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Evaluating the Efficacy of Silica Nano-Particle "Liquid Glass" Protective Coatings for Outdoor Marble Sculpture and Monuments

ABSTRACT

"Liquid glass" products have been proposed for use as inert and versatile coatings that may have applications in the cultural heritage protection field. These coatings are advertised to consist of silica nano-particles and are held without adhesives or binders to various substrates including metals, textiles, stone, plastics, wood, and glass. By creating a nanoscopic surface texture, these coatings emulate the "lotus effect," demonstrating a variety of characteristics including hydrophobicity, oleophobicity, water vapour permeability, anti-microbial properties, and "easy to clean" qualities. As these coatings potentially offer protection against several forms of deterioration, they may aid in the preservation of stone architecture, sculpture, and monuments. Conservators and conservation scientists have not yet extensively tested these coatings, and thus further research may determine their suitability and ascertain possible applications in the conservation field.

Research conducted at Queen's University investigated three coatings: Portol Pro from CeNano GmbH & Co. KG and both a Stone Finish and a two part Anti-Graffiti Coating from Nanopool GmbH. Tests determined the efficacy of the coatings as water repellent and anti-graffiti materials. The substrate tested on was the Olympia White marble used to construct the Canadian Navy Memorial Monument in Ottawa. The coatings were characterized by X-ray diffraction, inductively coupled plasma optical emission spectroscopy, Fourier transform infrared spectroscopy with a DRIFTS attachment, and gas chromatography mass spectroscopy. Environmental scanning electron microscopy investigated the surface morphology of the product on marble and color change was monitored after application and after exposure to high humidity and temperature. Water repellency was measured with RILEM tubes and water contact angle measurements. Water vapour transmission rates were also compared. Empirical tests were performed to evaluate ease of cleaning following the application of test graffiti, as well as an investigation into the removability of this coating.

1. INTRODUCTION

Water instigates many forms of deterioration of stone-based cultural heritage. Water repellents may aid in the retardation of this deterioration, however the conservation profession has not yet produced a product that is known to be successful long term without shrinking, yellowing, or allowing sufficient water vapour permeability. "Liquid glass" products have been proposed as inert and versatile coatings that may be extremely applicable in the cultural heritage preservation field. These coatings consist of silica nanoparticles, held to various substrates without adhesives or binders. Following the "lotus effect," by imitating the self cleaning abilities of the lotus flower's nanoscale texture, these coatings demonstrate a variety of characteristics including superhydrophobicity, oleophobicity, water vapour permeability, anti-microbial growth, and anti-graffiti. New materials introduced to conservation practice should adhere to ethical guidelines set by the prominent organizations in cultural heritage protection, including the United Nations Educational, Scientific, and Cultural Organization (UNESCO), the International Council on Museums and Sites (ICOMOS), the American Institute of Conservation of Historic and Artistic Works (AIC), and the Canadian Association for the Conservation of Cultural property (CAC). These organizations encourage minimal intervention and future maintenance, treatments that are visually integrated, and the use of materials that are proven scientifically to be advantageous, detectable, and removable. Silica nanoparticle coatings may potentially be a low impact, stable, versatile solution providing protection from several agents of deterioration and aiding in the preservation of stone architecture, sculpture, and monuments. Unfortunately, these coatings have not been tested sufficiently in regards to certain specific concerns for conservators, and thus further research may provide confidence in their efficacy and uses for these coatings or their derivatives in the conservation field.

The evaluation of a new product for use in conservation presents several queries: How effective is the product? How stable is it? What are the safest and most successful ways to apply it? How would a conservator detect its presence or remove it? This study was designed to consider these queries, while addressing some top concerns for stone conservators. First, the product was characterized to provide confidence in the manufacturer and to ensure no known harmful additives are present. Second, the product's water repellence performance was evaluated. Third, the water vapour permeability was measured, a priority for any coating on stone. Considering that many other concerns were not addressed, further study of this product may continue in the Queen's University, Master's of Art Conservation Program or by the author. Additionally, a collaboration was developed through Alexander Gabov, private conservator in Kingston, Ontario, with the National Capital Commission in Ottawa, Ontario, to research this coating for use on the marble Navy Memorial Monument (fig. 1). This monument had been previously coated with an antigraffiti coating that had failed, and thus these silica nanoparticle coatings could be investigated additionally as an anti-graffiti solution. The National Capital Commission graciously provided samples of previously coated marble, as no uncoated marble was available.

Fig. 1.
Navy Memorial Monument in Ottawa with scaffolding.

1.1 STONE AND COATINGS

As described in most stone conservation literature, but quite clearly by Torraca (2009), the conservation of stone-based cultural heritage often begins with evaluating several sources of deterioration resulting in a series of solutions to slow deterioration. It is clear that no single coating will be the sole solution to the protection and conservation of stone. Based on the amount of water-induced forms of deterioration of stone, water repellents are seemingly logical solutions. Stone is a hydrophobic material, rich in atoms that carry electric charges that attract water molecules and enable them to spread on the surface. Water repellents include hydrophobic materials, which have few or no electrical poles or ions and are unable to attract water, changing the surface properties of the stone and preventing the penetration of liquid water through capillary action. Charola (2003) emphasizes that these treatments are applied to stone surfaces to protect them from chemical and physical decay processes induced by contact with water. These include soiling and decay from the environment and biocolonization, frost damage from the absorption, freezing, and expansion of water, and from salt crystallization in the same manner. Additionally, water repellents aim to protect against corrosion and leaching from acids in atmospheric water (rain or dew) and from wet deposition from the dissolution of chemical constituents.

Doehne and Price (2010) state that the current most common water repellent treatments include silicone resins, alkyl siliconates, alkyl silanes, siloxanes, and polysiloxanes in addition to fluorine-containing polymers. Silica in itself is not hydrophobic, however silanes are used because they have the ability to bind the actual water repellent material, organic polymers, to the inorganic stone substrates. These treatments have been proven as effective, however are often not safe to remove from the object. Other concerns raised for the use of water repellents include insufficient adhesion to the surface or lack of water vapour permeability, incompatibility with salt accumulation, reactivity between the repellent and the stone, as well as loss of efficacy through the oxidation of organic non-polar groups, thus resulting in the need to reapply additional non-removable coatings.

One of the greatest concerns for any coating on stone, is water vapour permeability, which is significant if the stone has defects or characteristics which allow for water to penetrate the stone and condensate behind the repellent surface, causing spalling. At the present time, all available protective materials show flaws including darkening upon aging, dust attraction, loss of hydrophobicity outdoors, and are not water vapour permeable (Doehne and Price 2010; Charola 2001, 2003).

1.2 THE LOTUS EFFECT, SILICA NANOPARTICLES AND LIQUID GLASS COATINGS

The silica nanoparticle products examined in this study attempt to mimic the surface of *N. Nucifera,* the lotus flower's leaves. Lee et al. (2010), describe this effect as superhydrophobicity, which is defined by a very high water contact angle (>150^{o}), and as having a very low roll-off angle. Hsieh et al. (2008), describes the lotus leaf as having a two-tier micro/nanostructural surface textured with 3-10um bumps that are then coated with nanosized particles of a hydrophobic wax-like material. The bumps, or hills and valleys, ensure the surface contact area available to water is low, while the nanoparticles prevent the penetration of water into the valleys. This effect has been studied on other super hydrophobic surfaces in nature and has been attempted to be reproduced extensively (fig. 2). Thus, the water cannot wet the surface, forms spherical droplets, and can easily roll off the surface often carrying dirt and particulates with it.

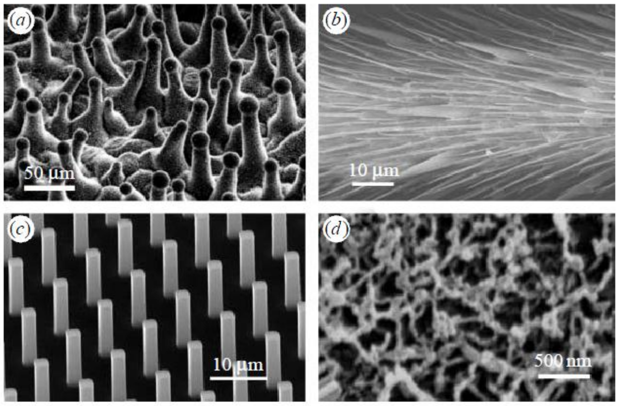


Fig. 2.
Different superhydrophobic surfaces under electron microscopy, displaying nanotextures
a) bumps on a magnolia leaf,
b) hairs on a slider's leg,
c) regular microposts on a synthetic surface,
d) fibrous or spongey design from a synthetic material

Courtesy of: Quere et al. (2008)

Various forms of nanoparticles are being manufactured in industry for use in cosmetics, drugs, printer additives, varnishes, and food, in addition to use in the health industry, including as an antimicrobial growth coating for surfaces in hospitals and even as an antimicrobial growth spray for the hands of health practitioners, according to NanoGlassIreland and Nanopool (2011). There are a few researchers studying the use and the effectiveness of silica nanoparticles in particular for their ability to increase the hydrophobicity of a surface in order to mimic the lotus effect. This can be especially useful in the field of cultural heritage preservation as additions to consolidants or water repellents.

Napierska et al. (2010) explained that the hydrophilicity of silica materials increase with the number of silicon-bonded hydroxyl groups, also known as silanols, present in the composition that are capable of forming hydrogen bonds with physical water molecules. The fewer these bonds, the more hydrophobic a material will be. Colloidal silica, precipitated silica, ordered mesoporous silica, and silica gel are hydrophilic because of a high concentration of silanols. It is useful to note that in some studies, superhydrophobicity was induced on a surface by the addition of inherently hydrophilic materials without chemical modification to their surfaces, thus determining that only the material's surface texture was attributed to the materials hydrophobicity (Mandoudis et al. 2008). Silica is the common name for silicon dioxide (SiO_2) and occurs in both crystalline and amorphous form. Silica nanoparticles are characterized using primary particle size, agglomeration or aggregation state, size distribution, shape, crystal structure, chemical composition, surface chemistry, surface charge, and porosity. Companies selling silica nanoparticle coatings, Nanopool Eu, CeNano, LiquidGlassIreland, call these coatings "liquid glass" thus suggesting that either the particles are amorphous, since glass is amorphous, or that the coating forms in an amorphous way. These companies describe manipulating the sol-gel process of producing silica to create these nano sized particles. Napierska et al. (2010) thoroughly explains this method of manufacturing silica nanoparticles, describing how amorphous silica particles are formed through the polymerization of monomers in an aqueous solution supersaturated with silicic acid, forming various silica materials from the liquid phase processes.

Recent research on hydrophobic coatings has employed inorganic oxide nanoparticles of silica (SiO_2), alumina (Al_2O_3), and tin oxide (SnO_2) as additions to enhance the hydrophobicity of commercial products, including polyalkylsiloxanes. Ferri et al. (2011) investigated silica nanoparticles (average size of 14nm) functionalized with 1,1,1-trimethyl-N-(trimethylsilyl)silanamine (Aeroxide LE1®, Degussa-Evonik) mixed with proportions of tetra-ethyl-orthosilicate oligomer (Dynasylan 40 ® Degussa-Evonik) or Glymo (3-(2,3-epoxypropoxy)-poly-trimetoxysilane or 3-glycidoxypropyl-trimetoxysilane), on limestone, sandstone, and granite samples. Aiming to improve the hydrophobicity of the surfaces, while reducing the shrinkage drying effect of the silanes on the surface, the addition of the silica nanoparticles improved the hydrophobicity up to a 148^o water contact angle (hydrophobic) on all three stone types and capilliary absorption was reduced only on the granite samples.

Manoudis et al. (2007) tested two methods of increasing hydrophobicity: etching marble surfaces with hydrochloric acid to create a surface roughening followed by Akeogard P, a functionalized perfluorinated polyether (PFPE), and the second as adding hydrophilic silica nanoparticles (Aldrich, 7nm and 14nm diameter) in different concentrations mixed with either acrylic poly(methyl methacrylate (PMMA) or the Akeogard P coating on calcium carbonate tablets. These methods resulted in pronounced effects on water repellency, increasing contact angles from 108 to 157 ±3degrees for the PMMA-SiO_2 and 112 to 162 with PFPE-SiO_2 on calcium carbonate surfaces. This study utilized the polymers as binding media between the nanoparticles and the substrate, requiring the particles to be covered with the polymer and utilized to only induce additional roughness.

Manoudis, et al. (2009) studied poly(alkyl siloxane) products from Rhodorsil 225 and Porosil VV in combination with nanoparticles (5-50nm diameter) of silica, alumina, tin oxide, and titanium oxide on Opuka, Bozanovsky, and Horicky stones used for restoration in Prague. Contact angles of almost 160^o (superhydrophobic) were obtained on the samples treated with the siloxane-particle composite films at a particle concentration of 2% w/v concentrations. This study showed that the stones had reductions in water vapour permeability on both the siloxane-particle composite and pure siloxane treated stone, showing inconsistent reduction in vapour permeability with the particles added than the pure siloxane treatments. Manoudis, et al. (2010) investigated white Greek marbles with a 1% concentration of silica nanoparticles (7nm) in the polyalkylsiloxane Rhodorsil Hydrof. Superhydrophobicity was achieved by increasing water contact angle measurements up to about 160 degrees with the particle additions in comparison to the pure siloxane treatments. This study shows that micron sized (about 3um) particles did not produce the same hydrophobic effect as nano sized particles. Additionally, water vapour permeability demonstrated a reduction with the addition of polymer, and further reduction with the nanoparticles, however this study states that it is maintained at an acceptable level, while capillary absorption was decreased similarly. Colorimetry measurements were also taken utilizing the CIE L*a*b* scale, resulting in higher increase of total change for stones coated with the siloxane-particle composite than the pure treatment, increasing as much as 10 units. Additionally, this study provided a comparison of particle sizes with different composition: alumina (40-50nm), tin oxide (22-43nm), and titanium oxide (5nm), all producing similar values of superhydrophobicity.

Hsieh et al. (2008) tested silica nanoparticles on carbon fibers to measure how they affect the fibers's wetting properties. This study utilized the commonly used sol-gel method to prepare the particles, and utilized a scaning electron microscope and Fourier transformed infrared spectroscopy to examine the surface. Their particles produced were 300-500nm in diameter and produced contact angles higher than 150^o resulting from the microscale texture of the carbon fabrics and the nanoscale texture of the particles, increasing hydrophobicity with increased concentration of nanoparticles on the surface. What is significant from this study is that there were no wax-like or fluorinated coatings added to the solution to lower the surface energy and no adhesives, simply nano sized silica particles.

CeNano and Nanopool (2011) are producers of liquid glass coatings advertised as solely silica glass nanoparticles that bond to the surface without polymers or adhesives. These coatings are being used in various sites in Europe for the protection of stone based cultural heritage, such as the Ataturk Mausoleum in Turkey (fig. 3), Nomura Bank in London, St Martin's Church and the Jewish Memorial in Kaiserslautern, the Menin Gate in Belgium, and on war graves and headstones cared for by the Commonwealth War Graves Commission. Reports from the companies state that the visual aesthetics of the stone are unaffected, they are free from biological growth, that soiling by oil and water is repelled, environmental erosion is inhibited, and cleaning is quicker.

Fig. 3.
Nanopool GmBH applying their products to the Ataturk Mausoleum in Turkey

Courtesy of: Nanopool GmBH

Considering proprietary information, Nanopool and CeNano do not discuss the exact composition of the liquid glass coatings, other than mentioning that the silica particles are formed through the sol-gel process and held in a solvent of either water or ethanol. Since organic components are usually what polymerize and become yellowed or are difficult to remove, it is important for conservators to determine if there are organics in the coating. In the previously mentioned studies, polymers were utilized. Nanopool and CeNano describe their coatings as silicon dioxide in composition without additions of resins or additives, citing the "lotus effect" and the particle's size as reason for the hydrophobicity and quantum forces for the coating's bonding to the surface. Each stating that they use the sol-gel process for production of their particles, Liquid Glass Ireland, which is partnered with Nanopool, references in their web-based literature that their coating is "almost pure silicon dioxide."

2. EXPERIMENTAL

The aim of this study is to provide qualitative and quantitative information of the efficacy of three nano-silica coatings on marble. The first phase included a characterization of the coatings alone, utilizing X-ray diffraction, inductively coupled plasma atomic emission spectroscopy, Fourier transform infrared reflectance spectroscopy, and pyrolysis gas-chromatography mass-spectroscopy to gain an understanding of the contents of the coatings. The surface morphology of the product on marble was investigated with environmental scanning electron microscopy and atomic force microscopy, while the aesthetic difference between coated, uncoated, and aged surfaces was investigated through CIE L*a*b* colorimetry measurements. Water repellence was measured with water absorption RILEM tube tests and advancing contact angle measurements. Water vapour transmission rates were also compared to determine if the coatings were "breathable". Finally, an empirical and qualitative examination was performed to evaluate ease of cleaning once graffiti is applied to the stone surface, as well as an investigation into the removability of this coating.

2.1 COATINGS

The products tested in this project were Portol Pro Sealant from CeNano GmbH & Co. KG, a porous stone water repellent and a two-part Anti-Graffiti coating from Nanopool GmbH & Co. The Portol Pro Sealant coating arrived as a solution of silica solved in water, with a spraying attachment for the bottle and was recommended to be sprayed, brushed, or wiped onto the surface. The water repellent from Nanopool arrived in one bottle, also with a spray attachment. The Two-Part Anti-Graffiti came in two bottles, a part A and part B. The two part system was meant to be applied part A first, and part B applied on to the wet surface.

2.2 HEALTH AND SAFETY CONCERNS

Napierska et al. (2010), discuss the health and safety implications of silica nano-particles, stating that it is clear that while silica nano-particles are being produced on an industrial scale for many commercial products, little is known of their true physiological effect. Crystalline micron sized silica has been extensively researched physiologically, however little is known about the toxicity of amorphous and nano-sized forms of silica, which have extremely different properties. In the Nanopool GmbH and CeNano GmbH&Co KG literature, these liquid glass coatings are considered physiologically safe, even safe enough to spray on hands when working in a hospital environment for treating patients. Although many studies have been performed on nano-silica, many have not included a full characterization of the particles thus meaning that the information obtained is incomplete and less reliable. The most common health implications of micro-sized crystalline silica are silicosis, lung cancer, chronic obstructive pulmonary disease, and pulmonary tuberculosis. The epidemiological studies of silica nano particles in comparison to fine sized particles on the microscale show greater risk of inflammatory responses and lung injury. Considering this information, all necessary precautions were taken while handling the nano-particles, in addition to while cutting the marble samples.

ASTM E2535 – 07 Standard Guide for Handling Unbound Engineered Nanoscale Particles in Occupational Settings was consulted when developing a health and safety plan for this project.

Considering silica nano-particles are respirable, or are able to reach the gas-exchange region of the lung, extreme caution was taken to prevent the particles from becoming airborne. Any inhalation risk was limited by applying the coating in a fume hood, in addition to fixation strategies which included including handling the particles in a solution and by brushing the liquids onto the stone substrate as opposed to spraying. For administrative controls, all products were labelled with handling restrictions and health and safety information. The products were only to be handled by the author and were kept in a safe location away from colleagues. Additionally, no dusting or dry mopping was used in cleanup, and only wet cleaning methods were used in the testing area. Equipment and surfaces worked on were smooth and non porous to allow for easy cleaning. In terms of personal protective equipment, if working with a large amount of the dried substance without a fume hood, a particulate mask was worn. Nitrile gloves were worn to protect from skin absorption and goggles were worn to protect against eye exposure.

2.3 SAMPLE PREPARATION

The marble substrates were Olympia White Marble from Vermont Quarries, donated by the Canadian National Capital Commission. The marble had been part of the Navy memorial Monument which had been coated with Graffiti Solution System from the American Polymer Corporation. The marble was tested in the Department of Geological Sciences at Queen's University using X-ray diffraction and a semiquantitative analysis found the marble to consist of 91% calcite, 8% muscovite, and 1% clinochlore. The Graffiti Solution System coating had failed and was peeling off the monument. The coating was mechanically removed from the substrate surface with a scalpel and warm water. These surfaces were marked and tested alongside cut and sanded surfaces for a comparison between previously treated surfaces and fresh surfaces. It is noteworthy that it is unknown how far the Graffiti Solution System coating had penetrated the marble and that all samples may have some of this polymer in it.

Samples were cut with a diamond saw according to sizes necessary for each test, ranging from between two inches by two inches to eight inches by eight inches. Sides that had not been coated with the Graffiti Solution System were sanded to a 120 grit, to match the surface of the monument. Each stone was cleaned according to the manufacturer's suggestions, with ethanol and a brush, and a final rinse of distilled water. Once cleaned, the stones were equilibrated for three days to the Artifacts laboratory testing environment (30-35%RH and 20-22^{o}C) at the Art Conservation Program, Queen's University. At this time, labels were printed on regular printer paper and applied with a strip of 15% Paraloid B72 first, with a top coat of 40% Paraloid B72 to delineate sample sites. The nanoparticle coatings were applied by brush to the samples, in the orientation they were to be tested, thus vertical surfaces were coated while left vertically. The coatings were brushed instead of sprayed for safety reasons. For each set of tests, a duplicate control set of samples was made and left uncoated. The samples were then left to dry and equilibrate for one month, with the exception of the nine samples made for the Portol Pro Sealant water vapor permeability test, which were contaminated through the use of Plasticine as a sealant around the testing cups, recreated as described earlier, and left to equilibrate for 1 week before testing commenced.

2.4 PRODUCT CHARACTERIZATION

The following tests were followed to attempt to identify the product, in order to confirm that the product contained silica nano-particles and to attempt to determine any other constituents. Characterization of the particulate based products followed the recommendations of ASTM F1877 - 05 Standard Practice for Characterization of Particles and followed the terminology recommended in ASTM E2456 – 06 Standard Terminology Relating to Nanotechnology. These standards are usually used for particulates obtained from biological specimens in health-related studies, however it was useful to understand common practice in identifying nano-particulates.

2.4.1 Fourier Transform Infrared Reflectance Spectroscopy

Often the first technique used to determine the content of an unknown substance, Fourier transform infrared spectroscopy (FTIR) was used to analyze samples of the coatings to see if their composition can be determined. The FTIR at the Queen's University laboratory is a Nicolet Avatar 320 FTIR with a Golden Gate, employing a single pass diamond Attenuated Total Reflectane (ATR) attachment, operating with 32 scans and at a resolution of $4cm^{-1}$. Analysis was performed by Dr. Gus Shurvell and the author. Samples were prepared by evaporating drops of the products on glass slides and scraped off onto the apparatus for analysis. The FTIR produces a spectra that can be compared to known spectra to determine the content.

2.4.2 Inductively Coupled Plasma Optical Emission Spectroscopy

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed to determine what elements of the thirty analyzed by the ICP-OES were present, especially to see if silica was present and in what quantity comparatively between products. A Varian Vista Axial ICP-OES was used. The samples were diluted from 1 mL with an Attendorph 1mL pipette, to twenty five milliliters in 2% nitric acid. Results reported below were adjusted for this dilution factor.

2.4.3 Environmental Scanning Electron Microscopy with Elemental Analysis

The environmental scanning electron microscope has the capacity to detect both the surface morphology of a sample and to detect elements present on a surface. An FEI Mineral libation analysis 650 Field emission gun environmental scanning electron microscope was used in the Department of Geological Sciences at Queen's University. Samples were cut into small highly polished cubes, each with copper tape down the center, with half coated with the product and half uncoated (fig. 4). Analysis was performed by Alan Grant (Geological Sciences, Queen's University) and the author.

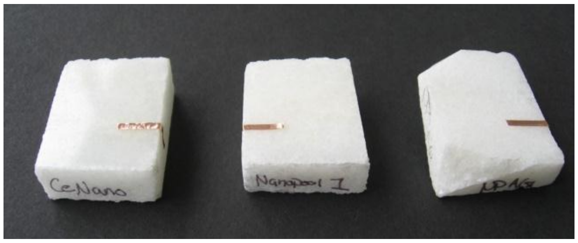


Fig. 4.
Samples prepared for ESEM: Larger areas designated for the coating; tape was cut after coating.

2.4.4 X-Ray Diffraction

X-ray diffraction detects crystalline materials and was used to confirm the amorphous nature of the silica nano-particles. Sample preparation for XRD was to evaporate the products on to glass disks and mounted in the apparatus. This was also used to analyze the marble samples. These were ground to a fine homogeneous powder. The XRD took place in the Department of Geological Sciences at Queen's University; the samples were scanned with a Philips X'Pert Pro MPD diffractometer fit with an X'Celerator high speed strip detector. Cu Kα radiation (Ni filtered), 0.02 rad incident beam soller, 15 mm mask, ½º divergence slit, 1º anti-scatter slit, 0.02º diffracted beam soller were used. The count time was 10 seconds at 0.02º 2θ increments scanned from 3º to 60º, 2θ; the sample was rotated at 2 sec/revolution. PanAlytical HighScore Plus software was used for phase identification. The software compares the peak positions and peak intensities for the unknown sample to data in a large database of known phases. The database is Powder Diffraction File Release 2001 published by International Centre for Diffraction Data in 2001. Analysis was performed by Alan Grant.

2.4.5 Pyrolysis Gas-Chromatography Mass-Spectroscopy

Pyrolysis gas-chromatography mass-spectroscopy was performed at the Analytical Services Unit, Queen's University, to determine what organic compound components are in the products. Samples were prepared by evaporating drops of each product on a glass plate, scraping them into a glass vial with a fiberglass plug, and inserting into the CDS Pyroprobe 5000 series Pyrolysis unit to be processed by the 5890 Series II Plus Gas Chromotography unit. Data was analyzed by the Analytical Services Unit.

2.5 SURFACE MORPHOLOGY AND COLOR

Methods of analysis was performed to determine the difference in surface morphology between uncoated and coated surfaces. Analysis was also used to determine if the coatings changed the color of the marble surfaces with application, as well as with artificial aging in an extreme environment.

2.5.1 Optical Microscope

An Olympus Reflected Fluorescence System, BX51 System microscope with the X-Cite Series 120 Q, XFO excitation lamp paired with the Olympus DP2-DSW software was used was used to examine the coatings on for their distribution, size, and crystalline or amorphous features. The sample preparation was to evaporate 2-3 drops on a glass slide. Samples were placed under the microscope and examined under 10x, 20x, 40x, and 100x magnification, and were examined using crossed polars as well as with ultraviolet light.

2.5.2 Environmental Scanning Electron Microscope

The surface morphology of the coatings on the stone were examined with the same environmental scanning electron microscope as previously described, in order to compare an uncoated surface with a coated surface. The samples were half inch by half inch cubes, one for each of the three coatings, partitioned with copper tape to delineate coated and uncoated surfaces (fig. 5). The surfaces of the 120 grit sanded samples was too rough for visualization, therefore these were highly polished by the Geological Sciences unit.

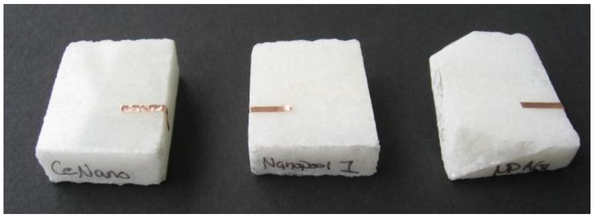


Fig. 5. Samples prepared for the ESEM.

2.5.3 Colorimetry

The colorimetry test was performed to determine the aesthetic color change before and after application, and then again after exposure to an extreme environment. Samples used were two inch by two inch blocks, with two blocks designated for each coating and control set, thus leaving ten testing sites for each product. One site on each block had been previously coated with the Graffiti Solution System, which had been mechanically removed.

The apparatus used is the Folio Instruments Minolta Chroma Meter (model CR300 D.P.) (fig. 6) which took CIE 1976 L*a*b* measurements, which is based on the Opponent-Colors Theory. The extreme environment was created using a Despatch LEA 1-69 chamber.

Measurements were taken before coating with the exact location marked, and then after coating in the same location a month later once the coating had cured. The blocks were then placed in the Despatch chamber for a week with a 60^{o}C and 60% relative humidity. The blocks were measured after this, and then placed again in a laboratory oven at 120^{o}C for another 5 days and measured again. The change in color using the CIE L*a*b* is calculated with the following equation with L* as the level of white (L*=100) to black (L*=0), a* as the red (+a*) to green (-a*), and b* representing yellow (+b*) to blue (-b*) to classify the object's color.

Fig. 6. Apparatus during testing.

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

2.6 WATER INTERACTION AND REPELLENCE

Tests were performed to determine how water interacted with the coated surfaces in comparison to uncoated surfaces. This was performed both by testing repellence on the exterior surface of the stone as well as vapor transmission rates of water through the interior of the stone.

2.6.1 Water Contact Angle

Water contact angle testing was performed to determine the change in hydropobicity that the coatings impart on the surface. ASTM D7334-08 Standard Practice for Surface Wettability of Coatings, Substrates, and Pigments by Advancing Contact Angle Measurement was followed while measuring the angle of contact when a drop of liquid applied to a coated surface. The contact angle is the interior angle that a drop makes between the substrate and a tangent drawn at the intersection between the drop and the substrate. The drop of approximately 10 microliters was applied to the specimens using a syringe, and the contact angle was be measured by capturing an image of the drop and measuring it with software.

The marble samples were cut and sanded as described earlier, did not contain any visible blemishes or defects, and were coated as previously described. Nine samples were prepared for each of the three coatings, including one set of control samples. Of the nine, two had been previously coated with the Graffiti Solution System, which was removed mechanically. This particular set of samples was used first for the water contact angle test, and then used for the water vapor transmission test.

The apparatus required for this test was an AST Products Inc, VCA Optima in the Chemical Engineering Department at Queen's University (figs. 7, 8). This model is composed of a horizontal stage, a syringe to place the droplet on surface, a light source to illuminate the droplet, and a microscope with still camera. The liquid used was deionized water (purified with a Millipore system).

Fig. 7.
VCA Optima apparatus

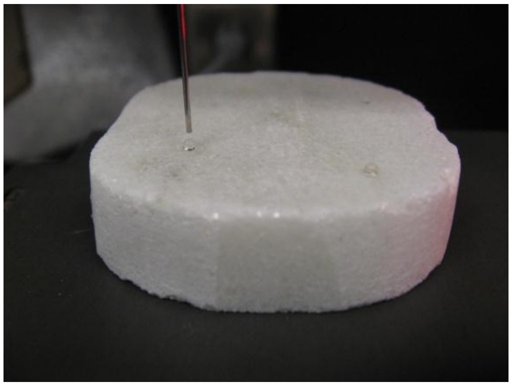


Fig.8.
Droplet being dispensed from syringe onto sample

The stage and the camera were leveled. Approximately ten microliter drops (1-2mm diameter) were applied to the marble surface by starting a drop on the tip of the needle, touching the drop to the surface, lowering the stage to deposit the drop on the surface, and taking a picture after waiting for the drop to settle after two seconds. Two angle measurements were taken, one on either side of the drop edges (fig. 9). At minimum, four drops were analyzed on each sample and contact angle results were the average of all eight angles. Possible sources of error may include dirt or fingerprints on surface, a rough or porous surface, or low humidity. The image capture and contact angle calculation was performed using the VCA Optima XE software. Analysis was performed by the author.

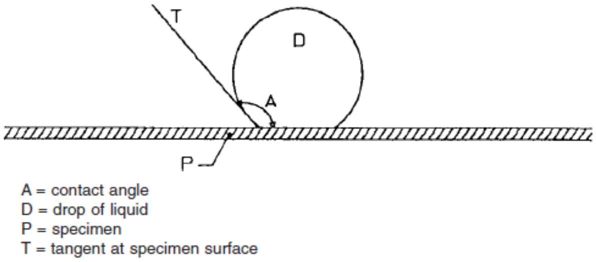


Fig. 9.
Diagram of the angle that is measured for the water contact angle test.

2.6.2 Water Absorption Tube Test RILEM II.4

The RILEM water absorption tube test II.4 was also used to determine water repellence. This test provides a means for measuring the rate at which water moves through porous materials such as masonry. This test can be performed on site or in the laboratory, and is used mainly for unweathered and untreated masonry, however it can also be used to determine the degree of protection of a water-repellent treatment. An effective treatment should reduce permeability of a surface to liquid water, and reduce vulnerability to water-related deterioration.

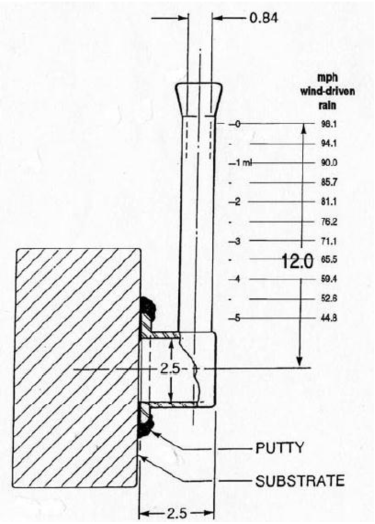


Fig. 5.
Diagram for RILEM tube on substrate.
Courtesy of: AMT Laboratories

Four blocks approximately eight inches by eight inches were prepared as discussed previously, each with fourteen sites for testing. The tubes were affixed with Plasticine putty to the surface of the stone with manual pressure. The vertical surface RILEM tubes were used, and have a zero ml to five ml gradation, where the amount of water in the column corresponds to the amount of dynamic wind pressure of 98.1mph. Tubes were obtained from PRG Masonry Products.

Water was added through the upper end of the tube until the water reached the zero graduation mark, and at intervals the level of water in the tube was recorded (fig. 10). At least eight data points were obtained for each site and the slope was determined for the data points.

2.6.3 Water Vapor Transmission

Water vapor permeability measurements were taken to determine the vapor transmission of water through the coated surface by following the suggested guidelines from ASTM E96/E95M-10 Standard Test Methods for Water Vapor Transmission of Materials. Water vapor permeability is defined as “the rate of water vapor transmission through unit areas of flat material of unit thickness induced by the vapor pressure difference between two specific surfaces under specified temperature and humidity” (ASTM E96/E95M-10 2011) The standard is designed primarily for materials with a thin, even thickness like paper, plastic films, sheet materials, plaster products and wood products and are limited to specimens not over 1.24 inches thick. Jacob and Weiss’ (1989) alteration of the ASTM E96-E95M-10 test for evaluating the water vapor transmission rates of masonry mortars and paints, was used to guide this test method.

The samples used for this test had previously been used for the water contact angle tests. The samples were approximately two inches by two inches. Nine samples were selected for each of the three coatings, with one set for a control. ASTM E96-E95M-10 suggests a minimum allowable extension of the sample beyond the cup set up, therefore the samples, originally square, were rounded and edges were cut to extend no more than 1/8th of an inch beyond the diameter of the cup. Each sample was a uniform thickness in itself, and averaged 11.25mm±0.98mm, (measured with a PowerFish digital caliper) did not contain visible blemishes or gashes, and remained uncontaminated. They were each coated as mentioned previously, and then handled with gloves. Before attaching to cup assembly, the weight of each sample was recorded.

Containers selected for the experiment were polypropylene and have a circular diameter of 4.5cm, giving the sample a 6.3cm^2 test surface. Since the samples were not of a consistent total size, a circle was cut in Cantech 91-21 Premium Aluminum Foil tape (adhesive is solvent based acrylic, used for waterproofing) in the same diameter and was adhered to the top of the sample (fig. 11. left). This test was to be performed with the coated side of the stone facing downwards (fig. 11. right), so a hole was cut in the bottom of the cup to fill the cup with water later, and then the open face of the cup was adhered to the uncoated side of the stone with hot glue, then further sealed with aluminum tape.

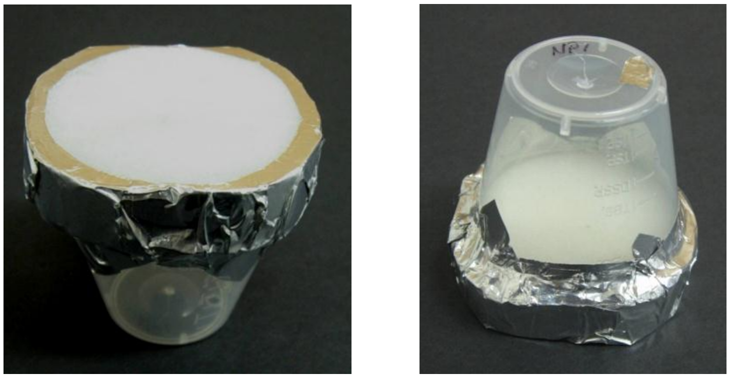


Fig. 6. Cup assembly
Left: coated stone surface with aluminum foil circle replicating cup diameter
Right: orientation of cup assembly for testing with hole cut in bottom of cup and plugged with aluminum foil tape.

The apparatus used for this test included a plastic storage container to maintain a steady temperature and relative humidity (fig. 12). Inside the chamber was a plastic grate to set the samples on, and conditioned silica gel along the bottom of the container. Since the samples were consistently emitting moisture, a consistent RH was unobtainable, thus the variation was recorded with a HOBO data logger and compared to the results. This varied between 22.8 and 21.1^{o}C and between 60% to 11% RH as the silica gel was stirred daily, and replaced every other day.

The cup assemblies were filled with 6mL of deionised water, and the hole was covered with the aluminum tape. They were weighed immediately with a Sartorius analytical balance (BP 211D). Eight or ten data points was necessary to determine a good result, therefore the samples were weighed once every day for 10 days, with a precision of approximately 1% between weightings (between 15 minutes of 5:00 pm daily).

Fig. 7.
Chamber set up with sample assemblies on the grate and data logger in the center of the chamber.

2.7 EASE OF GRAFFITI REMOVAL AND REMOVABILITY INVESTIGATION

The final phase included empirical tests to determine how much the coatings improve the ease of removal of graffiti, as well as investigations into how to remove the coatings themselves.

2.7.1 Graffiti Removal Test

This test was performed to compare the ease of removal of multiple types of graffiti from the coated surfaces, to an uncoated surface to simulate the coating's graffiti resistance. This was performed on both samples created for this test, as well as on a mockup created for the construction of the Navy Memorial Monument.

The samples created were four eight inch by eight inch by two inch blocks, coated and sanded as described earlier. Graffiti was chosen to utilize four different types and solubilities. Graffiti material used were: 1) Krylon Indoor/Outdoor spray paint (glossy) (blue), containing: acetone, propane, toluene, petroleum distillates, butane, timethylbenzenes 2) Staples brand Black permanent marker (black), containing: alcohol, 3) Windsor and Newton Oil color: permanent green light shade, containing: linseed/safflower oil, and 4) Motomaster Color Match Lacquer touch up paint (47-2527) (red), containing petroleum distillate, acetone, or toluene.

The Navy Memorial Monument mockup tested had been coated with the Graffiti Solution System polymer, which was then removed from most areas, but kept as an additional comparison surface. On the mock up four different graffiti materials were used: 1) Rustoleum**,** Specialty Fluorescent Bright neon colors, (orange), containing: aliphatic naphthas, propane, xylene, isobutanone, acetone, hexanone, toluene 2) Staples brand black permanent marker (black), containing: alcohol, 3) Windsor and Newton Oil color: ultramarine green shade, containing: safflower oil, and 4) Motomaster Color Match Lacquer touch up paint (47-2527) (red), containing: petroleum distillate, acetone, or toluene. Photography was taken of each side.

The samples were left for two days to cure, then three methods were utilized in attempting to remove the graffiti: 1) mechanical action with a scalpel, 2) water scrubbing with a natural hair bristle brush and deionized water with Orvus WA paste was used in a 0.2% solution, 3) and Smart Strip, an environmentally safe alcohol based paint stripper used by the National Capitol Commission for removing graffiti. After photography was taken of each block and compared.

2.7.2 Detectability and Removability

Coated samples as well as residue remaining after evaporation of the solvent in vials were exposed to ultraviolet light to determine if this was a plausible method of detecting the coatings. This may also provide clues as to how to remove the coatings in future studies. Additionally, observations were made about the remaining hydrophobicity of the surfaces that graffiti was removed from.

3. RESULTS

These experiments wielded a great amount of general information about these products, maintaining that there is much to be learned still about their potential use in conservation.

3.1 PRODUCT CHARACTERIZATION

3.1.1 Fourier Transform Infrared Reflectance Spectroscopy

FTIR produced very complex spectra for all of products. The CeNano Portol Pro, Nanopool Finish, and the Nanopool AntiGraffiti part A were all the same, while the Nanopool Antigraffiti part B had a spectrum much more similar to silica (fig. 13). The most important finding, was that the spectra did not appear similar to that of a spectrum of just silica particles, however whether or not the size of the particles affects the spectrum is unknown.

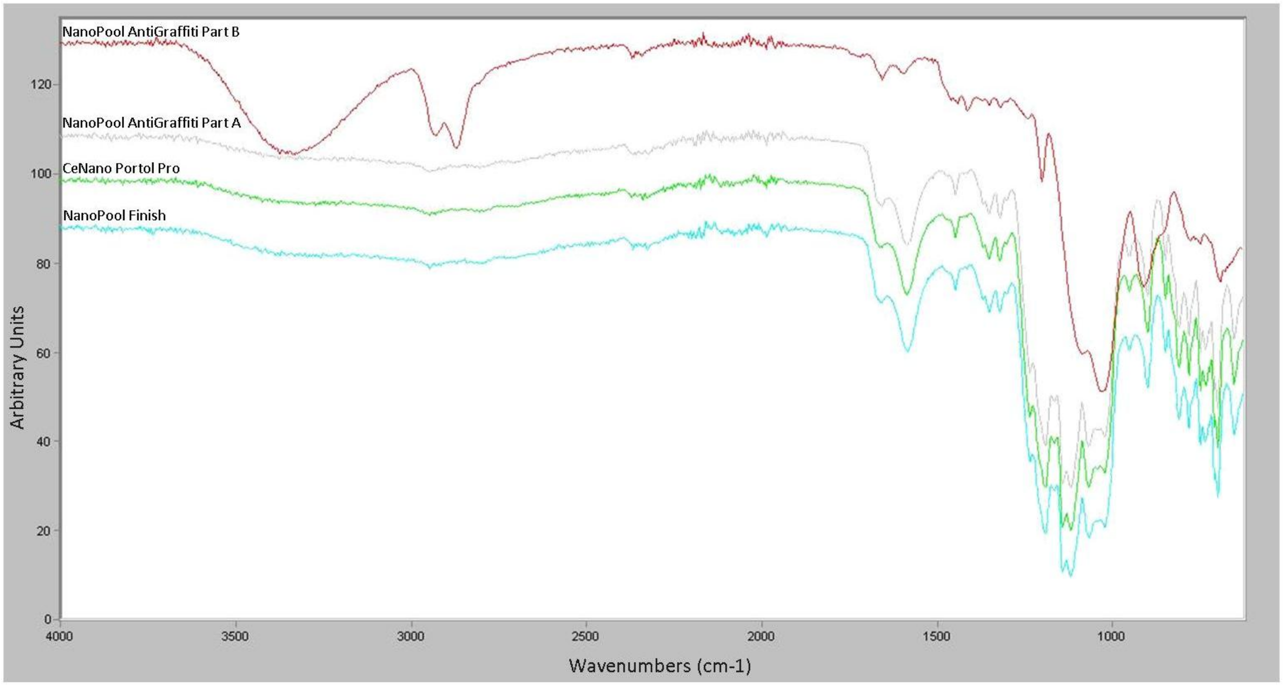


Fig. 8.
FTIR spectra of Nanopool AntiGraffiti Part B (top), Nanopool AntiGraffiti part A (second to top), CeNano Portol Pro (third from top), and Nanopool Finish (bottom)

3.1.2 Inductively Coupled Plasma Optical Emission Spectroscopy

The results from the 30 element inductively coupled plasma optical emission spectroscopy (ICP-OES) determined that silicon is the only element of the 30 detectable to be present in the product. Table 1 lists the relative amounts in the products, with part B of the Nanopool two part Anti Graffiti product containing the most detectable silica. However, the amounts detected are very low, and considering silica is difficult to detect with ICP-OES paired with the reportedly small size of the silica, this method is not to be considered appropriate.

Table 1: Silicon Content From ICP-OES

	Si (ppm)
CeNano Portol Pro	141.0
Nanopool Finish	181.0
Nanopool AntiGraffiti Part A	175.0
Nanopool AntiGraffiti Part B	13600

3.1.3 Environmental Scanning Electron Microscopy Elemental Analysis

Environmental scanning electron microscopy was successful in determining what elements were present in comparison between the coated and uncoated sides of the samples. It was evident in all samples that the silicon content increased and that fluorine was only present in the coated areas. It is noteworthy that on each of the sample surfaces there were areas where the coating had pooled while drying. In these areas the silicon and fluorine contents were even higher than those where the coating was not as thick. Figure 14 is demonstrative of all products tested.

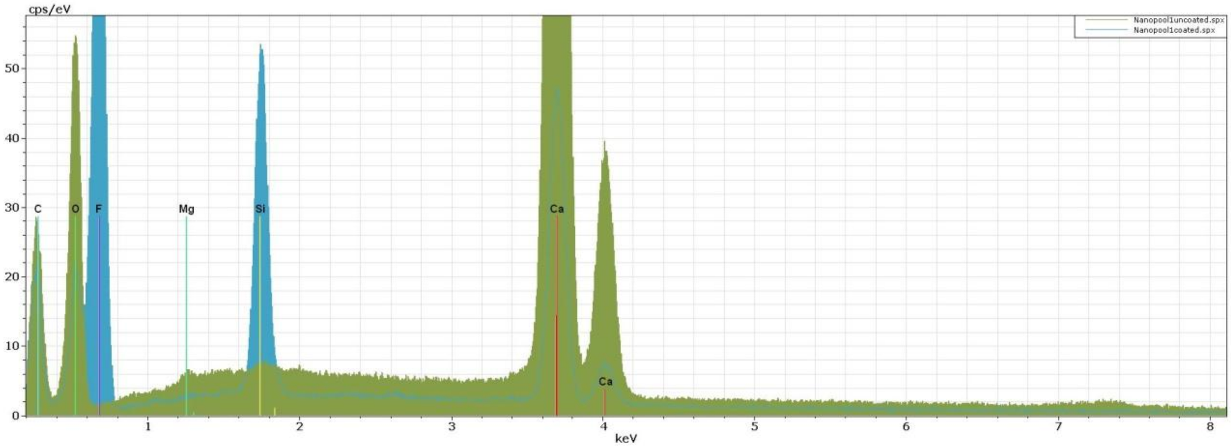


Fig. 9.
Nanopool Finish comparison between coated area (blue) and uncoated (green).

3.1.4 X-Ray Diffraction

The diffractograms produced from all three products produced characteristic amorphous peaks (fig. 15) and confirmed the manufacturer's statement that the silica in the matrix is amorphous.

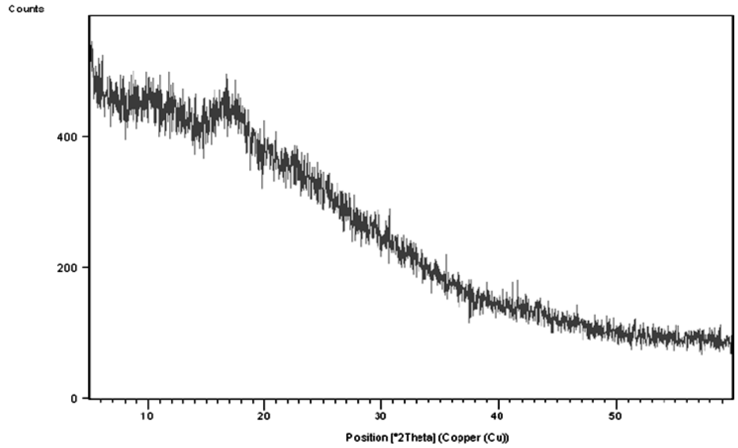


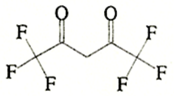
Fig. 10.
Diffractogram from Nanopool Finish.
Shows characteristic amorphous peaks.
This diffractogram is representative of all tested coatings.

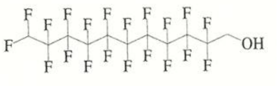
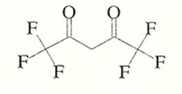
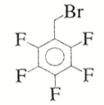
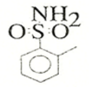
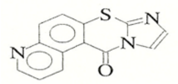
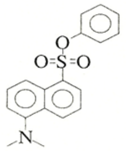
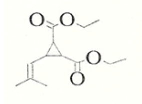
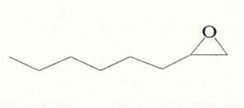
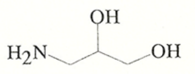
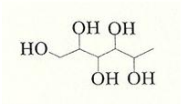
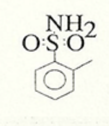
3.1.5 Pyrolysis Gas-Chromatography Mass-Spectroscopy

Samples from CeNano Portol Pro, Nanopool Finish, and NanoPool AntiGraffiti part B were analyzed. Using the pyrograms, the Analytical Services Unit analyzed the first few major peaks, the majority of the area, to determine the base of the product. A mass spectra was then produced and compared with compounds listed in the National Institute of Standards and Technology library searched for matches, shown in table 2.

Nanopool Finish was determined to be very similar with the CeNano Portol Pro product however it produced possible bromine and sulfur compounds. For Nanopool AntiGraffiti Part B, the Py-GCMS did not detect the possibility of fluorine in the product, but did find an epoxide bond in one of the potential compounds. It is also notable that silicon or any form of silane or siloxane bone was not proposed as a potential compound from the majority of the product. To make an absolute identification, standards would have to be run and compared with these results.

Table 2. Py-GCMS Results

	Time (Min)	Proposed Compound Name	Proposed Structure
CeNano Portol Pro	0.991	2,4-Pentanedione, 1,1,1,5,5,5-hexafluoro-	
	2.493	Benzene, (bromomethyl)pentafluoro-	

	6.749	1H,1H,2H,2H-Perfluorooctan-1-ol	
	8.830	1H,1H,2H,2H-Perfluorooctan-1-ol	
Nanopool Finish	.810	1H,1H,11H-Eicosafluoro-1-undecanol	
	1.418	2,4-Pentanedione, 1,1,1,5,5,5-hexafluoro-	
	2.858	Benzene, (bromomethyl)pentafluoro-	
	18.249	Benzenesulfonamide,2-methyl-	
	19.895	(11H)Pyridol[3’2’:4,5]imidazo[2,1-b]benzothiazin-11-one	
	21.025	1-Naphthalenesulfonic acid, 5-(dimethylamino)-, phenyl ester	
	23.539	1,2-Cyclopropanedicarboxylic acid, 3-(2-methyl-1-propenyl)-, diethyl ester	
Nanopool AntiGraffiti Part B	3.467	Oxirane, hexyl-	
	4.960	3-Amino-1,2-propanediol	
	10.485	1-Desoxy-d-mannitol	
	18.333	Benzenesulfonamide,2-methyl-	

3.1.6 Product Characterization Discussion

The intention of performing the compositional analysis was to confirm that the products contained amorphous silica and to determine if any organic matter was present. FTIR showed that the product may have a complicated composition and consisted not only of silica. This investigation was then encouraged by the discovery of a yellowed residue during the solids content analysis, which led to the GCMS experiment, which determined a variety of complex fluorinated polymers may be in these products, none of which contained silicon in their composition. The ICP-OES confirmed that silicon was in fact present, and the XRD analysis determined that this silicon was likely silica of an amorphous nature. Both the presence of silicon and fluorine was further supported by the ESEM elemental analysis. In comparison between products, Nanopool AntiGraffiti part B was found to likely contain more silicon through the ICP-OES results, which was supported by it forming a seemingly thicker film and produced more residue when evaporated in a vial. These results were discussed with the CeNano manufacturer, who stated that that product is a per fluoride silica matrix.

3.2 SURFACE MORPHOLOGY AND COLOR

3.2.1 Optical Microscope

Visualization was performed up to 100x magnification, with the best resolution at 40xmagnification and under crossed polars for contrast. However, because of the transparency of the coatings, a definite surface morphology or particle size was not determined using this method. Along the edges, it appeared that a form of crystallization occurred on the CeNano Portol Pro product (fig. 16) and some tide lines appeared along the edges of the Nanopool Finish Product (fig. 17). The edges of the Nanopool AntiGraffiti product seemed to give a much more diffuse appearance and almost seemed to have smaller particles than the other products (fig. 28).

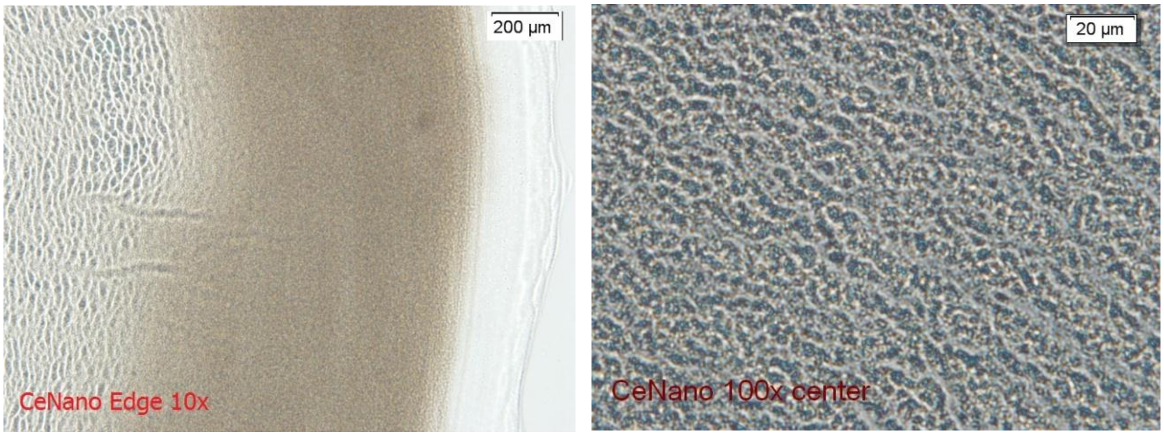


Fig. 11. CeNano microscopy images, showing surface texture or drying pattern as well as small spherical shapes.

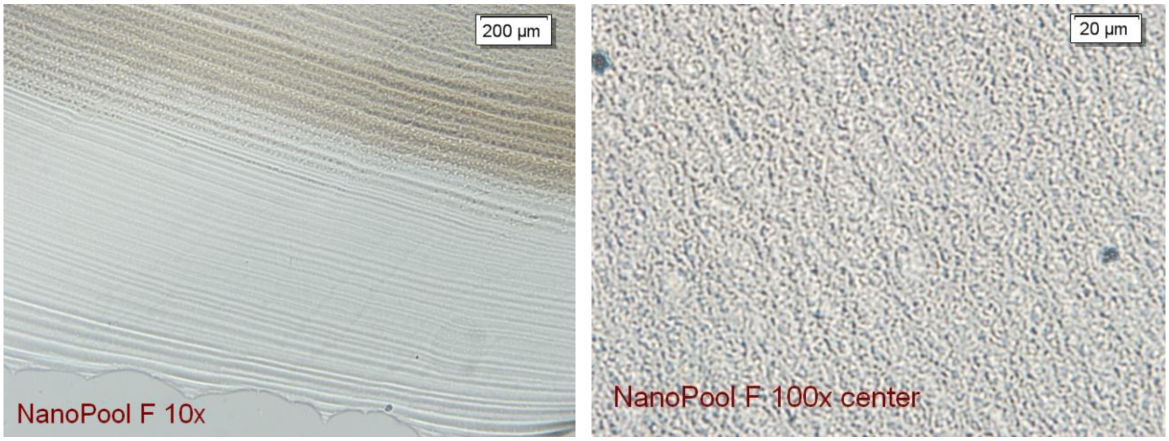


Fig. 17. Nanopool Finish showing surface texture or drying pattern and small spherical shapes.

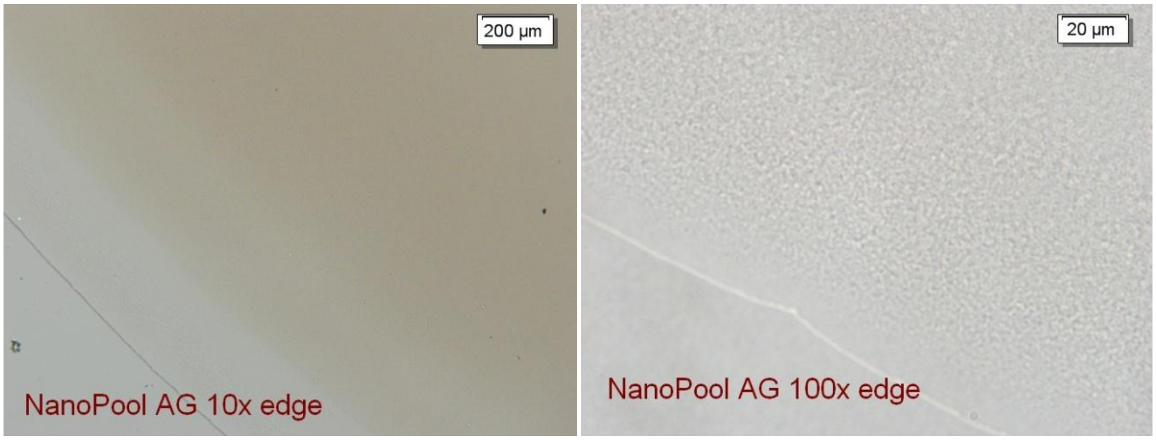


Fig. 18. Nanopool AntiGraffiti products showing a more dispersed edge and potentially smaller particles.

3.2.2 Environmental Scanning Electron Microscopy

Environmental scanning electron microscopy was successful in imaging coated and uncoated areas of the products, and was especially interesting when examining pooled areas of the products as well as lines where the products had been applied up to the copper tape edge, with the tape then removed. Unfortunately, a high enough resolution to determine the nano-scopic surface texture of the samples was not possible with the settings used.

The CeNano Portol Pro product may not have been applied thick enough along the edges, considering no tape line was visible (fig. 19) and pooled areas were infrequent. A pooled area found on the surface revealed small specks (fig. 20), which were determined to be likely organic matter, either from dust or from residue in the product (fig. 21).

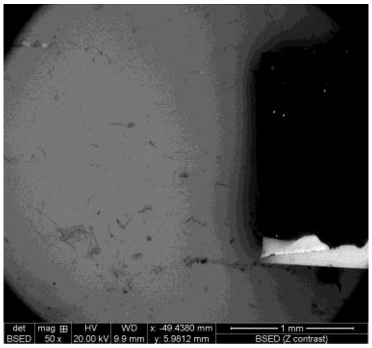


Fig. 19.
CeNano Portol Pro: tape lines were not as easily distinguishable in comarpison to the other products. Potentially not enough product applied.

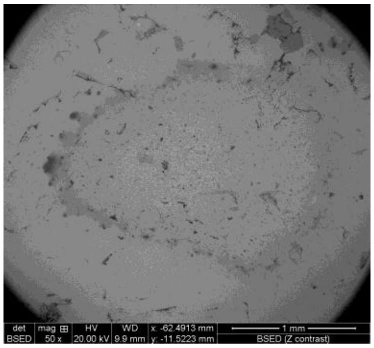


Fig. 12.
CeNano Portol Pro: Areas where the noted pooled areas that had small specks of possible organic matter in them (increased carbon content in spectra).

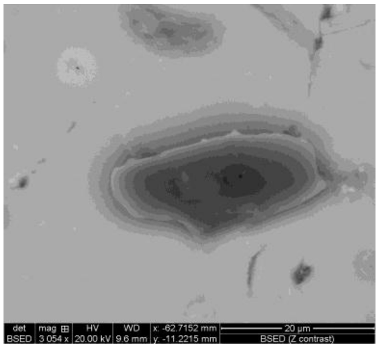


Fig. 21.
CeNano Portol Pro: Detail of small speck in pooled area of CeNano Portol Pro sample. Likely organic matter that was deposited on the surface while drying or was in the product. The black dot indicates beam damage indicative of organic matter.

The Nanopool Finish product was easily imaged with this method and produced a very distinct tape line (figs. 22, 23). Additionally, pooled areas (fig. 24) were easily distinguishable, as it seems this product produced a thicker layer than the CeNano Portol Pro product.

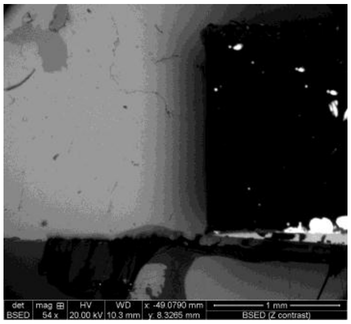


Fig. 22. Nanopool Finish: Tape lines are easily distinguishable. The dark black residue in the image is tape adhesive, while the light grey is the product.

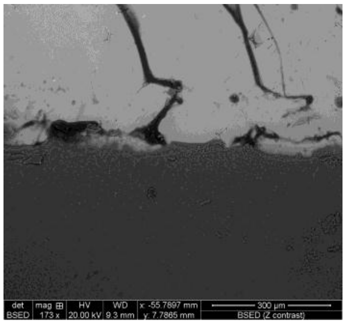


Fig. 23. Nanopool Finish: At higher magnification, the tape line is clearer. The black is adhesive residue.

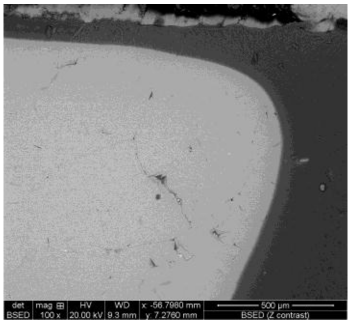


Fig. 13. Nanopool Finish: In pooled areas, it appeared that there was more of a distinguishable boundary line than other products.

The Nanopool AntiGraffiti coating was also easily imaged using ESEM. The tape lines were well defined (figs. 25, 26). Also, the appearance of the pooled areas differed distinctly from the CeNano Portol Pro and Nanopool Finish products, as they appeared more dispersed (fig. 27).

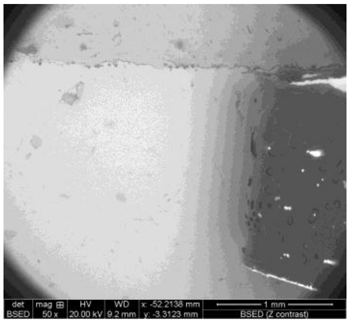


Fig. 25.
Nanopool AntiGraffiti: Tape lines were easily distinguishable with this coating.

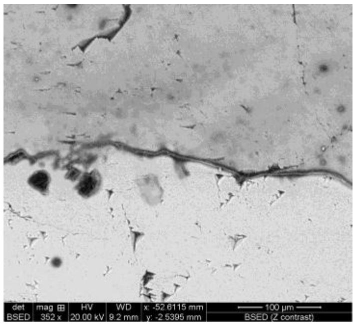


Fig. 26.
Nanopool AntiGraffiti: At higher magnification, the tape line is even easier to distinguish. The darker grey areas are coated.

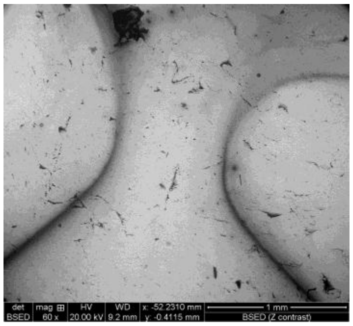


Fig. 27.
Nanopool AntiGraffiti: Pooled areas appeared more dispersed than the Nanopool finish and were easier to identify than the CeNano Portol Pro product.

3.2.3 Colorimetry

The colorimetry results are illustrated in figure 28. With application , the most significant change was the L*(white-black) value, which for most samples was found to be slightly lighter, except with the Nanopool AntiGraffiti coating where it appeared slightly darker. The a* and b* values showed no statistically significant differences. Total change, ΔE, is visible above a value of 1, so a visible difference was seen with the Nanopool Finish previously coated samples, the Nanopool AntiGraffiti coating, and on the Control previously coated samples.

After 5 days with 60°C and 60% RH environment, the most significant change was with L*, as it appeared all samples became significantly lighter with the previously coated samples (GSS) for each set being 0.50 (Nanopool AntiGraffiti) to 3 values higher (control) than the not previously coated set. Again, the a* values were not significant, however the b* values all changed between 1.07 (Nanopool AG) to 3.52 (CeNano GSS). The average change, E, was a total of between 4.00 (Nanopool Finish) to up to 6.50 (Control GSS), with those having been previously coated consistently a larger change than those not.

After an additional 5 days with an environment of 200°C and an uncontrolled relative humidity, these samples all samples became significantly lighter, between 9.65 (CeNano) to 10.32 (Control) units. The a* values were also slightly higher, from 0.64 (Nanopool AntiGraffiti) to 0.91 (CeNano) units, and similarly behaving were the b* values between 0.90 (CeNano) to 1.95 units (Nanopool 1). The b* values were significantly higher for the previously coated samples, between 1.95 units (CeNano) up to 3.79 units (Nanopool AntiGraffiti). The total change then was very high for this test, due to the amount that the L* values changed. According to Student's t-test of the ΔE values, the only values statistically significantly different when compared to the control are the differences between the Nanopool AntiGraffiti coating and the control after application, and between the control and the CeNano after the 120°C exposure, with the CeNano changing less than the control.

It is notable that with all of these tests, it appears that the control samples changed just as much as the test samples changed. Thus, these products do not aesthetically change the appearance of the stone under these conditions. However, the samples that had been previously coated with the Graffiti Solution System were more affected by the conditions than the other samples. Also, it should be considered that the marble may have been dehydrated during this process, thus causing the samples to appear lighter. The Nanopool AntiGraffiti coated surfaces did appear slightly glossy, whereas the other surfaces all retained a similar matte surface without obscuring the natural shimmer of the marble. This was not tested or quantified and should be further investigated.

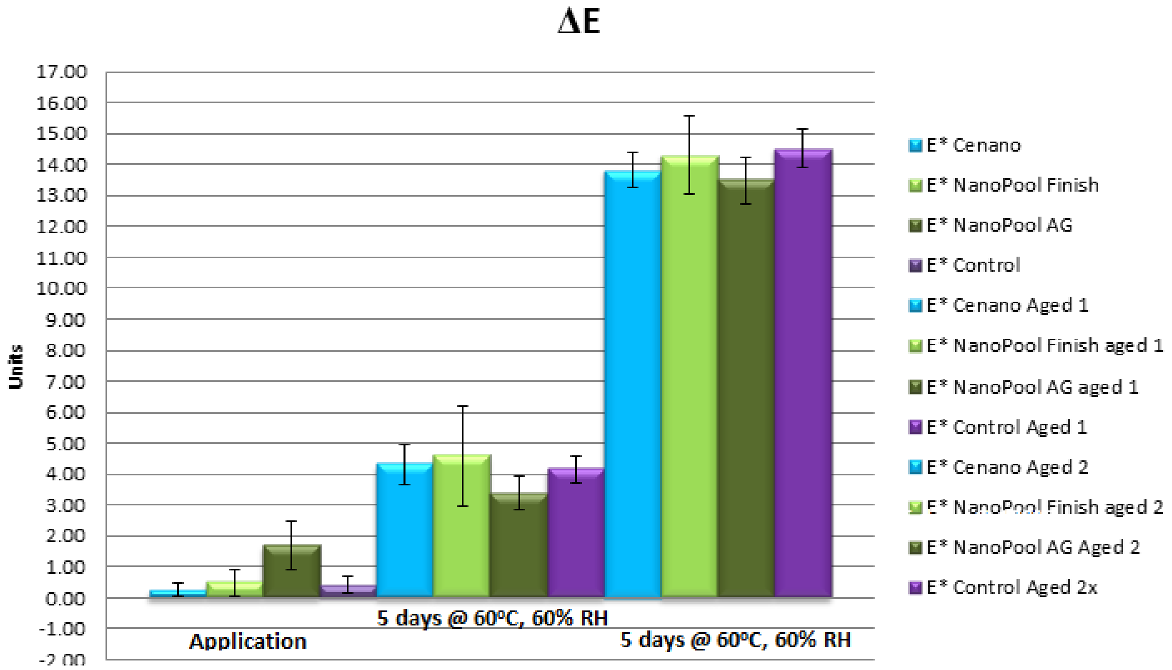


Fig. 28.
Total color change. It is significant to note that the Control samples changed just as much as the coated samples.

3.2.4 Discussion of Surface Morphology and Color

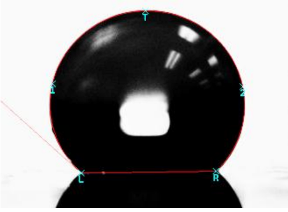
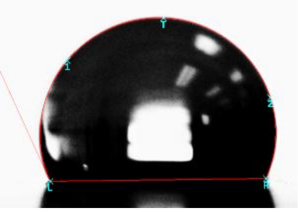
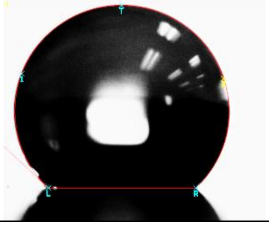
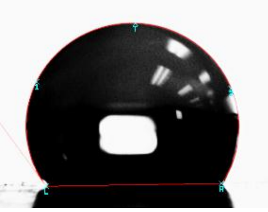
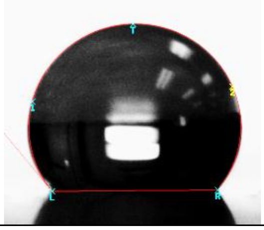
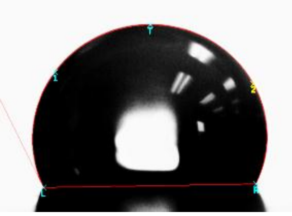
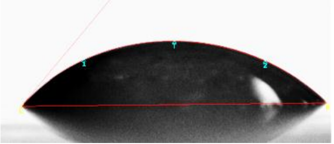
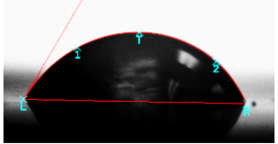
Microscopy indicated crystallization around the edges of the some the drops, which was confirmed under ESEM. The ESEM was able to examine the coating and their interaction with this surface, noting that the coating was unable to provide an even finish and became concentrated in some areas, which may be useful for examination. Colorimetry indicated that there is not a significant change before and after application of any of the products, as well as with exposure to extreme environments when compared to an uncoated control set, which is an excellent finding.

3.3 WATER INTERACTION AND REPELLENCE

3.3.1 Water Contact Angle

Angles of 10-20^{o} are indicative of excellent wetting of the surface and hydrophobic an angle greater than 90^{o}. According to Lee et al. (2010), water contact angles higher than 150^{o} are considered superhydrophobic, and indicative of the lotus effect. By comparing the coated samples with the controls, as indicated in table 4, the water contact angle was improved by a maximum of about 88^{o} by the addition of the CeNano Portol Pro product and Nanopool finish products, and by about 78^{o} with the Nanopool AntiGraffiti product. It is also of note, that on samples that had been previously coated with the Graffiti Solution System, the water contact angle was improved by 10^{o} with just that product, and only about 56^{o} with Nanopool AntiGraffiti product, 67^{o} with the Nanopool Finish, and 55^{o} with the CeNano Portol Pro. According to the Student's t-test, the only values statistically significant are between the Nanopool Finish and the Nanopool AntiGraffiti coating, and all values when compared to the control (table 3).

Table 3. Water Contact Angle Comparisons

	Average Contact Angle	**Previously coated with GSS**
CeNano Portol Pro	138.91 ±3.00 	113.31±0.64 
Nanopool Finish	138.83 ±4.01 	125.25 ±0.14 
Nanopool AntiGraffiti	128.60 ±7.55 	114.90 ±1.45 
Control		

3.3.2 Water Absorption (RILEM Tube Test)

These values were calculated as stated in the experimental. The water absorption at 260 minutes was calculated by a line from the data points (table 4). It is notable that some data sets were discarded due to the RILEM tube detaching from the substrate and alternate methods to adhere the tubes to the stone substrate should be considered in reproducing a similar study. Considering the standard deviations (better visualized in fig. 29) and the Student's t-test, it was determined that the only statistical difference between values was between the Control and the Nanopool AntiGraffiti Finish coating.

Table 4: Water Absorption Comparison

	Mean (sd) water absorption at 260 minutes	**Samples with GSS**
CeNano Portol Pro	0.48 (±0.23)	*0.24 (±0.03)*
Nanopool Finish	0.31 (±0.07)	*0.36 (±0.18)*
Nanopool AntiGraffiti	0.53 (±0.30)	*0.31 (±0.10)*
Control	0.45 (±0.06)	*0.44 (±0.10)*
Water evaporation rate	0.10 (±0.08)	

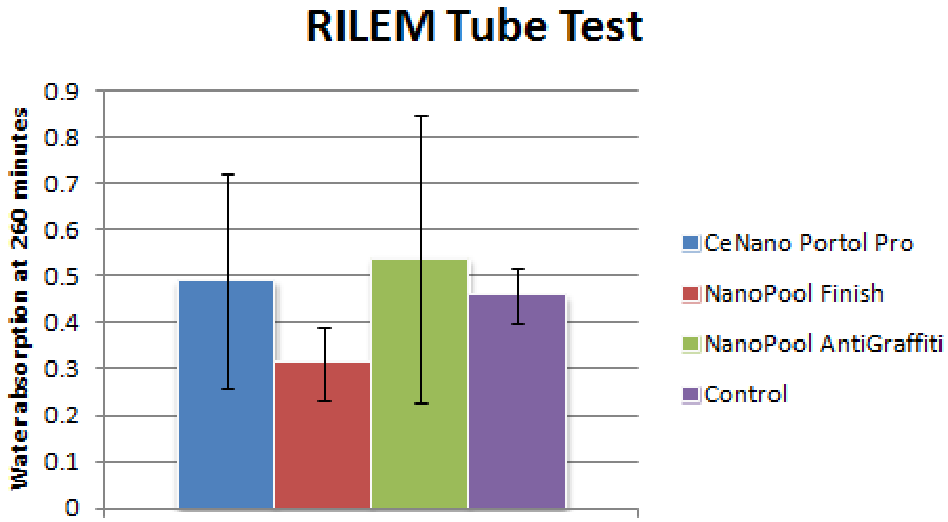


Fig. 29.

3.3.4 Water Vapor Transmission

This test was very successful in determining the water vapor transmission and permeability of the coatings. It is notable that the set of CeNano Portol Pro samples became contaminated before the testing, and more samples had to be made. Samples that had leaked were not included in the average of the water vapor transmission rates. Water vapor transmission rates of the products were significantly different from each other, as seen in table 5, however the CeNano behaved quite similarly to the control (fig. 30). According to Student's t-test, all of the results were statistically significantly different than the control, with the CeNano having a score almost representative of not statistically significant. The only t-score values not significant was between the Nanopool Finish and the Nanopool AntiGraffiti test.

Table 5. Water Vapor Transmission Rates
No standard deviation for the GSS samples indicates a sample had been eliminated

	WATER VAPOR TRANSMISSION RATES	
	Water Vapor Transmission Rate (grains per hour per area m^2)	**samples with GSS**
CeNano Portol Pro	61.240 (±1.963)	7.361
Nanopool Finish	42.489 (±17.62)	12.614
Nanopool AntiGraffiti	12.097 (±3.348)	11.950 (±3.122)
Control	63.619 (±0.632)	60.293 (±2.334)

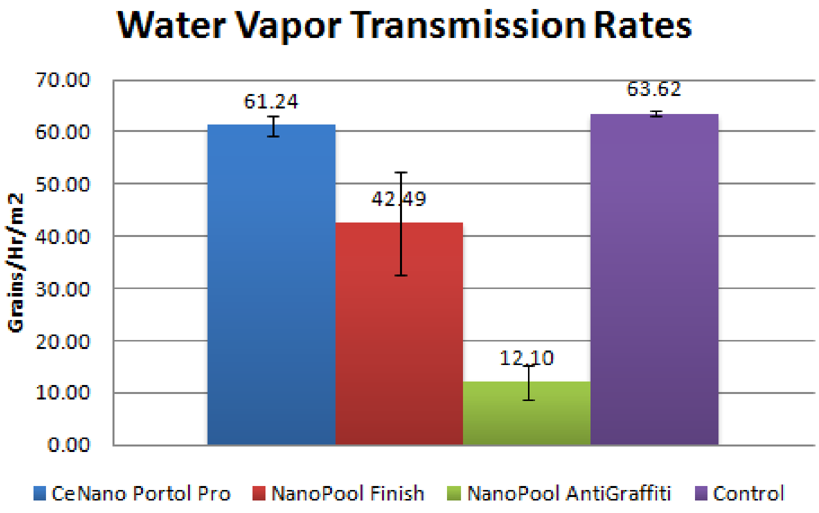


Fig. 30.

3.3.5 Water Interaction and Repellence Discussion

The water contact angle measurements showed that all three products increased the water contact angle in comparison to the control. It is also notable that those that had been previously coated with the Graffiti Solution System gave a reduced water contact angle when coated with the products. The RILEM tube tests unfortunately provided no statistically significant difference between the amount of water absorbed into the substrate after 260 minutes. An immersion test may provide a more significant indication of water absorption differences. Water vapor transmission rates determined that the rate of transmission through the CeNano Portol Pro Portol Pro and the Control set are extremely close, with the Control having a greater rate of transmission. The Nanopool Finish product had an extremely wide standard deviation. The Nanopool AntiGraffiti Product showed the product allowed a much slower rate of vapor transmission. Based on these results it appears that these products increase the immediate water repellence, however if water is held to the surface for a prolonged period of time, the stone will absorb water. This may be due to the product losing repellence over time or becoming solubilized in water. This hypothesis was reinforced by the resolubilization of residue in the vials when more product was added. Prolonged water contact angle measurements or immersion tests may provide a better indication of these results.

3.4 GRAFFITI REMOVAL AND REMOVABILITY OF COATING

3.4.1 Graffiti Removal Test

This testing showed that these products all make the graffiti somewhat easier to remove than the control surface, however the Nanopool AntiGraffiti coating did provide a more protected surface in comparison to all others. Unfortunately, ghosting was still evident (fig. 31) in all situations and better results may come from more efficient methods of removal or with an additional coat of the product.

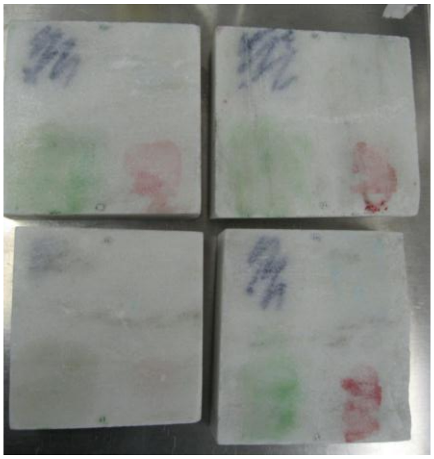


Fig. 31.
Samples after graffiti removal
Top left: CeNano
Top Right: Nanopool Finish
Bottom Left: Nanopool AntiGraffiti
Bottom Right: Control

On the mock up from the Navy Memorial that had been previously coated with the Graffiti Solution System, it was found that the permanent marker was repelled by the nano surfaces, and remained on the top of the surfaces. Most of the other graffiti materials adhered to the surface sufficiently. Removal of all graffiti was much more effective on this mock-up and less ghosting was apparent, likely due to the impermeability of the Graffiti Solution System. When removing graffiti from the remaining Graffiti Solution System, the graffiti tended to smear around, and removal methods weakened the polymeric surface. Drops of water were applied to the surfaces where graffiti was removed and all nano coated surfaces still appeared water repellent, except for the remaining Graffiti Solution System surface.

3.4.2 Detectability and Removability

The 32 mL samples were evaporated at a temperature of 200°C, and they were found to be yellowed once evaporated, thus producing a possible degradation product. It is noteworthy here, that according to the CeNano product developer, the organic constituents of their product is unstable above 100°C. The products became yellowed (fig. 32, left) and fluoresced under ultraviolet light (fig. 32, right).

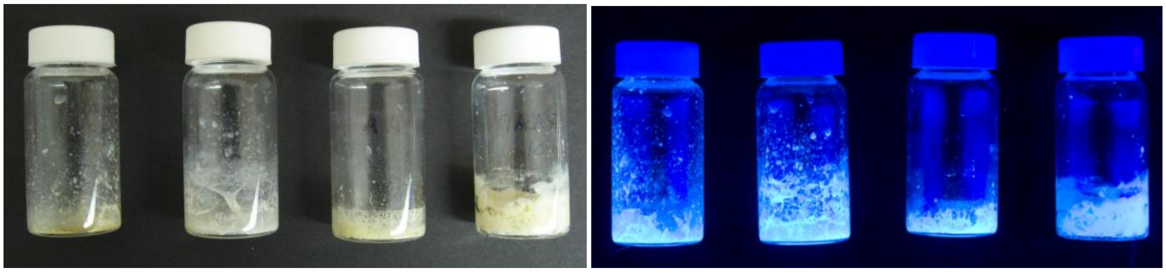


Fig. 32. (Left) After evaporation of 32 mL under mixed lighting; (Right) After evaporation under ultraviolet light.

It is also notable that areas where the products had pooled on the surface of the ESEM samples also fluoresced (fig. 33). This may provide a good method to determining if the coatings are affected by removal methods.

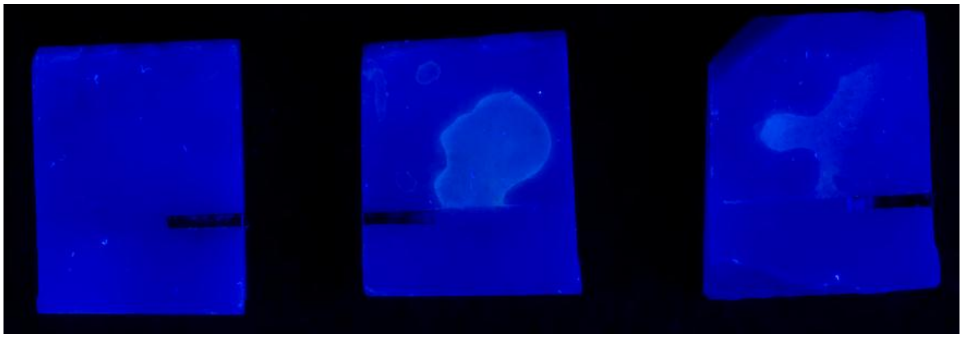


Fig. 33. ESEM samples under fluorescent light. (Left) CeNano, (Middle) Nanopool finish, (Right) Nanopool AntiGraffiti

3.4.3 Graffiti Removal and Removability Discussion

With the above testing, it was evident that these coatings provided some protection against graffiti and soiling. The most effective was the Nanopool AntiGraffiti product, which seemed to form a greater barrier than the other products. This may be due to the product’s diffuse nature and smaller particles, as well as greater silicon content and possible epoxy nature. These products are detectible under ultraviolet light, which may mean that these products can be detectable in concentrated areas or microscopically. These products seemed unaffected by the graffiti removal methods, as they retained a water repellence behavior after the cleaning ended. In conversation with the CeNano manufacturer, it was stated that the products are not affected by acids, and can be removed with a solution with a pH of higher than 13.

4. CONCLUSIONS

This project was able to give a successful basic understanding of these silica nano-particle “liquid glass’ coatings, however proved that much more research must be done. It was confirmed that amorphous silica was present in the products, and found that some form of fluorinated polymer also existed. The ‘lotus effect’ surface morphology was not determined through these methods, however the coating’s thin layer and various surface features were found, indicating that a nanoscale texture is likely to be present. The coatings were found to repel water initially as seen in water contact angle measurements, however may lose repellency over prolonged periods of time as indicated through the water absorption RILEM tube tests. Water vapor transmission was found to just below that of the control for the CeNano Portol Pro product, however was reduced with the Nanopool Finish and greatly reduced with the Nanopool AntiGraffiti product. For graffiti resistance, these products improved the stone’s cleanability and aided in preventing the products from penetrating deeper into the pore structure however did not completely prevent ghosting of the graffiti. For all tests, it appeared that the few replicates whose surfaces were previously coated with the Graffiti Solution System did not perform performed as well as those that had not been previously coated, and were found to decrease the hydrophobicity of the newly coated stone slightly, yellowed slightly in extreme environments, and were much less transmissible to water vapor. In terms of detectibility, it was found that the coatings fluoresced in concentrated areas, which may be useful in determining how effective removability methods are.

These products show potential for use in conservation, and may prove more useful as a protective layer from surface dirt, pollution, and graffiti than as a water repellent for more modern and newer surfaces. Future research is necessary and could include: prevention of biodeterioration, long term stability and reapplication, removability, re-treatability, and use on other substrates.

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