

## Abstract

Titanium dioxide (titania) is frequently used in materials to break down common pollutants. A poly(carbonate urethane) coating composed of Idrocap 993PF and Titanium dioxide doped with Erbium and Ytterbium was prepared via sonication. This was done to evaluate its possible use as a coating for stone surfaces in cultural heritage preservation and rehabilitation.

Coquina, a limestone rock that presents unique preservation challenges, was used for testing as limestone typical of Florida heritage sites.

The coating was tested for its photocatalytic properties using methylene blue degradation in response to simulated sunlight. Rock surfaces were monitored for changes in morphology and color after treatment to determine if the coating would be suitable for preserving the aesthetic quality of heritage sites. The coated stones will be tested for their static contact angle and their ability to repel water while still allowing for the flow of water vapor.

The properties assessed indicate that the coating tested could be suitable for use in the preservation of stone structure heritage sites but further tests must be completed.

## Background

Stone heritage sites are under constant assault from a variety of assailants including weathering, pollution, and climate change. Florida stone faces unique challenges as well with fragile rock like coquina making up many significant sites. With so many factors to account for, efforts to preserve and rehabilitate these structures are met with complex challenges.

Protective and self-cleaning coatings offer a possible solution to some of the problems faced in the field of cultural heritage preservation but these coatings must fulfill certain criteria. A coating cannot impact the aesthetic quality of a structure, the coating should protect the structure from new contaminants while having no harmful byproducts, it should repel water while at the same time allow water trapped below the surface to escape to minimize damage from spalling.

The goal of this research was to test possible coatings for use on stone structure heritage sites to see if they met most or all of these criteria.

## Objectives

- Evaluate doped titania coatings for their ability to break down pollutants and handle the flow of water without damaging the heritage site
- Evaluate the benefits of doped titania and the upconversion process for use in coatings for stone heritage preservation.
- Evaluate the value of doped titania coating use for the preservation of coquina

## Approach

The coating was prepared using a commercial poly(carbonate urethane), Idrocap 993PF, and cold mixing it with 1% of the photocatalyst samples via sonication. 25mL of the coating was then brushed evenly onto the surfaces of both travertine limestone samples and white marble samples. The stone samples dried within an hour allowing the aesthetic impact of the coating to be evaluated.

The coating was transparent and did not change the color of the stone. The only noticeable difference was a slight sheen which could be seen only when the stone was hit by light at certain angles. The TiO<sub>2</sub> particles could be seen using a magnifying glass but, due to the natural porous appearance of stone, had negligible impact of the aesthetic quality of the stone surface.

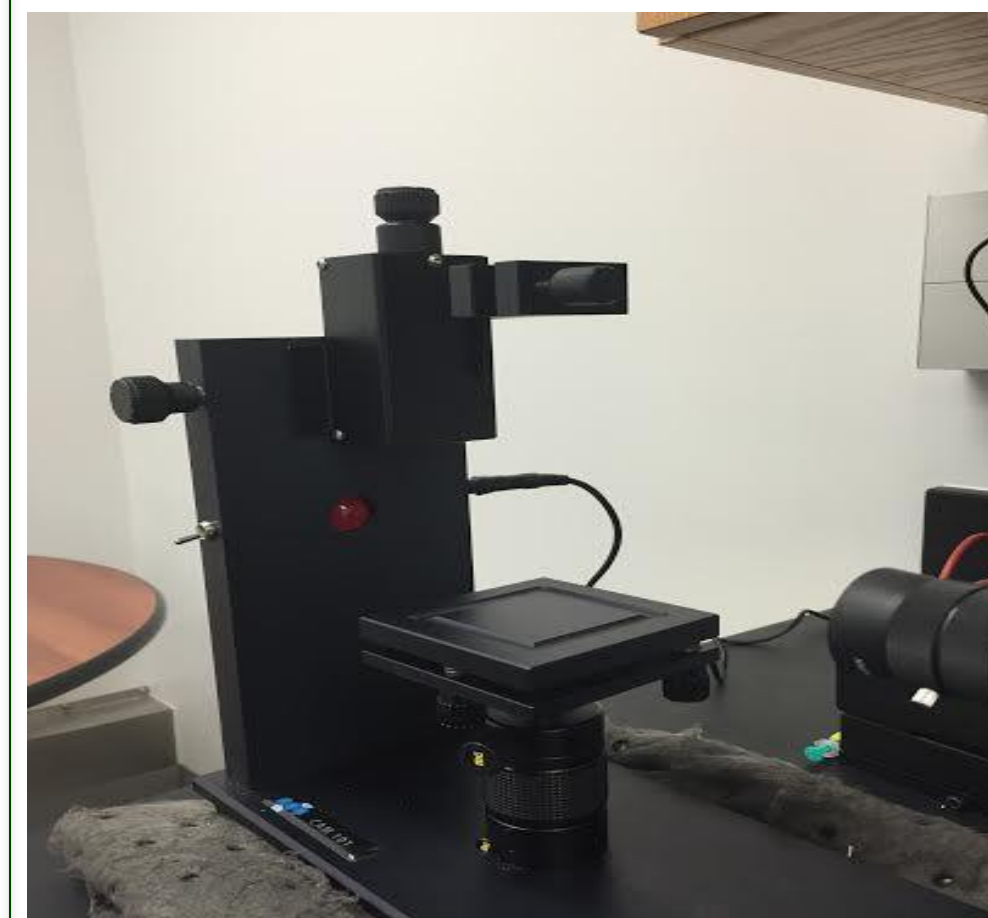
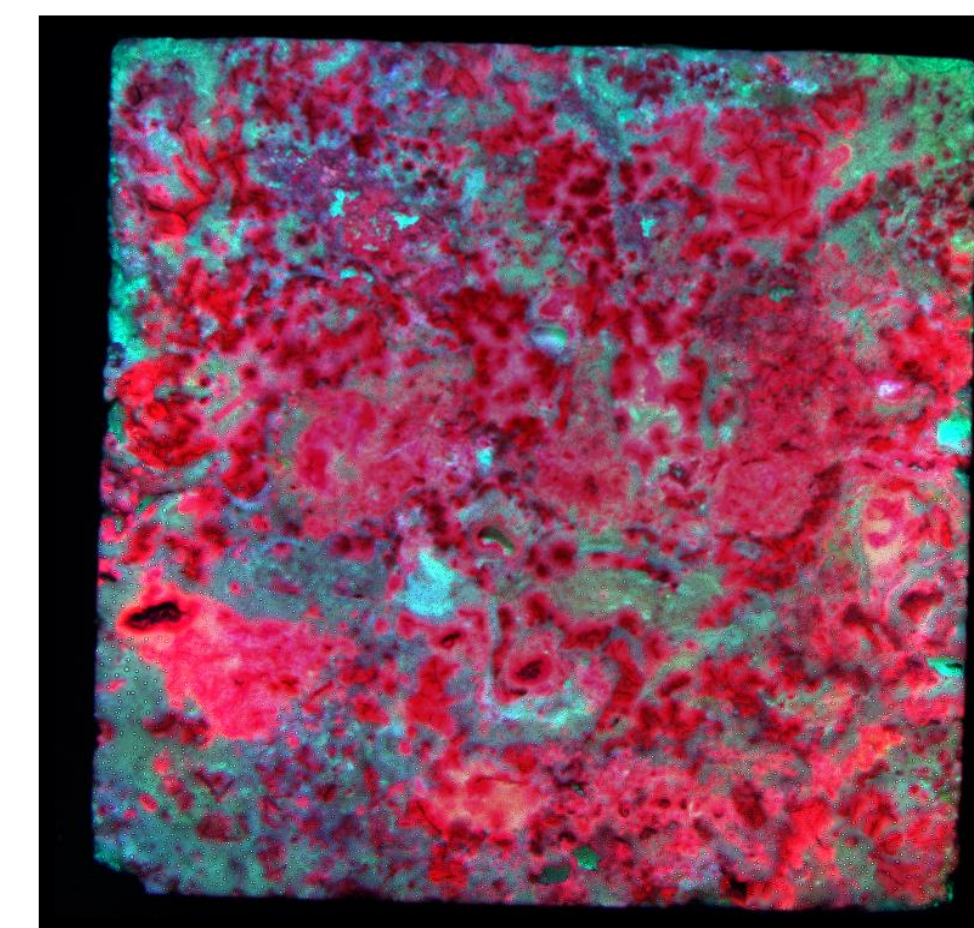


Figure 1

Coatings were then evaluated for their hydrophobicity by measuring static contact angles. A KSV CAM 101 (figure 1) was used to conduct these tests. We tested the approximate center of 4 quadrants of each sample and then averaged out the contact angle to compare the following samples: No coating, Idrocap only, Idrocap with commercial TiO<sub>2</sub>. Further tests must be conducted on the pure and 10% coatings.

Figure 2



Once the coating had dried some of the samples were treated with methylene blue dye representative of contaminants in the environment. Coquina samples were set up using the following coatings: Idrocap 993PF only, Idrocap plus 1% of pure TiO<sub>2</sub>, Idrocap plus 1% commercial TiO<sub>2</sub>, and Idrocap plus 1% of TiO<sub>2</sub> 2% Er 10% Yb, 83% (labeled 10%). An uncoated coquina sample was used as a control. Once treated with the dye samples were exposed to simulated sunlight in low humidity for 20 hours.

Before and after exposure pictures were taken of all the samples. The degradation of the dye for the simulated sunlight (sunbox) samples will be analyzed at a later date using the NIH program Image J. At the time of the printing of this poster only the picture of the "before" samples were available. In order to take the pictures in a controlled environment Protein Simple's Multiflour was used to image the samples RGB spectrum. This can be seen in figure 2, a picture of a coquina sample coated with Idrocap and pure TiO<sub>2</sub>.

## Conclusions

The results showed that the coatings tested have potential for use in heritage preservation endeavors. The main criteria that was evaluated: the aesthetic impact of the coatings on stone samples, the hydrophobicity of the coatings, and the photocatalytic quality of the doped Titania in simulated (still in progress). There is little to no impact on the aesthetic quality of the stone samples making these coatings appropriate for use on cultural heritage sites.

Static contact data (figure 3-5) shows that the coatings improved the hydrophobicity of the coquina which is a desirable characteristic for stone heritage preservation. Further tests will be conducted on doped coatings.

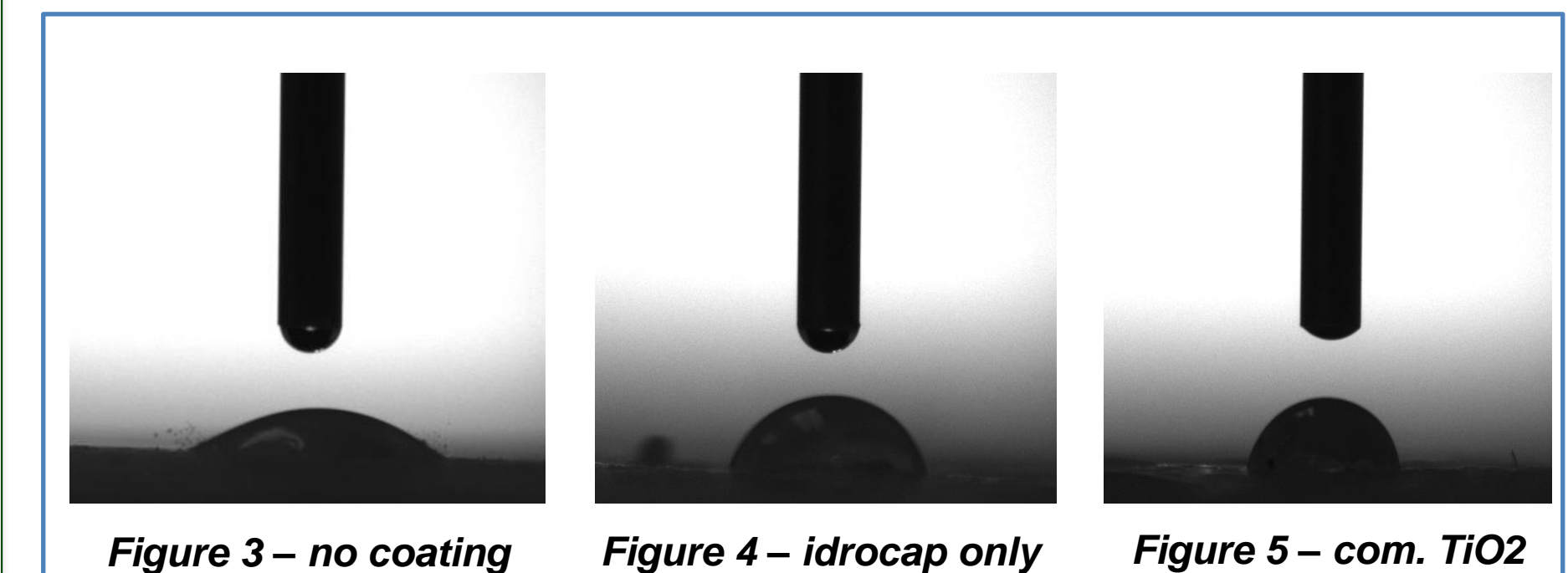


Figure 3 – no coating    Figure 4 – idrocap only    Figure 5 – com. TiO<sub>2</sub>

Preliminary tests, on limestone and marble, indicate the doped coatings do improve the self cleaning properties of titania (results from preliminary testing can be seen with figure 6). Further results are being process with more sophisticated imaging techniques (figure 2).

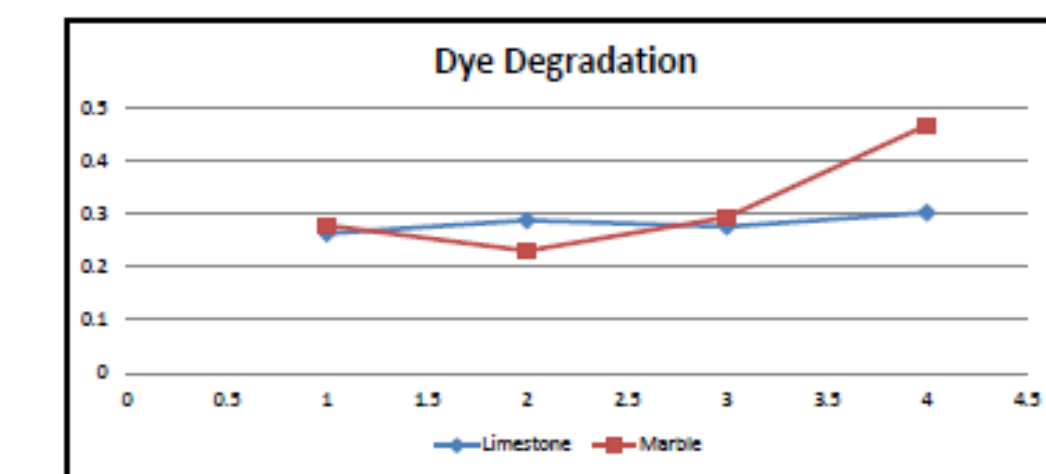


Figure 6

figure 6: 1) Idrocap only, 2) Pure, 3) 0%, 4) 10%

Further tests are needed to measure the effect the coatings have on water absorption rates as well as the ability to allow vapor to pass through the coquina sample to avoid spalling.

## Referenced Resources

- Colanguili, D., Calia, A., & Bianco, N. (2015). Novel multifunctional coatings with photocatalytic and hydrophobic properties for the preservation of the stone building heritage. *Construction and Building Materials*, 93, 189-196.
- D'Orazio, L., & Grippo, A. (2014). A water dispersed Titanium dioxide/poly(carbonate urethane) nanocomposite for protecting cultural heritage: Preparation and properties. *Progress in Organic Coatings*, 79, 1-7.
- UNI EN 15801:2010. Conservation of cultural property – Test methods – Determination of water absorption by capillarity. Official Italian Version of EN 15801:2009. Milan: UNI; 2010.
- UNI EN 15803:2010. Conservation of cultural property – Test methods – Determination of water vapour permeability (dp). Official Italian version of EN 15803:2009. Milan: UNI; 2010.
- Watt, J., Tidblad, J., Kucera, V., & Hamilton, R. (2009). *The Effects of Air Pollution on Cultural Heritage*. New York: Springer Science.