FMRI RET 2015- Poly(carbonate urethane) and doped Titania coatings for Cultural Heritage preservation

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Abstract

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. Limestone and marble samples were used for testing as stones typical of heritage sites. The coating was tested for its photocatalytic properties using rose bengal degradation in response to simulated and natural 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 properties assessed indicate that the coating tested could be suitable for use in the preservation of stone structure heritage sites.

Background

Stone heritage sites are under constant assault from a variety of assailants including weathering, pollution, and climate change. 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, it must be easy to apply to the stone surfaces, 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, and finally it should be durable and long lasting to maximize time between reapplications. 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

- Recreate previous research in titania coatings, create new coatings, and test the results on actual rock samples
- Address concerns about coating use on American heritage sites
- Evaluate coatings for practical use on stone structure heritage sites

Approach

The photocatalyst samples (fig. 1) used had been prepared using a modified hydrothermal synthesis method for TiO_2. The photocatalysts were synthesized with erbium nitrate and ytterbium nitrate as the sources for the Er^{3+} and Yb^{3+} ions. Three synthesized samples were used differing in their percent of TiO_2, Er, and Yb. The composition of the samples in molar percent are: 100% TiO_2, 98% TiO_2 2% Er 88%, and TiO_2 2% Er 10% Yb, 83%.

figure 1

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_2 particles could be seen using a magnifying glass but, due to the natural grained appearance of stone, had negligible impact of the aesthetic quality of the stone surface.
Once the coating had dried some of the samples were treated with rose bengal dye representative of contaminants in the environment. Both limestone and marble samples were set up using the following coatings: Idrocap 993PF only, Idrocap plus 1% of pure TiO_2 , Idrocap plus 1% of 98% TiO_2 2% Er 88% (labeled 0%), and Idrocap plus 1% of TiO_2 2% Er 10% Yb, 83% (labeled 10%). Once treated with the dye half of the samples were exposed to simulated sunlight in low humidity for 20 hours while the other half were exposed to natural sunlight outdoors for 6 hours with an average humidity of 60%. Before and after exposure pictures were taken of all the samples. The degradation of the dye for the simulated sunlight (sunbox) samples were analyzed using the NIH program Image J.
The outdoor samples were only able to be analyzed for the visible differences at this time, although the contrast between the low and high humidity samples are readily apparent as can be seen in figures 2-5.

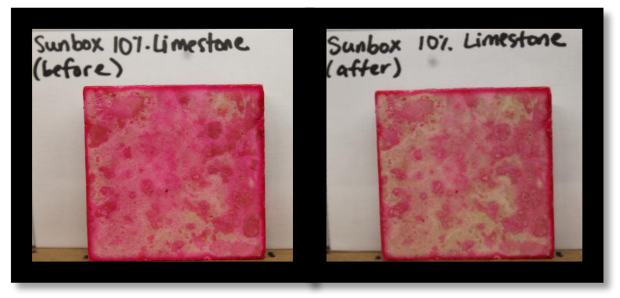

figure 2: Simulated Sunlight on Limestone

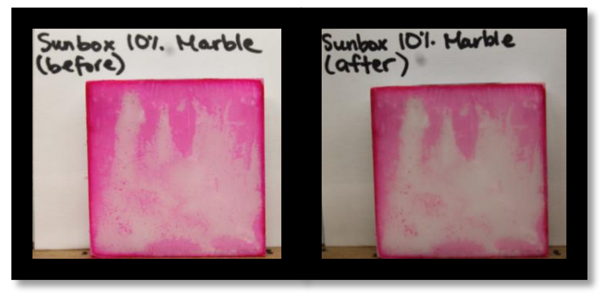

figure 4: Simulated Sunlight on Marble

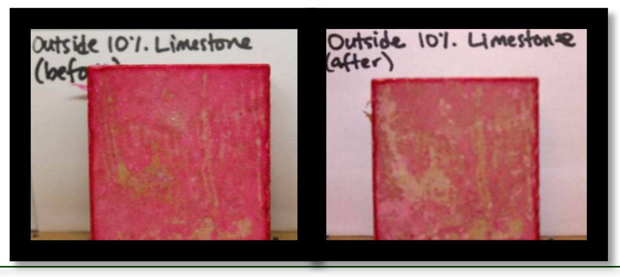

figure 3: Natural Sunlight on Limestone

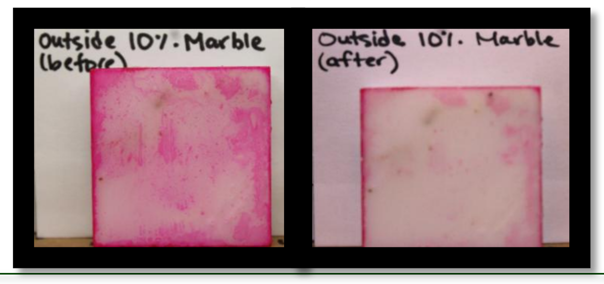

figure 5: Natural Sunlight on Marble

Conclusions

The results showed that the coatings tested have potential for use in heritage preservation endeavors. The main criteria that was evaluated falls into three areas: the aesthetic impact of the coatings on stone samples, the photocatalytic quality of the doped Titania in simulated sunlight (figure 6), and the impact of humidity on the reaction of the coatings with regards to dye degradation.
There is little to no impact on the aesthetic quality of the stone samples making these coatings appropriate for use on cultural heritage sites. Furthermore, when referring to the figure 6, it can be seen that the coating with the most impact was the 10% coating (4). The coating is more effective with the less porous marble samples but still makes a difference on the limestone.

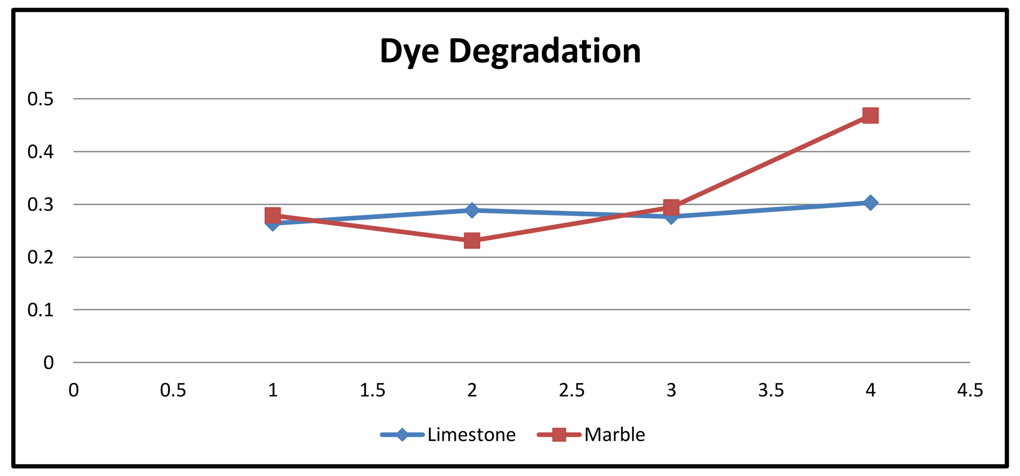

figure 6: 1) Idrocap only, 2) Pure, 3) 0%, 4) 10%

The visible differences of the reactions in low versus high humidity (when low humidity samples reacted for 20 hours and the high humidity samples reacted for only 6 hours) suggests that higher humidity leads to faster reaction times. This would make the coating beneficial to outdoor heritage sites, especially in high humidity areas such as Florida where the outdoor test were conducted.
Overall the use of doped titania coatings show promising initial results. Further testing will be done to determine the specific differences between the coatings including the reaction with UV versus visible and infrared light. Further testing should also be conducted to determine the effects of the coatings on spalling as well as the long term durability of the material. Outdoor samples will have to be analyzed for quantitative differences in dye degradation.

Referenced Resources

D'Orazio, L., & Grippo, A. (2014). A water dispersed Titanium dioxide/poly(carbonate urethane)nanocomposite for protecting cultural heritage: Preparation and properties. *Progress in Oragnic Coatings*, *79*, 1-7.
La Russa, M., Ruffolo, S., Rovella, N., Belfiore, C., Palermo, A., Guzzi, M., & Crisci, G. (2012). Multifunctional TiO2 coatings for Cultural Heritage. *Progress in Organic Coatings*, *74*, 186-191.
Watt, J., Tidblad, J., Kucera, V., & Hamilton, R. (2009). *The Effects of Air Pollution on Cultural Heritage*. New York: Springer Science.

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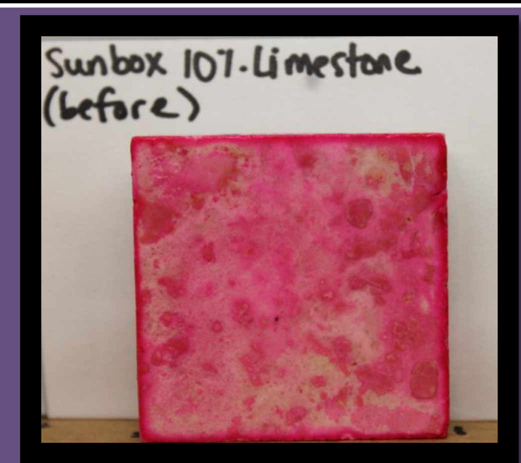
Sunbox 107-Limestone
(before)