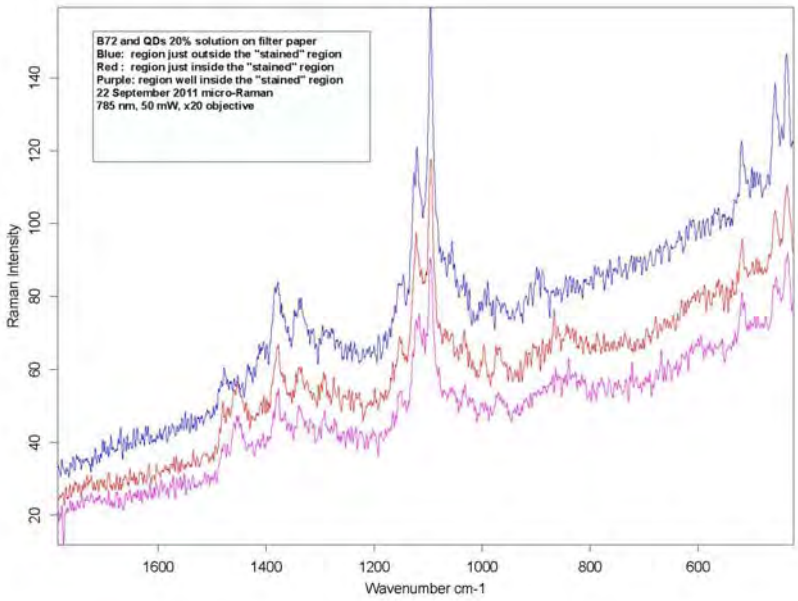
Test 4.7—Micro Raman Spectroscopy
The purpose of this test was to confirm that the nanoparticles traveled with the consolidant through the matrix. It is crucial that the nanoparticles travel with the consolidant through the matrix and not separate out of solution.

Micro Raman Spectroscopy (Raman) was performed to confirm the presence of Paraloid B72 on the filter paper used in Test 3.2. The sample was taken to Union College where the test was performed. A Micro Raman Spectroscopy Bruker Senterra with three lasers at 785 nm, 633 nm, and 532 nm was used to conduct this test.

- Micro Raman Spectroscopy identified the presence of Paraloid B72 within the outlined area. Confirming the nanoparticles traveled with the consolidant.
- No Paraloid B72 was detected outside the outlined area.



Graph 1.
Baseline for Paraloid B72(red) on Filter Paper, Filter Paper (green) & Paraloid B72 (purple).



Graph 2.
Detection of Filter Paper (blue) outside fluorescing area, Paraloid B72 (red) detected just within boundary of fluorescing area & Paraloid B72 (red) detected within boundary of fluorescing area.

Test 5: Pilot Project

The Coe Hall mural, painted by Robert Winthrop Chanler, Planting Fields, NY State Park, began flaking soon after its completion. In addition to unstable environmental conditions, Chanler's construction method may be partly responsible for the advanced deterioration. The mural's primary support is a masonry wall covered with wire mesh supporting multiple layers of plaster. On top of the finish plaster layer is a layer of heavy gesso with impasto strokes. Select areas have been prepared for gold leafing with a layer of red bole. Finally the surface features a thin layer of distemper based paint.

Diagram 1
Cole Hall Mural Section

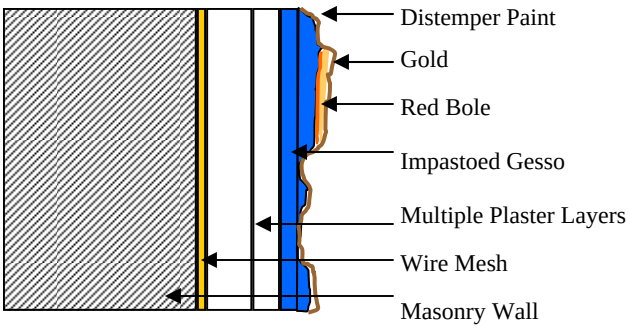


Image 1. Robert Chanler Mural c.1920's
Coe Hall, Planting Fields, State Park

The mural has been deteriorating since it's construction. There are letters documenting flaking paint just months after its completion. Investigations have found that the delamination is occurring primarily at the interfaces between the gesso layer and plaster layers.

Since New York State's acquisition of Planting Fields and Coe Hall, conservation campaigns have been undertaken at least three times. These treatments have all produced limited success and the mural's structural integrity has continued to fail. Before undertaking yet another conservation treatment the structure and materials of the mural were analyzed. We recognized the need to test consolidating materials for their penetrating abilities.

The nanoparticles tagging technique, developed and supported by a grant from National Center for Preservation Technology and Training and New York State Office of Parks, Recreation & Historic Preservation, was used to analyze the depth of penetration of consolidants. The structure and materials of the Coe Hall mural made it an ideal candidate for the successful application of this technique.

Mock Up Construction:
Mock up of the mural were constructed for testing purposes. The mock ups were designed to replicate the mural's construction and were artificially aged to replicate the deterioration. The mock ups were constructed on a sheetrock foundation with the surface paper removed. A base coat of rough plaster (scratch coat) was applied followed by a fine plaster layers. A layer of gesso with heavy impasto stokes was then applied. To this layer red bole and gold leaf was added. The entire surface was then painted with a thin layer of distemper paint.

Consolidant Testing on Mock ups:
A range of consolidants were selected for testing, these included Paraloid B72 (10% in xylene), Lascaux P500 (10% in xylene), PVA AYAA (10% in xylene) and Isinglass (10% in water). Each consolidant was tagged with the appropriate nanoparticle and applied by pipette to a square centimeter of the mock up. A total of .5mls of consolidant was applied to each sample location. The consolidant was allowed to dry and then the treated area was cut to reveal the crossection. The crossection was examined under the appropriate UV wavelength. The fluorescing nanoparticles revealed the location of the consolidant.

Image 2. Crossection
Mural mockup treated with Paraloid B72 tagged with Evident T2 Evi Dot™ Maple Red-Orange under halogen light. 100x magnification

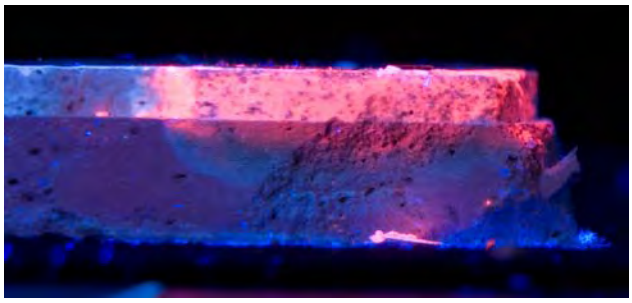


Image 3. Crossection
Mural mockup treated with Paraloid B72 tagged with Evident T2 Evi Dot™ Maple Red-Orange under 350nm UV light. 100x magnification

Image 4. Crossection
Mural mockup treated with Isinglass tagged with Sun Innovations™ YVE1005 under halogen light. 100x magnification

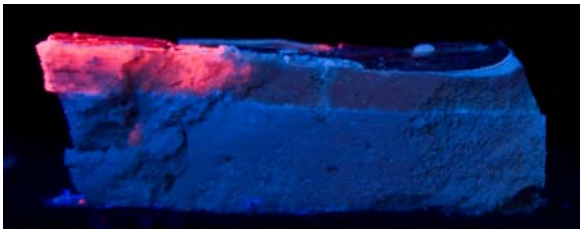


Image 5. Crossection
Mural mockup treated with Isinglass tagged with Sun Innovations™ YVE1005 under 325nm UV light. 100x magnification

The nanoparticles proved successful in penetrating through a complex multi-layer structure. The tagged Paraloid B72 (Image 3.)penetrated through the paint, gesso and plaster layers to reach the sheetrock foundation of the mock-up. The isinglass penetrated through the paint, gesso and plaster layers but only beginning to penetrate the sheetrock foundation layer. Since in each case a controlled amount of consolidant was applied to the mock up this indicated that the Paraloid B72 was more effective at penetrating the structure.

Consolidant Testing on Mock ups:
The artificial aging of the mock ups produced severe cracking and cleavage between layers. Copious amounts of the tagged Paraloid B72 was applied by brush along crack lines until saturation was achieved. The sample was then examined under UV light.

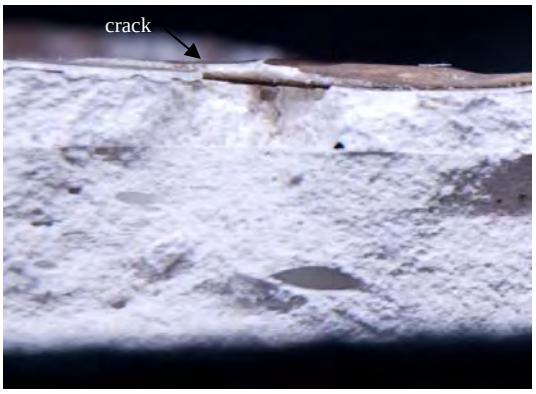


Image 6.
Mural mockup treated with Paraloid B72 tagged with Evident T2 Evi Dot™ Maple Red-Orange under halogen light.
100x magnification

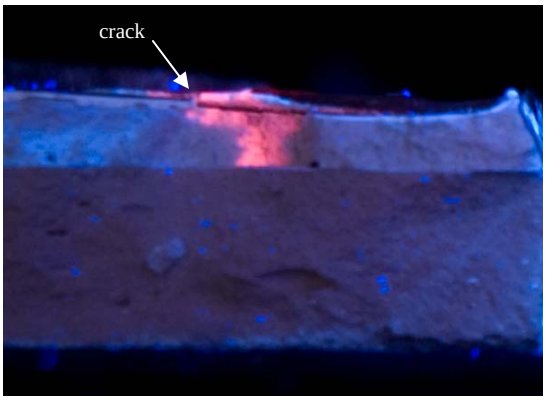


Image 7.
Mural mockup treated with Paraloid B72 tagged with Evident T2 Evi Dot™ Maple Red-Orange under 350nm UV light.

The fluorescing nanoparticles revealed the path of the Paraloid B72. It traveled through the crack, through and under the lifting gesso layer and into the fine plaster layer. The consolidant was drawn into the surrounding friable material by capillary action.

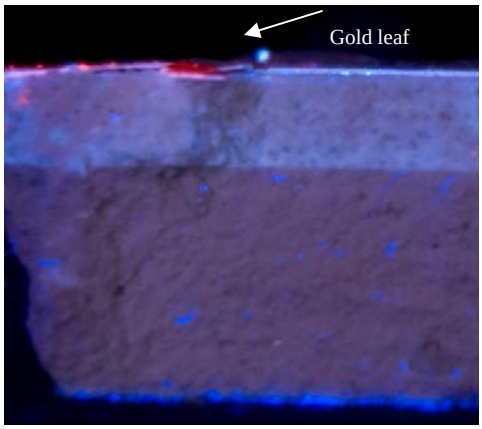


Image 8.
Mural mockup treated with Paraloid B72 tagged with Evident T2 Evi Dot™ Maple Red-Orange under 350nm UV light
100x magnification

In an additional test the tagged Paraloid B72 was applied over a gilded area of the mock up. The crossection of the area showed fluorescing nanoparticles sitting on the top surface of the gold. The gold acted as a barrier layer preventing the consolidant from penetrating the structure. The same result was achieved with isinglass and Lascaux P550.

Consolidant Testing on Coe Hall Mural Samples:
Small fragments of the Coe Hall Mural were collected after they had flaked off of the mural's surface. The fragment locations were carefully documented and samples were retained for analysis. Microscopic examination of the samples revealed that each sample had delimitated at the interface between the plaster layers of the mural's structure. The samples included layers of the distemper paint layer, the gesso layers and multiple layers of plaster.

Based on the information gathered from the testing of the mockups, the samples were prepared for testing using the nanoparticle tagging technique. The nanoparticles were prepared as required and solutions of Paraloid B72 (10% in xylene), Lascaux P550 (10% in xylene) and isinglass (10% in distilled water) were prepared. The Paraloid B72 and the Lascaux P550 were tagged with Evident T2 Evi Dots™ Maple Red-Orange (1μl of nanoparticles in 1ml of consolidant solution). The isinglass was tagged with Sun Innovation™ YVE1005 (1 μl of nanoparticles in 1ml of consolidant solution). The crossections were not mounted in resin or polished as the polishing action could produce transfer of the nanoparticles producing inaccurate results. As a consequence the uneven surface of the samples made imaging difficult.

Based on the sample available two sample groups were prepared.
Sample Group 1: East Wall & Sample Group 2: North Wall
The sample fragment from the east wall was divided into three samples, S-E1, S-E2 & S-E3.

Sample Group 1—S-E1:
This sample was immersed in isinglass tagged with Sun Innovation™ YVE1005 (1 μl of nanoparticles in 1ml of consolidant solution). The sample was allowed to dwell in the solution for over an hour with frequent agitation to encourage penetration of the consolidant. The sample was then removed from the consolidant and allowed to dry. A crossection of the sample was taken and examined under uv light. The nanoparticles revealed that the isinglass was completely unable to penetrate any of the layers of the samples.

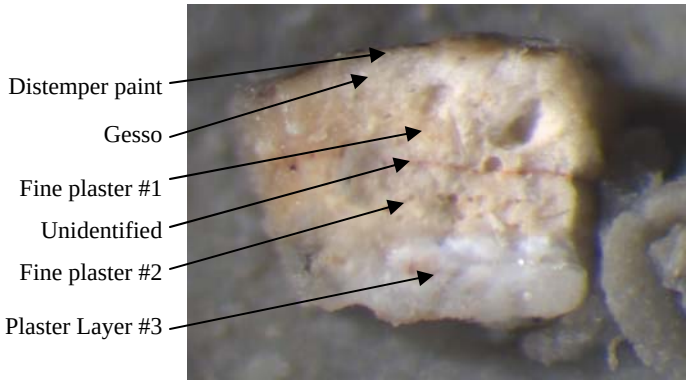


Image 9.
Mural sample S-E1 under halogen light
300x magnification.

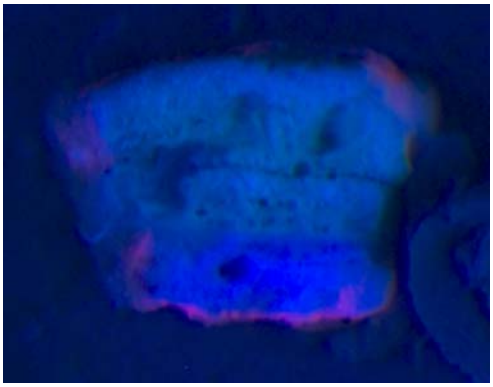


Image 10.
Mural sample S-E1 under 325nm UV light
300x magnification.

Sample Group 1: East Wall & Sample Group 2: North Wall
The sample fragment from the east wall was divided into three samples, S-E1, S-E2 & S-E3.

Sample Group 1—S-E2:
This sample was immersed in Paraloid B72 tagged with tagged with Evident T2 Evi Dots™ Maple Red-Orange (1µl of nanoparticles in 1ml of consolidant solution). The sample was allowed to dwell in the solution for over an hour with frequent agitation to encourage penetration of the consolidant. The sample was then removed from the consolidant and allowed to dry. A crossection of the sample was taken and examined under UV light. The Paraloid B72 did not penetrate through the top layers of the sample, but did penetrate through the bottom plaster layer.

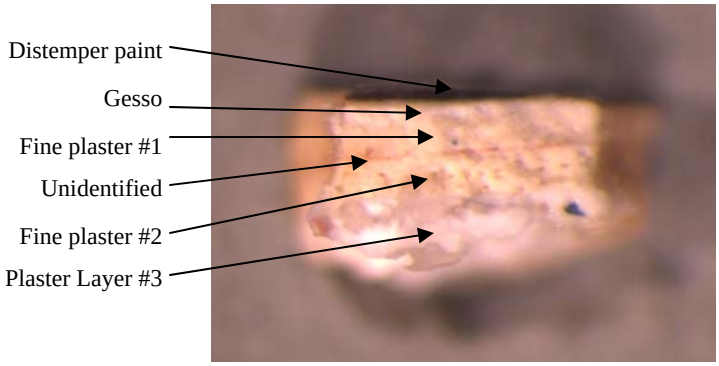


Image 11.
Mural sample S2 under halogen light
300x magnification.

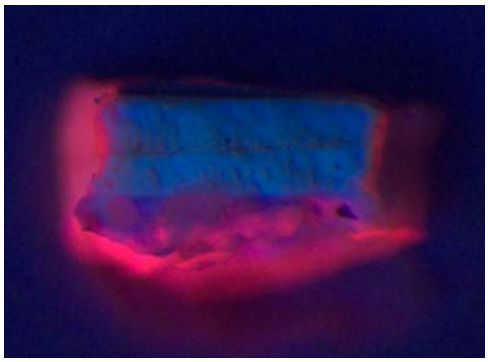


Image 12.
Mural sample S2 under 350nm UV light
300x magnification.

Sample Group 1—S-E3:
This sample was immersed in Lascaux P550 tagged with tagged with Evident T2 Evi Dots™ Maple Red-Orange (1µl of nanoparticles in 1ml of consolidant solution). The sample was allowed to dwell in the solution for over an hour with frequent agitation to encourage penetration of the consolidant. The sample was then removed from the consolidant and allowed to dry. A crossection of the sample was taken and examined under UV light. The Lascaux P550 did not penetrate through the sample.

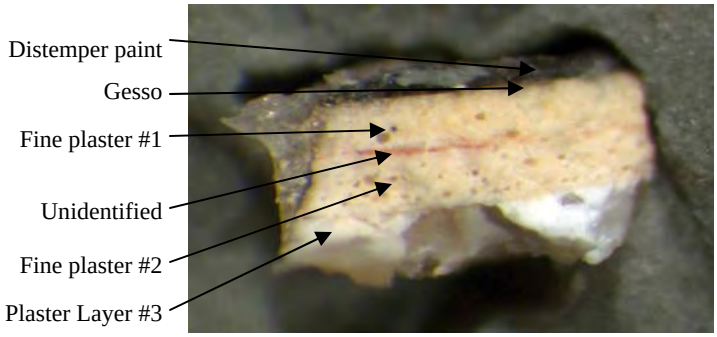


Image 13.
Mural sample S2 under halogen light
300x magnification.

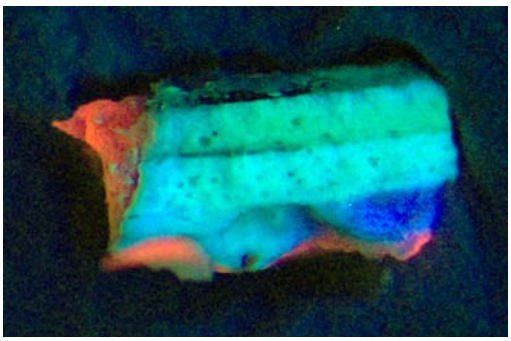


Image 14.
Mural sample S2 under 350nm UV light
300x magnification.

Sample Group 2—S-N1:
This sample was immersed in isinglass tagged with Sun Innovation™ YVE1005 (1 µl of nanoparticles in 1ml of consolidant solution). The sample was allowed to dwell in the solution for over an hour with frequent agitation to encourage penetration of the consolidant. The sample was then removed from the consolidant and allowed to dry. A crossection of the sample was taken and examined under UV light. The nanoparticles revealed that the isinglass was completely unable to penetrate any of the layers of the samples.

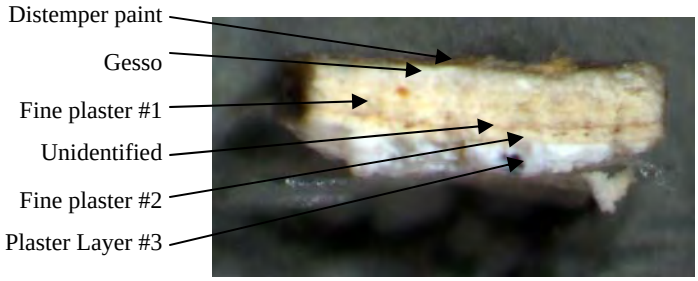


Image 15.
Mural sample S-N1 under halogen light
300x magnification.

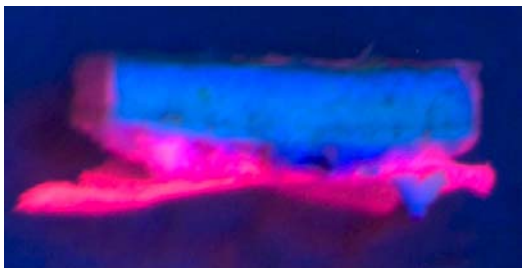


Image 16.
Mural sample S-N1 under 325nm UV light
300x magnification.

Sample Group 2—S-N2:
This sample was immersed in Paraloid B72 tagged with tagged with Evident T2 Evi Dots™ Maple Red-Orange (1µl of nanoparticles in 1ml of consolidant solution). The sample was allowed to dwell in the solution for over an hour with frequent agitation to encourage penetration of the consolidant. The sample was then removed from the consolidant and allowed to dry. A crossection of the sample was taken and examined under UV light. The Paraloid B72 did not penetrate through the top layers of the sample, but did penetrate through the bottom plaster layer.

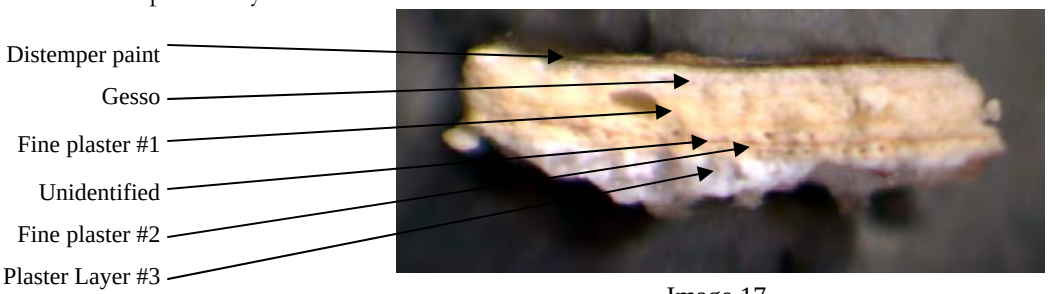


Image 17.
Mural sample S2 under halogen light
300x magnification.

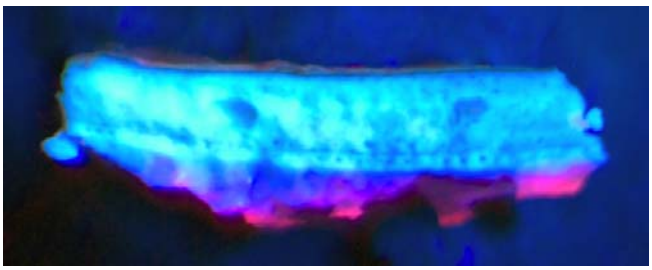


Image 18.
Mural sample S2 under 350nm UV light

Sample Group 2—S-N3:
This sample was immersed in Lascaux P550 tagged with tagged with Evident T2 Evi Dots™ Maple Red-Orange (1µl of nanoparticles in 1ml of consolidant solution). The sample was allowed to dwell in the solution for over an hour with frequent agitation to encourage penetration of the consolidant. The sample was then removed from the consolidant and allowed to dry. A crossection of the sample was taken and examined under UV light. The Lascaux P550 did not penetrate through the sample.

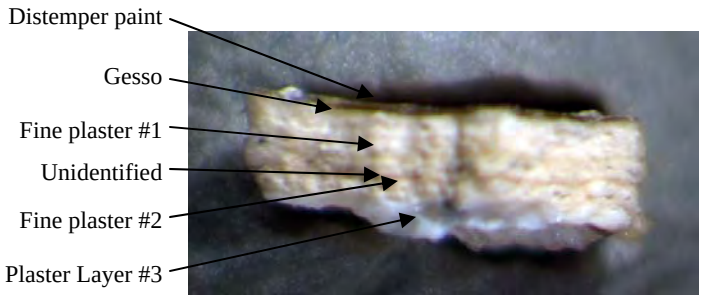


Image 19.
Mural sample S2 under halogen light
300x magnification.

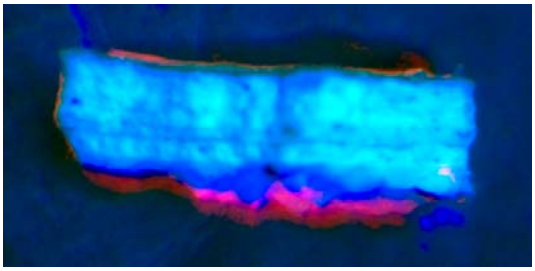


Image 20.
Mural sample S2 under 350nm UV light
300x magnification.

Conclusion:
The testing done during the Pilot Project identified the cause of the numerous failed consolidation treatments at Coe Hall. The materials and structure of the mural have created a barrier that prevents the consolidant from penetrating. The consolidant can not physically reach the unstable areas. The surface layers of the mural appear to be especially impervious to aqueous and non-aqueous materials.

This new insight creates another challenge. A way of reaching the unstable areas must be found that is not dependant on only consolidating the surface of the mural as has been done in the past. Conservators from the NY State Bureau of Historic Sites will be exploring alternate treatment methods such as: injecting consolidants, treating the mural from the back and using vacuum pressure.

6. Results & Discussion

Our initial premise was that nanoparticles could be ideal visual markers to determine the depth of penetration of a consolidant through a matrix. The manufacturer's literature on nanoparticles promoted them as stable, inert, highly fluorescent and nanosized.

Our research has found that nanoparticles may be successfully used to determine depth of penetration of a consolidant under the right circumstances. Unfortunately, our research has also found that there are circumstances where nanoparticles can not be used to determine the depth of penetration of a consolidant.

Nanoparticle Compatibility

A range of highly fluorescent nanoparticles were found to be compatible with consolidants in aqueous solutions and another class of nanoparticles were found to be compatible with consolidants in aromatics and ketones. We also found successful pairings between many types of nanoparticles and material matrices such as mortar, limestone, plaster, gesso, adobe, and marble. The intensely fluorescent nanoparticles tag the consolidant making the consolidant highly visible within the sample.

Nanoparticle Incompatibility

Compatibility issues between nanoparticles and materials can prevent the successful use nanoparticles to determine depth of penetration. We found the problem is two-fold. One problem is the lack of compatibility between some solvents and nanoparticle and the second is a lack of compatibility issue between nanoparticles and some material matrices.

1. Solvent-Nanoparticle Compatibility

The nanoparticles that are currently available are compatible with either aromatics or aqueous solutions. Despite manufacturer's assertions that their nanoparticles should be miscible with alcohols our tests were not successful.

2. Nanoparticle-Matrix Compatibility

Electrostatic forces present in some matrices inhibits the successful penetration of the nanoparticles through the matrix. The nanoparticle is separated out of the consolidant by these forces. Materials that exhibit these strong electrostatic forces include brick and sandstone.

Potential Uses

Unfortunately, these incompatibility limits the use of this technique for determining depth of penetration for building conservation. For example, the commonly used alcohol based ethyl silicate consolidation treatments are incompatible with all of the fluorescing nanoparticles currently available. In addition, commonly consolidated building materials (brick & sandstone) exhibit strong electrostatic forces preventing the success with this technique.

This technique can be used for determining the depth of penetration of a consolidant through complex laminate structures such as murals and ornamental and flat plaster. It can also be used for determining the best consolidation treatment for adobe and historic mortars

7. Conclusion

The initial goal of the project was to develop a technique using nanoparticles to tag consolidants to determine depth of penetration. This technique would help develop a treatment that would successfully consolidate the unstable mural at Coe Hall, Planting Fields, NY State Historic Park. The mural has suffered from chronic flaking and delamination since it was painted in the 1920s. The mural has failed to respond to several consolidation treatments. Before undertaking yet another conservation treatment, it was necessary to understand why the past treatments had failed.

After extensive testing and research a successful method for determining depth of penetration of a consolidant through the mural was found. The testing identified successful pairings of consolidant and nanoparticles that were compatible with the materials found in the mural. After conducting preliminary tests on mockups, select consolidant nanoparticle pairs were tested on tiny samples taken from the Coe Hall mural. Examination of the samples under UV light revealed that the consolidants were unable to penetrate through the surface layers of the mural. This finding explains why all previous consolidation treatment failed. The consolidant failed to reach the delaminating areas.

The technique of using nanoparticles to tag consolidants to determine depth of penetration has limited practical applications to the wider conservation field at this time. However, the field of nanotechnology is still growing and it is possible that more compatible nanoparticle may be developed.

Acknowledgments

Special acknowledgements are to be made to Rose Harvey, Commissioner, New York State Office of Park, Recreation and Historic Preservation, Ruth Pierpont, Director, Division of Historic Preservation, New York State Office of Parks, Recreation and Historic Preservation, John Lovell, Assistant Director, Bureau of Historic Sites, New York State Office of Park, Recreation and Historic Preservation and Christopher Flagg, Senior Historic Sites Restoration Coordinator, New York State Office of Parks, Recreation and Historic Preservation for their support and encouragement for this research project. Also thanks to Alexander J. Roth, Executive Director, Natural Heritage Trust and Michelle Phillips-Conlin, Natural Heritage Trust for their assistance and attention to detail. Finally, special thanks to Gregg Bosak, Senior Manufacturing Chemist of Evident Technologies and Travis Jennings, Research Scientist, eBioScience for patience and understanding throughout the project.

BIBLIOGRAPHY

Ahmadi, S. "Adobe Conservation: Evaluation of Silicone and Acrylic Consolidants." PhD diss., Queen's University, Canada, 2008.

Brajer, Isabelle. The Transfer of Wall Paintings: Based on Danish Experience. London: Archetype Publications, 2002.

Cather, Sharon, trans. *The Conservation of Wall Paintings: Proceedings of a Symposium organized by the Courtauld Institute of Art and the Getty Conservation Institute.* London: The Getty Conservation Institute, 1987.

Clifton, James R.. "Stone Consolidating Material: A Status Report." *National Bureau of Standards. (*2008).

Gowing, Robert, Robert Pender, trans. All Manner of Murals: The History, Technique and Conservation of Secular Wall Paintings. London: Archetype Publications, 2007.

Kumar, Rakesh , and William S. Ginell. "A New Technique for Determining The Depth of Penetration of Consolidants into Limestone Using Iodine Vapor." *Journal of the America Institute for Conservation* Volume 36, Number 2, Article 4. (1997):143-150.

Matero, Frank G., and Anne B. Oliver. "A Comparative Study of Alkoxysilanes and Acrylics and Sequence and in Mixture." *Journal of Architectural Conservation* Volume 2. Number 2. (1997): 22-32.

Mora, Paolo, Laura Mora, and Paul Philippot. Conservation of Wall Paintings. London: Butterworths, 1984.