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The ability of three commercial anti-graffiti products, Fluorolink® P56 (a fluoropolymer), Weather Seal Blok-Guard® and Graffiti Control (a silicone elastomer), and Protectosil® Antigraffiti (a silane), to provide protection from graffiti attack was evaluated on Wallace sandstone and Mississquoi marble. Results suggested that the coatings affected the colour of the stones, rendering samples darker with increased yellow values. Water absorption of the sandstone decreased with anti-graffiti coatings. The application of protective coatings can inadvertently provide a hydrocarbon source for microbial growth. To investigate this potential, anti-graffiti coatings were contaminated by common soil microbes through culture plate production and microbial isolate cultivation; the biodeterioration was measured with Electrochemical Impedance Spectroscopy (EIS). EIS data indicated that no coating was affected by microbes. Fourier-Transform Infrared spectroscopy in attenuated total reflection mode (FT-IR / ATR) was used to note changes in coating chemistry before and after exposure to microbes. FT-IR / ATR proved to be a more sensitive technique than EIS in detecting changes to the coatings and suggested that Blok-Guard® was susceptible to biodeterioration. Effective removal of paint and marker graffiti from the coatings was tested with water, ethanol (80% in distilled water), acetone, and a commercial product, Defacer Eraser® Graffiti Wipe. Defacer Eraser® Graffiti Wipe was more successful than other solvent systems in removing graffiti from stone coated with anti-graffiti coatings. When all the results were assessed together, Protectosil® exhibited the best results followed by Blok-Guard® and finally Fluorolink® P56.

Une étude a été menée dans le but d'évaluer la performance des enduits anti-graffiti commerciaux suivants : Fluorolink® P56 (un fluoropolymère), Weather Seal Blok-Guard® & Graffiti Control (un élastomère à base de silicone), et Protectosil® Antigraffiti (un silane). Ces tests ont été effectués sur du grès Wallace et du marbre Mississquoi. Les résultats indiquent que les enduits ont altéré la couleur des pierres, causant un assombrissement ainsi qu'une augmentation dans les teintes jaunes. De plus, le grès est devenu plus imperméable. L'application d'un enduit peut avoir comme effet secondaire, celui de créer une source d'hydrocarbure favorable à la croissance microbienne. Afin d'étudier cette question, les enduits anti-graffiti ont été mis en présence de cultures microbiennes typiques du sol et ont été examinés au moyen de la spectroscopie par impédance électrochimique (SIE). Les données de la SIE démontrent qu'aucun des produits étudiés ne sont vulnérables aux cultures microbiennes utilisées. L'analyse de changements dans la composition chimique des produits avant et après leur exposition aux cultures microbiennes a été effectuée par spectroscopie infrarouge à transformée de Fourier par réflectance totale atténuée (SI-TF / RTA). L'analyse par SI-TF / RTA s'est avérée être plus sensible que celle par SIE, et suggère que Blok-Guard® est vulnérable à la biodégradation. Le nettoyage des graffiti faits à l'aide de peinture en aérosol et de crayons feutres a été testé avec de l'eau, de l'éthanol (dilué à 80 % dans de l'eau distillée), de l'acétone ainsi qu'un produit commercial, le Defacer Eraser® Graffiti Wipe. Ce dernier s'est montré plus efficace que les autres solvants pour enlever les graffiti sur la pierre protégée par les enduits anti-graffiti. En évaluant les produits selon tous les critères, les meilleurs résultats ont été obtenus avec Protectosil®, suivi de Blok-Guard® et finalement de Fluorolink® P56.

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Introduction

Public art, monuments, historic structures, and heritage sites are a testimony to their creators, past cultures, and historic events. Preservation allows for continued exploration and appreciation of the material culture of past eras. Preservation also ensures that the physical and tangible realizations of today's culture are available for the future. While the goal of preservation is to provide stabilization for the longevity of historic and artistic objects using current knowledge, best practices, stable materials, and, where possible, minimal intervention, the task of protection from graffiti is not without some difficulties. Measures to prevent this form of damage from occurring in the first place such as physical barriers, landscaping, or object relocation are often not options in a preservation and conservation maintenance plan. Coatings that give an absorbing surface the ability to repel or to shed contaminating substances are commercially available and may provide a viable alternative. These coatings must be used with caution as they may cause discoloration, may negatively affect moisture movement in and out of substrates, and may degrade at varying rates of speed given the nature of the coating and exposure to agents of deterioration. These coatings contain solvents, so application can be complicated, and they must be renewed on a periodic basis. These anti-graffiti coatings (AGCs) can provide a viable means of prevention of damage from vandals when carefully reviewed and properly selected. However, it is important to examine the effectiveness of these compounds to protect stone while, at the same time, not causing other undesirable changes or damage. As AGCs are closely related to those water repellent and consolidant products designed to protect stone from weathering and to strengthen a damaged surface, the performance criteria for conservation testing of AGCs are similar to those used to test stone preservatives. As new AGCs and stone preservatives appear on the market and old ones are reformulated to meet laws regarding volatile organic chemicals, there is ample need to continue the investigation of these materials for conservation purposes.

Anti-graffiti Coatings

AGCs work by providing a film barrier between the substrate and the graffiti. Some coatings line the pores of materials so that pigmented carriers from graffiti cannot penetrate. Others swell upon exposure to moisture, blocking graffiti from the substrate. Coatings with repellent properties affect the ability of the graffiti to dry, facilitating removal.[1]

Investigations into the nature and performance of AGCs appeared concurrently with the rise of graffiti in the 1960s and 1970s in cities such as New York and Philadelphia, although documentation of the conservation treatments is scarce from that period. One of the earlier documented uses of a product as an AGC was Hydron 300 (an acrylic-based coating) used on public transportation vehicles in the 1970s. This is cited in a 1971 treatment report of the Federal Hall National Memorial in New York City.[2]

Today, the chemistry of AGCs includes: acrylic or polyurethane fluoropolymers, acrylic emulsions, solvent or water-based silicones and silanes, waxes, and sacrificial polysaccharides. To narrow the scope of this research, only a polyurethane fluoropolymer, a solvent-based silicone, and a water-based silane were selected because they were less represented in research literature while generally available as commercial products.

Fluorinated Coatings

Fluorinated polymers (fluoropolymers) exhibit promising properties for conservation purposes. Fluoropolymers have been used as stone coatings with published studies first appearing in the 1980s, some specifically referring to the use of fluorosilicates in the treatment of deteriorated stone and stone with graffiti problems.[3] Fluoropolymers have strong bonds between carbon and fluorine, which offer some resistance to aging and chemical alteration from environmental exposure. Moggi et al.[4] found that the perfluoropolyethers (PFPEs) have properties that facilitate graffiti removal. Woolfit[5] tested PFPE oils, and demonstrated that, although the PFPEs could not prevent the penetration of pigment or dye particles into stone and concrete, they could increase the effectiveness of removal of graffiti by different cleaning agents. The basic chemical structure for PFPEs is described by Moggi et al.[4] and Horie.[6]

The fluoropolymer selected for testing was Fluorolink® P56 (Solvay Solexis), a product in the developmental stages by the manufacturer with potential uses as an AGC. It is an aqueous dispersion of an anionic-based fluorinated polyurethane resin. Fluorolink® P56 is not a PFPE but a polytetrafluoroethylene (PTFE). The proprietary two-component resin system includes isopropyl alcohol, methyl ethyl ketone, water, a diisocyanate catalyst cross-linker CX-100, and a polyfunctional aziridine (Zeneca). Polyfunctional aziridines are based on trimethylolpropane tris(2-methyl-1-aziridine propionate.[7] Fluorolink® P56 has been evaluated by the manufacturer with positive results for protecting ceramic tiles, stone, and leather against soiling from water, oil, marker, and dirt.

Silicone Coatings

Studies on silicone coatings are quite numerous in conservation. A review of the chemistry, degradation, and biodegradation of silicones and silanes is detailed by Graiver et al.[8] Major drawbacks of some silicone products have been noted: colour changes, difficulty in reversibility, and, in rare cases, acceleration of stone decay due to the blocking of water inside the substrate during freeze-thaw cycles. The silicone coating selected for testing was the product Weather Seal Blok-Guard® and Graffiti Control (henceforth referred to as Blok-Guard®), a proprietary solvent-based silicone elastomer in mineral spirits and 1,2,4 trimethylbenzene (PROSOCO Inc.).

Silane Coatings

The third AGC selected was Protectosil Antigraffiti® (henceforth referred to as Protectosil®), a proprietary water-based fluorosilane in ethanol (Degussa Corporation). Silanes have been commonly used as stone consolidants and may have anti-graffiti potential, but recent research on the effectiveness of silanes as AGCs is sparse.

Evaluating the Performance of AGCs

The evaluation of the performance of AGCs is very similar to that used for the testing of stone preservatives, [1,9,10,11] and while prevention of damage from both physical and chemical weathering or from graffiti is desirable, there remains concern for utilizing AGCs in conservation and preservation efforts. Undesirable changes in the colour of the original surface can occur from the AGC upon application or from aging of the AGC in the stone after prolonged exposure to an outdoor environment. There are issues of reversibility for any coating applied to stone as chemical removal can be difficult or ineffective and abrasive removal or water-jet systems can damage the original materials. Rates of aging and ease of reapplication can be of concern as the coating itself will require maintenance in reapplication and, in some instances, eventual removal. It is desirable that the coating remains permeable to water vapour. Moisture trapped inside the stone pores will freeze and expand at low temperatures, resulting in damage to porous stone. Road salts, sea salts and salt residues from cleaning solutions can be damaging to stone; the damage occuring as salts crystallize inside the stone, increasing pressure and causing a breakdown of the stone structure. Surface efflorescence from the evaporation of water-borne salts is less harmful than salt deposition within the stone.[12] Therefore, the coating should maintain some degree of water vapour permeability to allow moisture absorbed into the stone to evaporate.[9]

Performance criteria specific to AGCs was reviewed recently by von Plehwe-Leisen et al.[13] and included:

- ease of graffiti removal from coated substrate,
- changes in colour and gloss of the coated substrate,
- changes in water absorbance and vapour diffusion after coating application,
- drying time of the coating,
- effect of coatings on microbiological growth,
- reversibility.

Special considerations of the difficulties involved in comprehensive analysis of preservative stone coatings were discussed by Price[14] and included: meaningful comparisons between samples tested by natural weathering, durability tests to simulate decay mechanisms for stones of different porosity prior to testing the stones with coatings, salt crystallization tests on coated specimens that can be nullified by water repellency, and the accuracy of accelerated aging tests to simulate the natural environment. The investment in time, materials, equipment, and overcoming the complexity of these tests, described by Price, do not warrant their inclusion in an initial testing scheme of AGCs but could certainly be included in a second round of testing after less complicated tests identify potential coatings that display promise.

The Performance Criteria for this Study

The performance criteria selected for the present study focused on the following important, but less complicated factors for coated Mississquoi marble and Wallace sandstone samples:

- coating application and drying,
- substrate colour change due to coating,
- changes in moisture absorption of the stone due to the coating,
- coating failure due to biodeterioration by microorganisms,
- the ability of each coating to repel graffiti,
- graffiti removal from the coating.

Evaluation of film drying and reversibility of graffiti damage were done visually. Measuring colour change on a flat, monochromatic surface is a straightforward procedure, but in this case, a method for determining colour change on outdoor sculpture using templates made for 3-dimensional surfaces was used, as described by Binnie.[15] The templates fit over the top and sides of the samples to ensure that the colour readings are taken in the same place each time, before and after coating of the samples. The ability of the coatings to protect the substratum layer without trapping moisture inside was tested by the RILEM [16] method for water absorption. This test is employed in field studies to evaluate stone consolidants, and was used in this study to compare control samples to coated stone samples.

The variety of existing standards for the evaluation of AGCs do not usually include measurement of complex variables such as variations in performance due to the changes of behaviour of the AGC on different substrates, nor the effects of microbiological growth on coating failure. For example, *ASTM D 6578-00 Standard Practice for Determination of Graffiti Resistance* [17] evaluates the performance of coatings in respect to graffiti removal and resistance to outdoor exposure, on clean stone as the standard fixed variable.

Since one cause of coating failure in the outdoor environment is biodeterioration, the testing scheme in the present study was designed to incorporate assessments of the biodeterioration of the coatings. There are two concerns with microbial deterioration of coatings. First, the coating may fail requiring removal and/or reapplication; and second, the substrate may be stained by microbes that produce pigments or may be utilized by the microbes for nutrition. For instance, Alakomi et al. found that stone was stained or discoloured by the microorganisms that inhabit stone, such as pigment-producing bacteria, coloured melanins and carotenes in fungi, and photosynthetic pigments from algae and cyanobacteria.[18] Other researchers found that the carbon source supporting microbial growth on stone may include organic and inorganic matter such as a coating.[8,19-21] Further, biodeterioration of AGCs has been studied by Krumbein, who found that microbial growth was possible on three different AGCs.[22] Many studies have shown Electrochemical Impedance Spectroscopy (EIS) to be a useful surface analytical technique to examine the failure rates of coatings used to protect metals.[23-29] EIS uses a low magnitude polarizing voltage that cycles from peak anodic to cathodic values over a range of alternating current frequencies to provide information about coating properties. In the present study, microorganisms able to use AGCs as the sole source of carbon for nutrition were isolated. Electrolyte solutions were inoculated with the isolates to measure the subsequent biodeterioration of the coatings on steel substrata inside EIS cells.

Fourier-Transform Infrared spectroscopy in attenuated total reflection mode (FT-IR / ATR) has been used by others for monitoring the development of structurally intact biofilms in-situ. A detailed description of the method is given by Schmitt.[30] In the present study, FT-IR / ATR was used to complement the EIS data by determining changes in the chemical bonds of the AGCs before and after biodeterioration processes.

The overall testing scheme, as outlined here, offers visual, physical, and chemical data that can be applied to the practical selection of a protective coating. Although the test results cannot be used to predict all future environmental and material interactions, they can assist in providing at least some missing technical information on a few promising, commercially available products. It is hoped that research in this field will continue to assess more factors, substrates, and products to provide the practitioner with much needed technical data for the selection of a commercial AGC product.

Methods

Stone Test Samples

Sandstone and marble test samples were used for some basic data-gathering tests. Mississquoi marble and Wallace sandstone samples coated with AGCs served for colour, water absorption, graffiti application and graffiti removal data. The stone samples were flat and unpolished. The marble samples served as a non-porous surface, and the sandstones as a porous surface for the coatings. The sandstone samples were 7.5 cm x 7.5 cm x 1.9 cm, and the marble samples were 8.3 cm x 8.3 cm x 2.5 cm. For each stone type, coating type, graffiti media, and cleaning method, three coated and three uncoated control samples were prepared.

Application of Coatings

The coatings were prepared according to manufacturer recommendations for mixing and dilution.[31] Stone samples received brush application of two coats, with a minimum of 24 hours drying time between coats.[32] All coatings were applied as liquids in a fume hood and as all preparations contained hazardous and volatile solvents, protective nitrile gloves were worn. For each sample, only one flat side was coated (7.5 cm x 7.5 cm for sandstone, 8.3 cm x 8.3 cm for marble). The sides and backs remained uncoated. Control samples remained completely uncoated on all sides. Drying of the coatings was carried out at 20ºC and 45% ± 5% relative humidity.

Colour Change Measurements

All sandstone and marble samples were measured for colour, prior to coating, using an X-Rite CA22 Spectrophotometer and QA Master 2000 software. Colour data was based on the 1976 CIELAB colour space system. After the samples were coated with the AGC and allowed to dry for 14 days, colour measurements were taken again. Measurements were taken five times per sample in the same area (using a template).

Water Absorption Measurements

Twelve sandstone and marble samples were measured, prior to coating, for water absorption with RILEM tubes using the RILEM test method.[16] Tubes were affixed to the surface with non-greasy putty and the observed water absorption was measured every five minutes for one hour. The process was repeated after the samples were coated and dried for one week.

Growth and Isolation of Microorganisms

A solution was prepared for each AGC containing: 1% coating, microorganisms (a mixed culture from outdoor soil in Cambridge, Massachusetts, USA), and sterile Rohan's Minimal Salt solution [0.22 g L^{-1} $(NH_4)2SO_4$, 1.20 g L^{-1} KH_2PO_4, 0.23 g L^{-1} $MgSO_4 \cdot 7H_2O$, 0.25 g L^{-1} $CaCl_2$, 1 L distilled H_2O]. The growth media remained on a rotary shaker for 27 days at 100 rpm, until growth was indicated by a change in solution from transparent to slightly turbid. The organisms were isolated on nutrient agar culture plates (DIFCO brand). Colonies of bacteria and fungi with morphological differences were selected and sub-cultured onto individual nutrient agar culture plates. The process was repeated until pure isolates were obtained. To identify the microorganisms that used the coatings as all or part of their metabolic cycle, a two step process of isolate solutions was used. A sterile loop was utilized to transfer isolates into individual solutions containing Rohan's Minimal Salt solution and 1% AGCs. After 1 week, the isolates indicated microbial growth by turbidity in solution, and were separated from solution gravimetrically. Because the 1% AGCs remained with the microorganisms when separated gravimetrically and were seen to obscure results when placed on slides, a sterile loop was used to sample the microbes into new Tryptic Soy Broth isolates with no coatings. Cells were separated from solution gravimetrically and placed onto glass slides without coating residue obscuring the results. Slides were stained using Gram's stain technique, coated with Cargille non-drying immersion oil (nD 1.4790±0.0002, type FF), and examined at 100x with an Olympus BX 60 microscope. Pure isolates were identified for each AGC, and prepared fresh in Tryptic Soy Broth solution. After one week, cells were separated from solution by centrifugation and resuspended in 1 mL of Rohan's Minimal Salt solution and this was used to inoculate EIS cells.

Electrochemical Impedance Spectroscopy (EIS) Measurements

Each EIS cell was constructed of multiple parts. The materials and working mechanics of the EIS cell are explained in **Appendix I**. The tri-electrode system had a saturated calomel reference electrode, a platinum mesh counter electrode, and a stainless steel coupon (coated with an AGC) as the working electrode. Four EIS cells total were made for each AGC. Cells were surface sterilized using germicidal UVC radiation (220-290 nm) in a laminar airflow hood for 24 hours. Two cells per coating type with no microorganisms served as controls, containing 100 L of formaldehyde in 40 mL of Rohan's Minimal Salt solution. To create an environment conducive to biodeterioration in the other two cells, 100 L of previously prepared microbial isolates were inoculated into 40 mL of Rohan's Minimal Salt solution. Sterile Rohan's Minimal Salt solution filled the EIS cells and acted as an electrolyte. EIS cells were connected to a Schlumberger 1250 frequency response analyser with a Schlumberger 1286 electrochemical interface (Solartron Analytical). A low magnitude polarizing voltage cycling from peak anodic to cathodic values over a low frequency range of 65 kHz to 0.1 Hz was used to measure the electrochemical impedance of each coating on steel. EIS cells were held at their open circuit potential and a sinusoidal perturbation of 20 mV was applied. Software Z-Plot and Z-View were used to collect and analyse the data (Scribner Associates Inc.) which allowed for data compilation from duplicate samples. Measurements of impedance responses were made in a laminar flow hood to prevent contamination of the cells. Sterile sponges were used to 'cork' the EIS cells when not in use to keep out dust and contamination. Between measurements, the calomel tube and platinum counter-electrode were sterilized with an ethanol solution to avoid cross-contamination of the cells. EIS spectra for all three AGCs were gathered regularly over a one month period and compared. Spectra were collected for a three month period for some cells (inoculated Protectosil® and sterile Blok-Guard®), but no further changes were observed.

FT-IR / ATR

All EIS cells in the experiment were kept after conclusion of EIS data collection for FT-IR / ATR analysis. The stainless steel coupons were removed from the EIS cells and air-dried. Dry residue from microorganisms was gently brushed away, and the steel coupons were sterilized overnight with a germicidal lamp and formaldehyde vapour. Replicate sections of the centre of each coupon were cut to 0.6 cm x 2.5 cm. FT-IR / ATR measurements were carried out on the sections in a Nicolet Nexus 670 infrared spectrometer. Samples were pressed on the ATR crystal to create close contact. All measurements were at 4 cm^{-1} resolution with 256 scans, using a liquid nitrogen cooled MCT detector. Spectra of the control groups were compared to spectra of cells subjected to microbial activity to document chemical changes due to biodeterioration.

Application of Graffiti and Effectiveness of Coatings to Prevent Graffiti Damage

Graffiti was applied to the AGC and uncoated stone samples using a black Super Sharpie® Permanent Marker (composed of dyes in solvent carriers)[33] and brown ColorPlace® enamel spray paint (carbon black and barium in solvent carriers).[34] Half of the surface of the samples was marked (tagged) with graffiti and allowed to dry for one week when a visual assessment of film formation, dry film appearance, and reaction of the graffiti on the coating was made. If the AGC prevented the graffiti media from forming an even film layer, this was noted as being "repelled" (**Figure 1**).

Cleaning Method to Remove Graffiti

To simulate the conservation field experience in the lab, the least aggressive agent to the most aggressive was tried to reduce or remove graffiti from the samples in order to find the least harsh but most effective solvent. Removal of graffiti, whether a film or dried pool of marker/paint on the surface of the AGC, was performed progressively with tap water, 80% ethanol in distilled water, acetone, and finally with commercially available pre-mixed proprietary solvent system Defacer Eraser® Graffiti Wipe (PROSOCO Inc.) (henceforth referred to as Defacer Eraser®). Defacer Eraser® contains nonionic surfactants, alkyl phenol ethoxylates, terpenes, and n-methylpyrrolidone.[35] To promote swelling and solvency of the graffiti media and to simulate what might be done in the field, each sample was wiped continuously for one hour with a cloth saturated in removal solution and rewetted as it became dry. Even, but not extreme pressure was used while wiping, similar to cleaning a mirror. The samples were dried and the process was repeated five more times for a total of 6 hours of continuous wiping. The testing pool included duplicate samples of each combination of stone, coating, graffiti type, and removal agent. The surface of each sample was divided into squares of 1 cm^2. The graffiti in each square was assessed as removed or not, and the results were averaged.

Results and Discussion

Colour Change Measurements

The results of the colour measurements are given in **Tables I** and **II**. Colour data was based on the 1976 CIELAB colour space system. The total colour change for each AGC on each stone was calculated using the following formula:

$$\Delta E*_{ab} = \sqrt{\left[(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2\right]}$$

Changes from light to dark are represented by a negative value for ΔL. A positive value for Δa is a shift from slightly green or slightly reddish to a more vivid red, while a positive value for Δb indicates a shift from slightly yellowish or yellow to a more vivid yellow. It is difficult to set threshold values for ΔE, ΔL, Δa and Δb that are perceptible to the eye because observation is affected by surface texture of the samples, gloss, the level and type of lighting used, and human perception. However, the colour changes calculated in **Table I** and **II** are sufficiently large that colour difference would likely be visible to the eye if coated and uncoated samples were viewed together under good viewing conditions.[36] Indeed, darkening and yellowing of all samples was visible to the eye under fluorescent and daylight viewing.

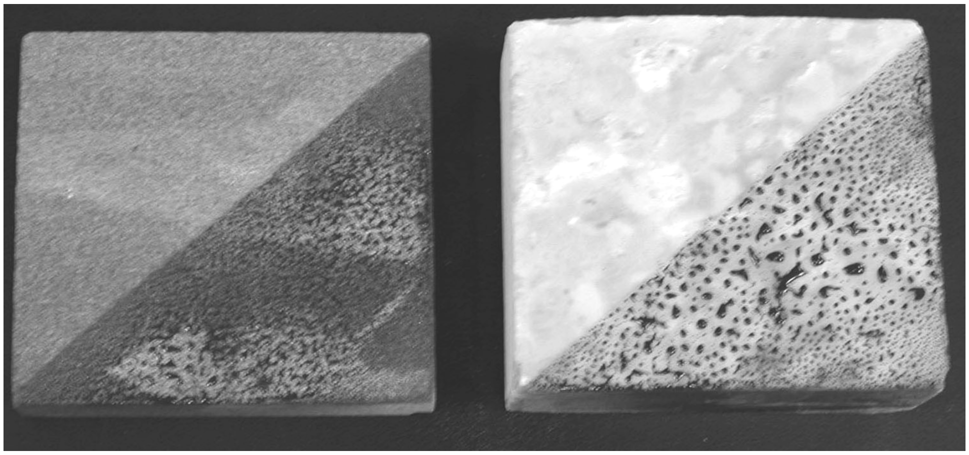

Figure 1. Stone samples of Wallace sandstone (left) and Mississquoi marble (right) coated with Protectosil® and tagged on half the surface with spray paint. The spray paint was repelled by the protected surfaces to the lower right.

Table I: Colour Changes After Application of AGC to Sandstone Surfaces.

Wallace Sandstone Sample	Coating	Average Colour Values ± Standard Deviation			Changes in Colour				Comment on Changes in Colour
		L*	a*	b*	ΔL*	Δa*	Δb*	ΔE*	
W3	uncoated	57.94 ± 0.07	1.09 ± 0.04	10.94 ± 0.34	-11.1	0.86	3.48	11.66	Darker, more orange/yellow
	Protectosil®	46.84 ± 0.15	1.95 ± 0.04	14.42 ± 0.06					
W8	uncoated	55.49 ± 0.23	0.80 ± 0.06	9.75 ± 0.08	-1.44	0.64	2.78	3.2	Slightly darker, more orange/yellow
	Protectosil®	54.05 ± 0.11	1.44 ± 0.04	12.53 ± 0.09					
W11	uncoated	60.58 ± 0.17	0.54 ± 0.06	9.39 ± 0.15	-21.19	2.01	6.52	22.26	Darker, much more orange/yellow
	Fluorolink® P56	39.39 ± 0.62	2.55 ± 0.07	15.91 ± 0.25					
W12	uncoated	59.43 ± 0.04	0.78 ± 0.16	10.16 ± 0.22	-14.53	1.48	6.32	15.92	Darker, much more orange/yellow
	Fluorolink®P56	44.9 ± 0.37	2.26 ± 0.04	16.48 ± 0.37					
W5	uncoated	59.60 ± 0.27	0.72 ± 0.04	10.39 ± 0.04	-12.56	1.07	4.09	13.25	Darker, more orange/yellow
	Blok-Guard®	47.04 ± 0.10	1.79 ± 0.03	14.48 ± 0.10					
W10	uncoated	57.44 ± 0.27	1.22 ± 0.01	10.42 ± 0.12	-8.54	0.94	3.26	9.19	Darker, more orange/yellow
	Blok-Guard®	48.90 ± 0.36	2.16 ± 0.11	13.68 ± 0.05					

The negative values for ΔL in **Tables I** and **II** indicate that all samples became darker when coated with the AGCs, with ΔL ranging widely from -1.44 to -21.19 for sandstone, and more uniformly from -6.00 to -9.92 for marble.

On sandstone, Fluorolink® P56 showed the most increase in yellow (+Δb) followed by Blok-Guard® and then Protectosil®. On marble, the greatest increase in yellowness (+Δb) was due to Protectosil® while the other two coatings had statistically similar smaller values. In most cases, the increase in yellow values (+Δb) combined with the slight increases in the red values (+Δa) resulted in an orange/yellow appearance of coated samples, with sandstone samples showing a stronger orange/yellow hue.

The total colour changes (ΔE) for Protectosil® and Fluorolink® on marble were statistically the same and although the Blok-Guard® on marble gave slightly lower values it was statistically the same as the Fluorolink® coating. Unfortunately, for the sandstone coatings, the data sets from the replicate samples (ie., W3/W8, W11/W12, W5/W10) for total colour change (ΔE) were inconsistent, eliminating certainty in ranking the coatings performance. For example, samples W3 and W8 had a wide margin between the ΔE values of 11.66 and 3.20. The data pairs were likely inconsistent due to three factors: natural colour and vein variances of the stone; a small data set of five measurements only; and utilizing a spectrophotometer with too small a target area (4mm). However, the darkening and yellowing on all coated sandstone samples was apparent to the eye.

As a final note, the non-porous surface of marble may actually minimize colour change when using AGCs because they cannot penetrate into the marble as they do on porous sandstone, but remain on the surface

Water Absorption Measurements

The RILEM method was used to measure water absorption of the Mississquoi marble and the Wallace sandstone in a one hour period. The marble in the coated or uncoated state did not absorb any water in the one hour period. The results for the sandstone can be seen in **Figure 2**.

The uncoated sandstone absorbed just over 1 mL of water in one hour. All AGCs performed as water barriers on the porous sandstone, reducing water absorption from 37 to 52%. It is not known what optimal level of water absorption is desirable for an AGC. More work in this area would be required to determine this level. However, the ideal water absorption for a protective

Table II: Colour Changes After Application of AGC to Marble Surfaces.

Mississquoi Marble Sample	Coating	Average Colour Values ± Standard Deviation			Changes in Colour				Comment on Changes in Colour
		L*	a*	b*	ΔL*	Δa*	Δb*	ΔE*	
M1	uncoated	73.46 ± 0.53	-0.57 ± 0.06	3.55 ± 0.35	-6.0	-0.47	5.02	7.83	Darker, much more yellow
	Protectosil®	67.46 ± 0.48	-1.04 ± 0.12	8.57 ± 0.41					
M2	uncoated	71.97 ± 0.04	-0.16 ± 0.02	-0.07 ± 0.06	-8.32	0.1	4.52	9.47	Darker, much more yellow
	Protectosil®	63.65 ± 0.62	-0.06 ± 0.04	4.44 ± 0.07					
M4	uncoated	77.77 ± 0.27	-0.30 ± 0.02	2.54 ± 0.46	-6.89	-0.28	2.69	7.4	Darker, more yellow
	Fluorolink® P56	70.88 ± 0.82	-0.58 ± 0.07	5.23 ± 0.26					
M11	uncoated	78.61 ± 0.14	-0.29 ± 0.02	-0.92 ± 0.04	-9.92	0.24	3.12	10.4	Darker, more yellow
	Fluorolink® P56	68.69 ± 0.47	-0.05 ± 0.02	2.20 ± 0.11					
M8	uncoated	73.44 ± 0.05	-0.02 ± 0.01	1.32 ± 0.03	-7.19	0.4	2.13	7.51	Darker, more yellow
	Blok-Guard®	66.25 ± 0.65	0.38 ± 0.07	3.45 ± 0.10					
M10	uncoated	72.67 ± 0.14	-0.06 ± 0.02	-0.42 ± 0.03	-7.29	0.4	1.98	7.56	Darker, more yellow
	Blok-Guard®	65.38 ± 0.26	0.34 ± 0.01	1.56 ± 0.05					

barrier would be related to the overall goal in a preservation program of reducing damage without causing the stone to become completely impermeable. Some considerations would include the pore size, the presence of salt in the stone, the current state of stability of the stone matrix, other coatings and consolidants on or in the stone, rainfall levels, and freeze-thaw cycling. The continued monitoring and documentation of the effects of a coating as part of the preservation program would reveal the success of the coating as a protective water barrier in minimizing or reducing damage caused by moisture. A completely impermeable surface would be detrimental especially where water can enter at points other than through the surface coating, as moisture and salts will then be trapped behind the coating.[11]

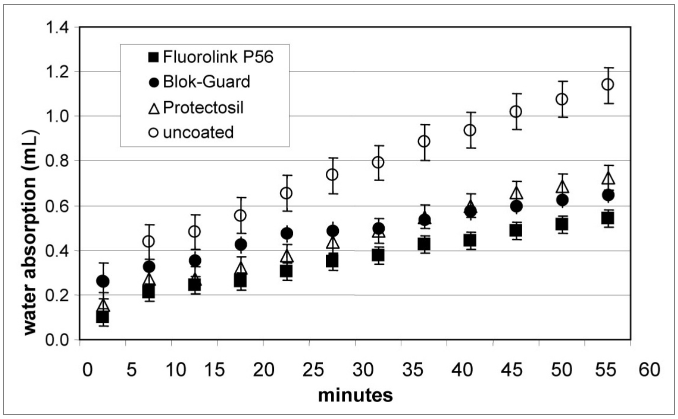

Figure 2. Water absorption changes for sandstone.

So advantageously, although all the AGCs reduced water absorption on sandstone, they did not render the samples completely impermeable, with Fluorolink® P56 being the most repellant, Protectosil® the least repellant and Blok-Guard® between the two.

Growth and Isolation of Microorganisms

Microorganisms from outdoor soil demonstrated an ability to utilize all three AGCs as the sole source of nutrition as mixed communities and as pure isolates. Gram staining revealed that a mixed community of gram-positive and gram-negative rod and coccus shaped bacteria was present on all coatings in the lab experiment setting. This is not surprising as several studies have demonstrated the ability of coatings to support microbial growth.[26,27] The results suggest that microbial growth on the AGCs would be expected and sustainable for many types of microorganisms; however, this requires further field testing.

EIS Measurements

EIS was used to quantitatively estimate the capacity of the microorganisms to degrade AGCs. A large (ie., orders of magnitude) reduction in the low frequency impedance ($|Z|_{lf}$) is indicative of coating deterioration. An example of an EIS graph can be seen in **Figure 3** for Protectosil®. Initial and final low frequency impedance magnitudes for the EIS measurements were determined and are plotted in **Figure 4**. The impedance for **Figure 4** was estimated at 0.1 Hz because it is in the frequency range that has been proposed as the optimal EIS parameter to evaluate performance of coatings.[37] Protectosil® (**Figure 4A**) showed no large changes in $|Z|_{lf}$ in either sterile or inoculated treatments. Differences in **Figure 4A** were the result of normal variation (ie., small fluctuations - not orders of magnitude) and were not large enough to indicate changes in the coating during the period of time in which measurements were made. The data suggests that Protectosil® is resistant to biodeterioration, consistent with the fact that silane coatings do not provide a carbon source for microbial nutrition unless they contain additives with organic carbon. Likewise, there was little change in the $|Z|_{lf}$ values for Blok-Guard® cells (**Figure 4B**). Differences between initial and final measurements were minor, the result of normal variation in the measurements, and did not indicate coating deterioration.

There was a large decrease (ie., greater than three orders of magnitude) in the $|Z|_{lf}$ of both sterile and inoculated Fluorolink® P56 cells (**Figure 4C**). The large drop in $|Z|_{lf}$ indicated coating failure of this AGC. Furthermore, the failure occurred rapidly after just one month of exposure. However, as these decreases occurred in both the sterile and inoculated cells, the coating failure was clearly not due to microbial deterioration.

In summary, the EIS measurements showed that no coating failed due to microbial deterioration, and that the Fluorolink® P56 coatings failed due to the experimental conditions utilized whether microbes were present or not.

FT-IR / ATR

FT-IR / ATR investigation of the Fluorolink® P56 coatings was not possible because they completely failed and were too deteriorated to yield any reliable information.

Major peaks present in the FT-IR / ATR spectra of Protectosil® before exposure to microorganisms were still present after exposure, indicating that the coating was not deteriorated by the microbes (**Figure 5**). This was consistent with EIS results which showed no effect of microbes on this coating.

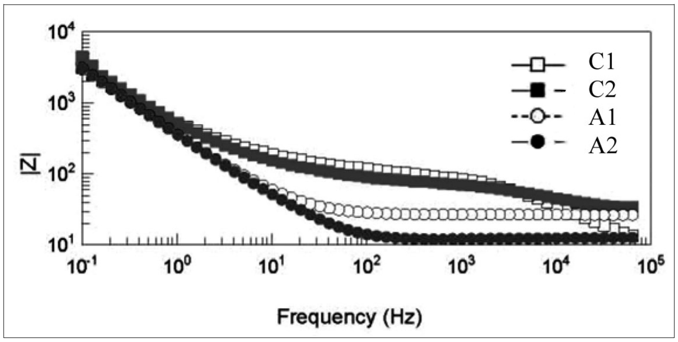

Figure 3. Example of a Bode Magnitude Plot from EIS for Protectosil®. A1 = initial value of EI cell with microbes, A2 = end value of EI cell with microbes, C1 = initial value of control EI cell without microbes, C2 = end value of control EI cell without microbes, |Z| = impedance (ohms).

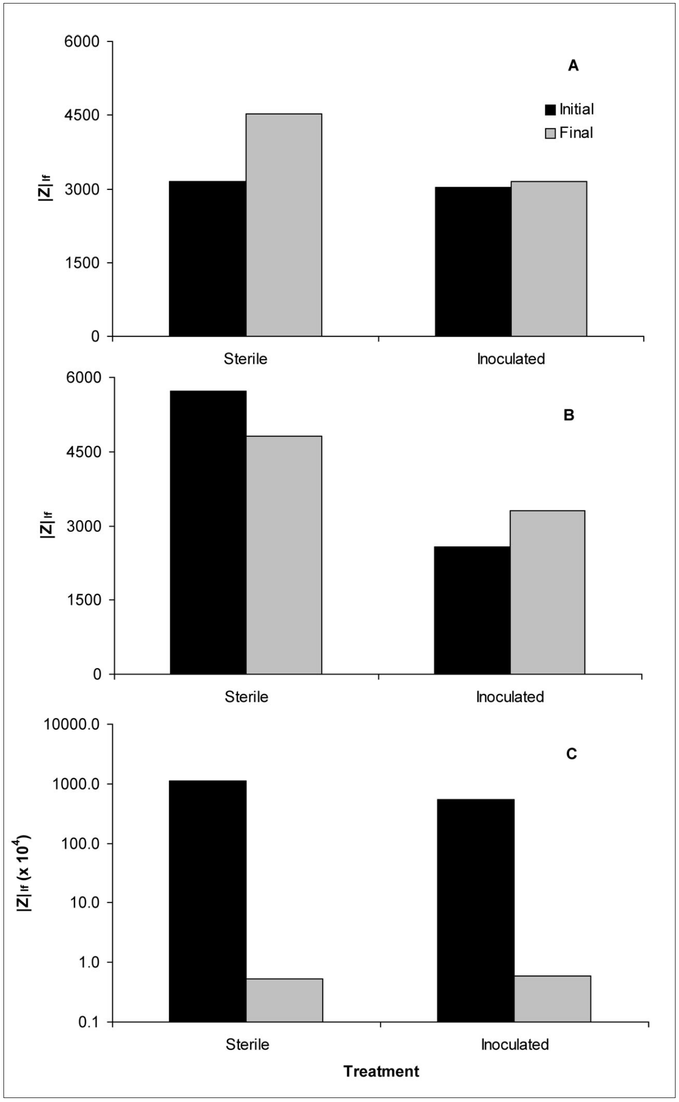

Figure 4. Initial and final (after 30 days) low frequency impedance magnitudes [$|Z|_{lf}$ (ohms), 0.1 Hz] for sterile (control, no microorganisms) and inoculated (with microorganisms) coatings of Protectosil® (A), Blok-Guard® (B) and Fluorolink® P56 (C).

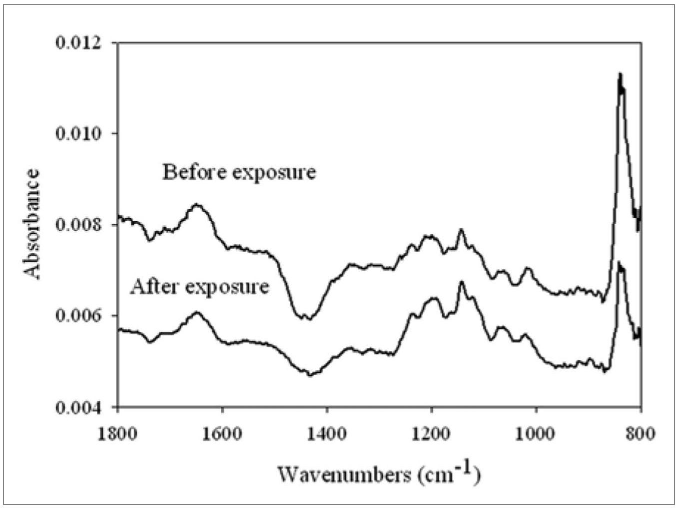

Figure 5. FT-IR / ATR of Protectosil® before and after exposure to microorganisms.

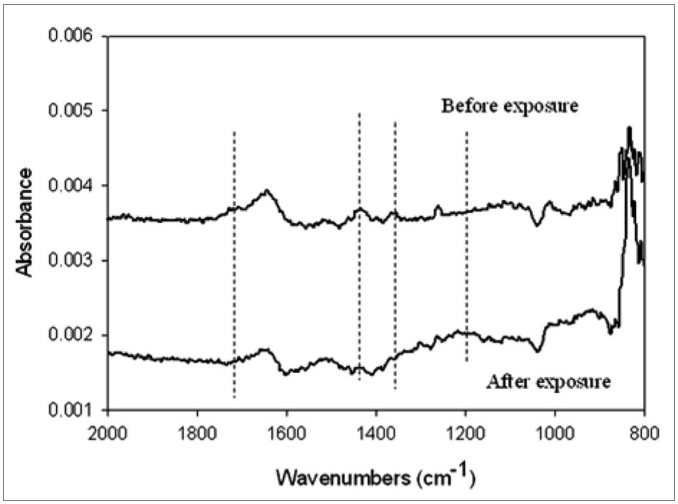

Figure 6. FT-IR / ATR of Blok-Guard® before and after exposure to microorganisms.

Blok-Guard® showed small changes as evidenced by the loss of peaks in the FT-IR / ATR spectra after microbial exposure (**Figure 6**). This suggested possible changes in some chemical bonds of Blok-Guard® which would indicate that microorganisms could degrade Blok-Guard®. These changes did not result in a coating failure detectable by EIS during the period of the experiment (**Figure 4B**), as there must be sufficient breakdown of the coating for water penetration to occur. Thus, it would seem that FT-IR / ATR is a more sensitive technique than EIS to detect changes in the coating. Potentially longer experiments are needed to determine if accumulated changes in the bond structure of Blok-Guard®, as detected in FT-IR / ATR, would result in enhanced water penetration detectable by EIS.

Ability of the Coatings to Protect Against Graffiti

A summary of the working properties of the coatings and the observed behaviour of the graffiti on the coatings is given in **Table III**. All AGCs appeared to dry to an uneven film on the porous and non-porous stone substrates in a short period of time (1-12 hours) with the exception of Fluorolink® P56 which required 48 hours to dry and still remained tacky after 2 weeks.

All AGCs repelled (prevented) the graffiti from reaching the substrate except for the Blok-Guard® which allowed the spray paint to penetrate the coating and stain the sandstone, and Fluorolink® P56 which did not repel the marker but allowed it through to stain the marble.

Graffiti Removal

Table IV summarizes the effectiveness of water and of various solvents to remove graffiti from the different AGCs and from the uncoated substrates. Water and solvents were not effective in removing graffiti from any of the uncoated samples.

Water was quite ineffective in removing marker and paint from the Blok-Guard® and Fluorolink® P56 coatings but had some success with removing marker and paint from the Protectosil® on marble but not sandstone. Ethanol 80% in distilled water was only effective in removing spray paint from Blok-Guard® on marble. Acetone had no effect on the spray paint at all, however, it was effective in removing the marker from all coatings except from Protectosil® on marble. Defacer Eraser® was the most successful solvent as it removed most of the graffiti from all the AGCs. The most successful removal of graffiti (100%) was from the Blok-Guard® with Defacer Eraser®.

After graffiti removal, staining of the stone through the coating was seen on a few samples. For the acetone, the marker staining through the Protectosil® and Fluorolink® P56 coatings but not through the Blok-Guard® coating might be due to the ability of the acetone to solubilize the Protectosil® and Fluorolink® P56 coatings but not the Blok-Guard® coating. For the Defacer Eraser®, the staining on the sandstone from the marker through Fluorolink® P56 is more difficult to explain. Perhaps the Fluorolink® P56 sank into the porous sandstone more than the other coatings and more than into the marble, resulting in a thinner coating that was more affected by the Defacer Eraser®.

Conclusion

When all of the results of the coatings were assessed together, Protectosil® exhibited the best results and Fluorolink® P56 the worst results. Protectosil® had the least effect on water absorption while still repelling graffiti, had an uneven surface film that dried in a reasonable period of time although with a tendency to crack if applied too thickly on marble, and did not deteriorate in the presence of microorganisms in the EIS experiments. On the other hand, the Fluorolink® P56 coating remained tacky which could result in dirt pickup and further discoloration of the substrate, showed the greatest alteration on water absorption, even though it totally deteriorated in the EIS experiments whether microbes were present or not, and failed to

Table III: AGC Film Forming Properties and Behaviour of Applied Graffiti on Sandstone and Marble.

Coating	Stone	AGC Film Formation Observations	Dry AGC Film Appearance	Reaction of Spray Paint on AGC	Reaction of Marker on AGC
Blok-Guard®	sandstone	Runny, dried in 2 hours	Film did not appear to be on the surface, but absorbed into stone	Not repelled, absorbed through to stain sandstone	Repelled
	marble	Runny, dried in 12 hours, second coat repelled by first coat	Uneven film on top of stone	Repelled	Repelled
Protectosil®	sandstone	Runny, dried in 1 hour	Uneven film on top of stone	Repelled	Repelled
	marble	Second coat repelled by first coat, each coat dried in 1 hour	Uneven film cracked & crumbled in thick areas, slight shine	Repelled	Repelled
Fluorolink® P56	sandstone	Very runny, dried in 48 hours, but remained tacky after 2 weeks	Shiny uneven film on top of stone	Repelled	Repelled
	marble	Very runny, dried in 48 hours, but remained tacky after 2 weeks	Shiny film on top of stone	Repelled	Not repelled, stained marble

Shading indicates that the graffiti was repelled by the AGC.

Table IV: Effectiveness of Graffiti Removal.

			% Removal Effectiveness (Assessed Visually)			
Coating	**Stone**	**Type of Graffiti**	**Tap Water**	**Ethanol 80% in Distilled Water**	**Acetone**	**Defacer Eraser®**
No Coating	sandstone	marker	0	0	0	0
		spray paint	0	0	0	0
	marble	marker	0	0	0	0
		spray paint	0	0	0	0
Blok-Guard®	sandstone	marker	30	0	95	100
		spray paint	0	0	0	100
	marble	marker	20	0	100	100
		spray paint	0	100	0	100
Protectosil®	sandstone	marker	0	0	95 black staining	100
		spray paint	0	0	0	100
	marble	marker	75	0	0	95
		spray paint	90	0	0	100
Fluorolink® P56	sandstone	marker	0	0	100 yellow staining	95 yellow staining
		spray paint	0	0	0	100
	marble	marker	0	0	100 yellow staining	100
		spray paint	0	0	0	100

Shading indicates desirable results. 100% = graffiti was completely removed; 90-95% = almost completely removed; 20-75% = partially removed; 0% = not removed. "Staining" refers to discoloration left behind by marker after near complete removal.

repel marker graffiti on marble. Blok-Guard® showed intermediate results: it dried in a reasonable timeframe, had intermediate impact on water absorption, failed to repel spray paint on sandstone, and showed slight changes in the FT-IR / ATR indicating susceptibility to biodeterioration. All films darkened and yellowed the substrates, especially on sandstone. Defacer Eraser® was the most successful solvent in removing graffiti from all the coatings while other solvents met with somewhat less success depending on the graffiti and stone.

None of the coatings repelled water 100%, so vapour permeability is possible with all coatings at varying levels. There remains uncertainty as to what exact percentage of water repellence is optimum, however, repellents are meant to prevent water (and graffiti) from penetrating into the stone while allowing for moisture evaporation. Any coating that sealed the surface completely would jeopardize the stability of the stone as trapped moisture and salts would have no avenue for escape.

As all coatings darkened and yellowed the substrates, especially on sandstone, the consideration of changes in colour of a selected coating for a newly commissioned sculpture or structure could be incorporated into the planning phases by artists, architects, and project conservators.

The integrated approach outlined in this paper can augment conservation maintenance plans. All coatings will eventually need to be removed and renewed as coatings are subject to weathering, physical abrasion and biodeterioration. The manufacturer of Protectosil® currently offers warranties for the product up to 5 years and suggests reapplication of the product in areas that have been tagged with graffiti and cleaned about 10 times. They also suggest that to determine if the coating is still intact and performing well, to apply droplets of 80-95% isopropanol to the surface to see if it is absorbed or repelled by the coating, and if repelled the coating is intact.[38] The manufacturer of Blok-Guard® currently offers warranties for the product up to 10 years and suggests reapplication of the product in areas that have been tagged with graffiti and cleaned 5-7 times.[39] Fluorolink P56 is not currently commercially available. It is important to be aware that manufacturers can reformulate their products, changing the properties of the coatings. Considering this, conservation maintenance plans should remain current with available testing of materials before use of any AGC on any historic or culturally significant object subject to graffiti attack. Testing schemes could include EIS and FT-IR / ATR, along with other tests mentioned in this paper, to determine whether the coating will support microbiological growth, and subsequently require more frequent applications or put the substrate at risk of discoloration and deterioration. Thus, owners responsible for maintenance of objects at risk can make more informed decisions for proper maintenance. This paper demonstrates the importance of involving the expert services of conservators and scientists on the decision-making team to weigh the benefits and potential risks of using anti-graffiti measures.

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Materials and Suppliers

Acrylic tubes (2” hollow rod outer diameter, 1 ¾” inner diameter, 6’ length): McMaster-Carr, 473 Ridge Road, Dayton, New Jersey 08810-0317. Tel: (732) 329-3200.

Baxter S/P pH Indicator strips: Baxter Diagnostics Inc., Deerfield, Illinois 60015-4633. Tel: 1-800-422-9837.

Cargille non-drying immersion oil (nD 1.4790±0.0002, type FF): Cargille Labs, Cedar Grove, New Jersey 07009, USA. Tel: (973) 239-6633.

ColorpHast Indicator Strips: Made in Germany, available from EM Science, 480 Democrat Road, Gibbstown, New Jersey 08027. Tel: (609) 423-6300.

ColorPlace® Interior and Exterior Spray Paint: Sherwin-Williams private spray paint brand for Wal-Mart Corporation.

DAP 100% Silicone Aquarium Sealant: DAP Inc., 2400 Boston Street, Suite 200, Baltimore, Maryland 21224. Tel: 1-888-327-2258.

Defacer Eraser® Graffiti Wipe: PROSOCO Inc., 3741 Greenway Circle, Lawrence, Kansas 66046. Tel: 1-800-255-4255.

DIFCO nutrient agar culture plate media and Tryptic Soy broth media: Becton Dickinson and Company, Sparks, Maryland 21152. Tel: 1-800-675-0908. Worldwide to the US: 1-410-316-4000.

Fluorolink® P56: Solvay Solexis, 10 Leonards Lane, Thorofare, New Jersey 08086. Tel: (856) 853-8119.

Protectosil® Antigraffiti: Degussa Corporation, 2 Turner Place, PO Box 365, Piscataway, New Jersey 08855-0365. Tel: 1-800-828-0919.

Rohan’s Minimal Salt Solution [0.22 g L^{-1} $(NH_4)2SO_4$, 1.20 g L^{-1} KH_2PO_4, 0.23 g L^{-1} $MgSO_4{\cdot}7H_2O$, 0.25 g L^{-1} $CaCl_2$, 1 L distilled

H_2O]: ingredients can be purchased from Fisher Scientific, 112 Colonnade Road, Ottawa, Ontario K2E 7L6. Tel: 1-800-234-7437, <http://www.fishersci.ca/>.

Stainless steel coupons (50 mm x 50 mm): Goodfellow Cambridge Limited, 800 Lancaster Avenue, Berwyn, Pennsylvania 19312-1780. Tel: 1-800-821-2870.

Super Sharpie® Permanent Marker: Sanford Corporation, 2711 Washington Blvd, Bellwood, Illinois 60104. Tel.: 1-800-323-0749.

Weather Seal Blok-Guard® and Graffiti Control: PROSOCO, Inc., 3741 Greenway Circle, Lawrence, Kansas 66046. Tel: 1-800-255-4255.

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    - good adhesion;
    - penetrate stone to a depth of at least 25 mm;
    - have low viscosity;
    - resistance to ambient temperatures;
    - not block the porosity of the stone;
    - not alter the porosity of the stone in order to prevent damage from freeze-thaw cycling;
    - match physical properties of the stone such as thermal expansion;
    - not discolour the stone, nor discolour over time;
    - not be vulnerable to decay by atmospheric pollutants, salts or biological activity;
    - match weathering of stone;
    - employ reasonably benign chemicals in view of health concerns.

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Appendix I. The Electrochemical Impedance Spectroscopy (EIS) cell.

The base of the EIS cells has dual functionality: to serve as the substrate for the anti-graffiti coatings and as the working electrode (A). Bases were pre-cut stainless steel coupons (50 mm x 50 mm, Goodfellow Cambridge Limited). The coupons were first abraded with 220 grit sandpaper and cleaned with acetone to remove grease. Coupons were coated by brush and received two coats of the anti-graffiti coating (B). Acrylic tubes (McMaster-Carr, 2" hollow rod outer diameter, 1 ¾" inner diameter, 6' length) were cut to 3" segments (C) and adhered to the steel coupons with DAP 100% Silicone Aquarium Sealant. Minimal salt solution was used to fill the cells as an electrode (D). The saturated calomel reference electrode (E) and platinum mesh counter electrode (F) were inserted into the medium, completing the tri-electrode system with the base (A).

Left: EIS cell diagram. **Right:** Blok-Guard EIS cell without electrodes E, F. Dark matter in the electrolyte solution is the microorganisms.