Rare Earth Metal Doped Titanium Dioxide Upconversion Photocatalysis for Historical Building Preservation Applications

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Abstract

Many historical buildings find themselves falling prey to hazardous pollutants and destructive weather patterns. In order to preserve the cultural heritage of these buildings, certain materials exhibiting photocatalytic abilities are being obtained. These materials are able to harness sunlight and use this energy to form reactions. In this experiment, I will be observing a prominent photocatylyst, titanium dioxide, on its effectiveness to degrade pollutants often found in nature. Titanium dioxide usually absorbs light found only in the visible light section of the electromagnetic spectrum. In order to improve efficiency, the titanium dioxide is being doped with rare earth metals, erbium and ytterbium, in order to "upconvert" lower frequency light waves to UV light waves. The amount of ytterbium added is manipulated in order to observe at what concentration pollutant degradation is the largest. The doped titanium dioxide samples are synthetized via a hydrothermal process. The samples are then applied on coquina and travertine, stones commonly used in the structures of historical buildings. A coating of Methylene Blue dye, a solution that has benzene-rings that mimic water-based pollutants, is then applied to each of the stones to study how much of the dye would degrade. Static contact angle and water absorption tests were run to assess the relationship between water and each of the various coatings. Static contact angle tests displayed that the use of the Idrocap993 PF does influence the wettability of a surface, and water absorption tests demonstrated that both the TiO_2 and Idrocap993 PF affect the penetration of liquid water into the tile.

Introduction

The concern about historical building conservation is an issue long overdue. Over time, pollutants and various other organic materials find themselves getting stuck to the side of many culturally-significant buildings, ultimately diminishing the buildings traditional importance and aesthetic beauty. These buildings will influence the socio, cultural, and economic aspects of our community. It is the responsibility of our generation to preserve cultural heritage as the legacy of physical artifacts and intangible attributes of these buildings must be maintained in the present and bestowed for the benefit of future generations. As they deteriorate from environmental consequences, past thoughts, beliefs, and opinions are fading away. Historical buildings remind humanity of our early beginnings and where we came from. Whenever such buildings are expressed, can we not only look into our past, but see how far society has come since then. With this perspective in mind, these buildings could even inspire us on what we are capable of doing in the future. These buildings have to keep their beauty in order to inspire people even after thousands of years. By observing historical monuments, we can learn about great human civilizations like Roman, Greek, Hindu, Egyptians, Mesopotamia. The buildings and architecture help to understand the evolutions of humans through centuries. Our future thoughts, beliefs, and opinions will become displayed through our architecture, as it did in the past.

In this experiment, I will be testing the claim that presence of rare earth elements in the titanium dioxide samples will lead to an increase in percentage of methylene blue dye degradation. I believe this will occur to the ytterbium ions taking part in an upconversion process with the titania. Lanthanide-doped nanoparticles have displayed prominent abilities in being able to decrease their wavelength when emitting light, therefore increasing their frequency. The doped titania will be able to showcase more light being absorbed, not just its default visible but also UV light. With more light being absorbed, there will be more energy being harnessed and therefore more dye can be degraded.

Background Research

In order to address the issue of heritage preservation, various treatments have been suggested. However, treatments can only be used if they fulfill a complicated list of conditions. In order to effectively restore and maintain natural stone, treatments must: clean; consolidate; adhere and seal; and protect the surface. When the issue was first addressed in the 1950s, vinyl resins were presented as a solution. Since then, new technologies and discoveries have been made, bringing the use of polyurethanes to attention. These materials have demonstrated that they can fulfill all the requirements need for an ideal surface consolidation treatment: good adhesion to the stone substrate, negligible color alteration, and no harmful by-products.

Similar to the heritage preservation application is the self-cleaning glass application, in which photocatalysts are utilized due to their ability to utilize the sun's light rays in order as energy to start up a reaction that ultimately disintegrates the pollutants found on the glass of building. A common compound used in self-cleaning glass materials is titanium (IV) dioxide. This metal oxide is notably known for its strong photocatalytic abilities. In order for the photocatalysis process to work, a photon of light equal to or greater than the bandgap's energy, 3.2 electronvolts (eV), must be absorbed. This stimulation of energy causes an electron to move from the valence band to the conduction band, leaving behind a positively-charged hole. Then, oxygen (O_2) in the atmosphere releases the electrons from the conduction band and combines with them to form superoxide anions. Simultaneously, the

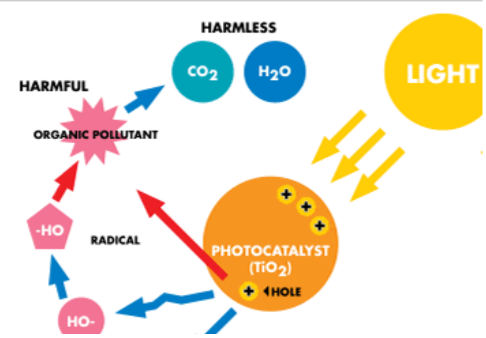


Figure 1. Diagram displaying the TiO2 photocatalysis process

positive hole attracts electrons from hydroxide (OH^-) molecules in the air appearing as moisture. By losing an electron to the positive hole in the valence band, the hydroxide become hydroxyl radicals. The superoxide anions and hydroxyl radicals together make up an active oxygen species that when combined with an organic substance result in an oxidative decomposition. The entire photocatalysis process ends with byproducts of carbon dioxide (CO_2) and water (H_2O).

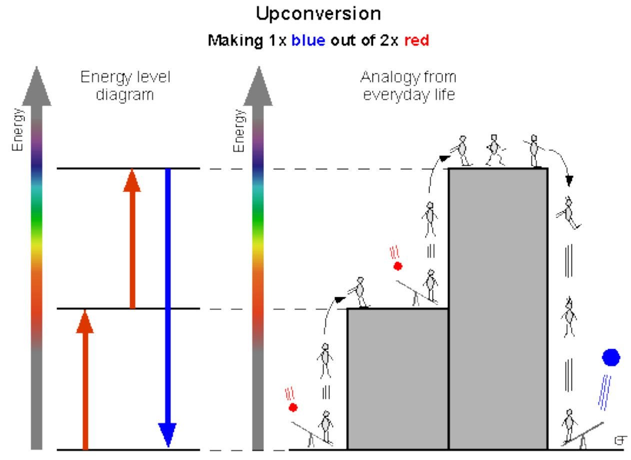


Figure 2. Graphic demonstrating the upconversion process

By default, the titanium (IV) dioxide is able to only utilize light with frequencies in the UV range. This range, however, only makes approximately 3% of the entire electromagnetic spectrum. In order to increase the range and therefore be able to utilize more light, titanium (iv) dioxide can be doped with lanthanide nanoparticles in an upconversion process. By doing this, the range expands and the titania can now absorb visible light. The upconversion process starts when a medium is excited and emits light at a shorter wavelength than the excitation wavelength. This is possible due to mechanisms which allow for more than one photon to be absorbed to emit a photon with a higher energy level.

Rare earth metals, like Erbium and Ytterbium, have been commonly used as dopants in many reactions. This doping process works as rare earth metal ions replace ions of a similar size in the host medium. Ytterbium is often doped alongside erbium. This process works as ytterbium ions absorb the pump radiation and transfer the excitation energy to erbium ions. Erbium ions can directly absorb radiation at 980 nm, however, codoping can be useful because of the higher ytterbium absorption cross sections and the higher possible ytterbium doping density. This will allow for a shorter pump absorption length and a higher gain can be achieved.

Titanium occurs naturally in nature through primarily the minerals anatase, brookite, and rutile. Of these minerals, only rutile has significant economic importance. As a metal, titanium is well known for corrosion resistance in sea water, aqua regia, and chlorine. Approximately 95% of titanium is consumed in the form of titanium dioxide (TiO_2). This can be attributed largely to its use as a white pigment in paints, paper, and plastics. The superiority of TiO_2 as a white pigment is due mainly to its high refractive index and resulting light-scattering ability, which impart excellent hiding power and brightness.

In recent years, photocatalytic TiO_2 has been receiving increased amount of attention for the conversation of the stone cultural heritage. It can preserve the integrity of the stone surface by protecting against the deposition of many urban particulates that feed on surface deposits. Therefore, photocatalytic stone coatings by TiO_2 nanoparticles can minimize the maintenance of the building facades by cleaning works. It is very effective in the degradation of uncombusted hydrocarbons, which retain on the stone surface in a polluted environment. A recent project was conducted at the Institute for Archeology and Monuments located in Lecce, Italy. They used a limestone substrate, train stone, for their experimental units. In order to further the applications, this project also a limestone called travertine. Travertine is a sedimentary rock with its sediments usually being found in geo-thermally heated geysers or springs. Unlike other limestones, it goes through the extra process in which hot water flows through the travertine, releasing carbon dioxide which accounts for all the pores in the stone. Due to many historical

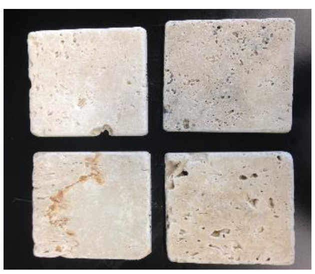


Figure 3. 4" x 4" Travertine Tiles with No Coating

buildings also being made of limestone and being porous, travertine tiles were used as the experimental units.

Polyurethanes are often used in the manufacturing of surface coatings and surface sealants. They are known for their outstanding performance in harsh weather conditions. Idrocap 993PF was used due to it having good water resistance, good abrasion, and rub resistance. It is a water-based emulsion with the dispersion of an aliphatic polycarbonate-based PU.

The dye imitator used in this experiment will be methylene blue. This organic dye contains benzene rings, as do many real water-based pollutants.

Materials and Methods

Hydrothermal Synthesis

First, glacial acetic acid (CH_3COOH) was added to 400mL of deionized water until a pH of 2 was achieved. Then, 38.4 mL of Ti^{4+}-isopropoxide ($C_{12}H_{28}O_4Ti$) and 38.2 mL of isopropanol ($(CH_3)_2CHOH$) were mixed together. At the same time, in the 10% doped sample, 1.3069 grams of erbium (III) nitrate pentahydrate ($Er(NO_3)_3 \cdot 5H_2O$) and 6.6197 grams of ytterbium (III) nitrate pentahydrate ($Yb(NO_3)_3 \cdot 5H_2O$) were added to the Ti^{4+}-isopropanol solution. The Ti^{4+}-isopropanol solution was then added to the acidic deionized water. The suspension was stirred for one week at room temperature until it became a homogenous solution. After one week, the suspension changed from a cloudy, heterogeneous mixture to a thick, white solution. After the allotted time period, trimethylamine ($(C_2H_5)_3N$) was added to the solution until a pH of 9 was reached. The suspension was then placed in an autoclave reactor and put in a hydrothermal treatment at 140°C for 20 hours. After the allotted time period, the resulting suspension was filtered with a Buchner flask with vacuum while using ethanol (C_2H_6O) to rinse. The precipitate was then dried overnight at 120ºC. The powder was then calcined at 500ºC for 2 hours in order to remove any organic compounds.

Preparation of Coatings and Methylene Blue Dye

For the purposes of this project, 5 groups were tested on. The first group consisted of travertine rocks with no treatment called No Coating. These tiles were used as a control group and for baseline comparisons. The second group consisted of tiles treated with only Idrocap993 PF and called Idrocap Only. The third group consisted of tiles treated with a sonicated mixture of Idrocap and manufactured TiO2 and referred to as TiO2 Control. The fourth group consisted of tiles treated with a sonicated mixture of Idrocap and synthesized TiO2, and this group was called Pure TiO2. The fifth group consisted of travertine tiles treated with a sonicated mixture of Idrocap and 2%Er/10%Yb doped TiO2, and it was referred to as 10%.

All of the sonicated mixtures were created by first mixing 99 milliliters of Idrocap993 PF and 1 gram of the respective TiO2 powder in a glass container for one minute. The containers were then placed in the sonicator at a setting of high for 10 minutes. The ratio for each of the mixtures between Idrocap993 PF and TiO2 powder was therefore 99:1. Each of the tiles were coated with 2.4mL of its respective coating.

The methylene blue dye ($C_{16}H_{18}ClN_3S$) was created in a 200 ppm concentration and 250 mL of the dye were created.

Static Contact Angle Tests

Prior to the dye treatment, the tiles were tested on to observe how the coatings affected the water static contact angle. The tiles were placed on a KSV CAM101, a computer controlled and user programmable video based instrument designed for the measurement of static contact angles. The tiles were divided into quadrants in order to prevent bias amongst taking a contact angle on different textures of the surface. The center of each quadrant was placed directly under the Manual Hamilton 1 ml, an adjustable precision syringe with proprietary easy to use "One Touch Dispenser" mechanism. Each of the quadrants served as a trial for each tile. 3 tiles, each with different coatings (No coating, Idrocap only, TiO_2 control), were used to each experimental group. Using a charge-coupled device (CDD) camera, the KSV CAM101 obtained pictures while the drop was applied and later exported the static contact angles were each tile. For each quadrant, 5 pictures were taken in a time span of 0.20 seconds.

Water Absorption Tests

A container with a flat base was obtained and used in this test. Filter paper, acting as a bedding layer, was placed along the bottom of the vessel. Enough filter paper was placed such that the layer was at least 5mm thick. Next, deionized water was added until the layer was saturated while noting that the water should not exceed the upper surface of the layer. The stones were then placed coating-side down upon the saturated bedding layer. Preliminary tests were run in order to obtain the appropriate time interval between massing. The time interval was concluded by massing every one minute until a change in mass occurred. For our tests, a time interval of 3 minutes was obtained. After the allotted time interval, the stones were picked up, dabbed to remove excess water, and massed via a balance. The test was completed for each tile after 5 weighings, resulting in a total of 15 minutes being submerged in the water.

Dye Degradation Tests

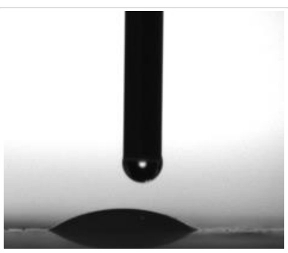
Once the coatings on the tiles dried, the tiles were each coated with 2.4mL of methylene blue dye. After the dye has dried, the tiles were each individually placed in a ProteinSimple FluorChem E, where multicolor fluorescent pictures were taken. The pictures were then analyzed via the NIH’s ImageJ program for the area, mean grey value, and integrated density of each tile.

The tiles were then placed in a sunlight-simulating lightbox for 20 hours. After the 20 hours have allotted, the tiles were once again placed in the ProteinSimple FluorChem E, and the same values were interpreted.

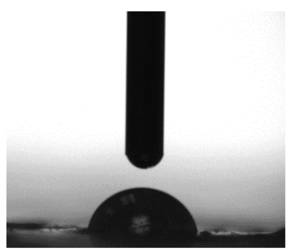
Results

Static Contact Angle Tests

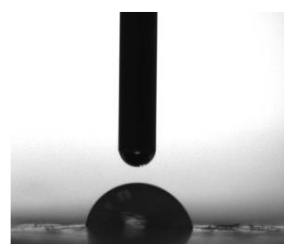
All the samples tested on displayed static contact angles less than 90 degrees. The average for each coating was calculated and a large disparity was present between tiles with and without the Idrocap993 PF. Natural travertine tiles with no coating had an average contact angle of 24.71843333 degrees, whereas tiles treated with the Idrocap, TiO_2 Control and Idrocap Only, had an average angle of 74.39776667 degrees (Figure 1). More specifically, Idrocap Only tiles had an average contact angle of 73.08786667, and TiO2 Control tiles had an average angle of 75.70766667 (Table 1). Over time, the angles remain fairly constant for samples treated with Idrocap, however, natural tiles with no treatment saw their angles decrease (Figure 2).



(a) Static Contact Angle of a Tile with No Coating



(b) Static Contact Angle of a Tile with Idrocap Only



(c) Static Contact Angle with TiO2 Control Coating

Figure 4. Detail of a water droplet on the surface of sample

Coating/Trial #	1	2	3	4	Average
No Coating	19.12393333	28.20053	18.3918	33.15747	24.718433

Idrocap Only	77.31226667	74.2973	78.70313	62.03873	73.087858
TiO2	79.50406667	82.0658	72.5456	68.7152	75.707667

Table 1. Contact angle averages (α) of each coating across different trials

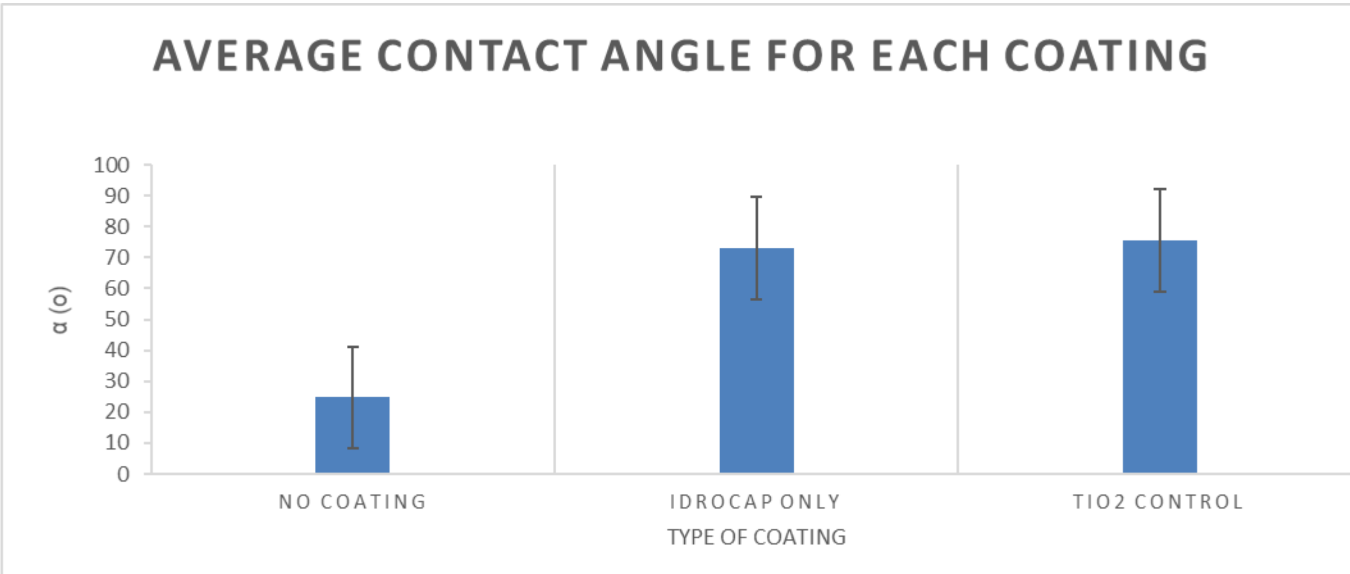


Figure 5. Graph displaying overall average contact angle (α) for each coating

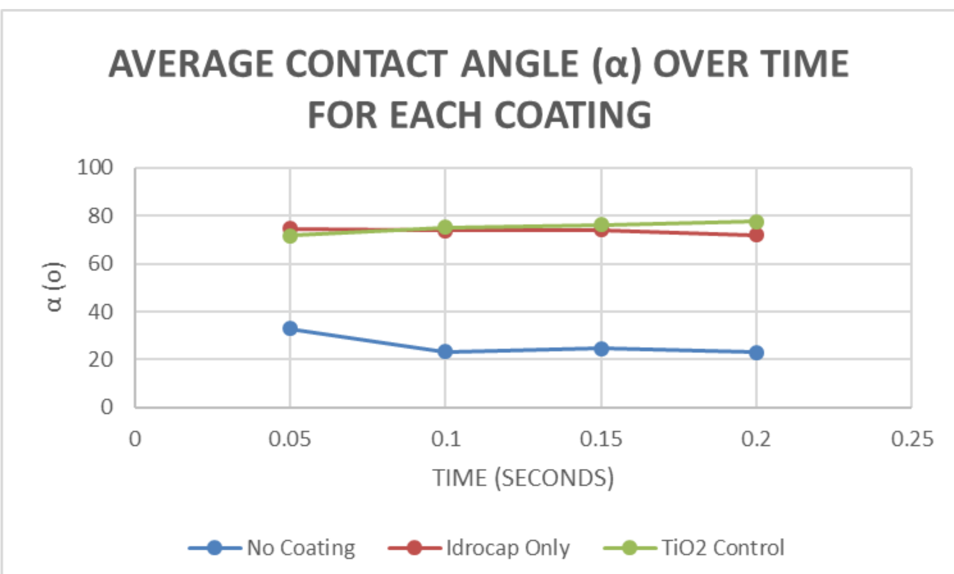


Figure 6. Graph displaying average contact angle every 0.05 for 0.20 seconds for each coating

Water Absorption Tests

Water absorption tests concluded that the 2% Er/10% Yb-doped TiO_2 had the best resistance to water. Out of all the coatings, the doped coatings displayed the highest ability to hinder water absorption. However, the presence of the rare earth metals did not contribute much to its hindering ability.

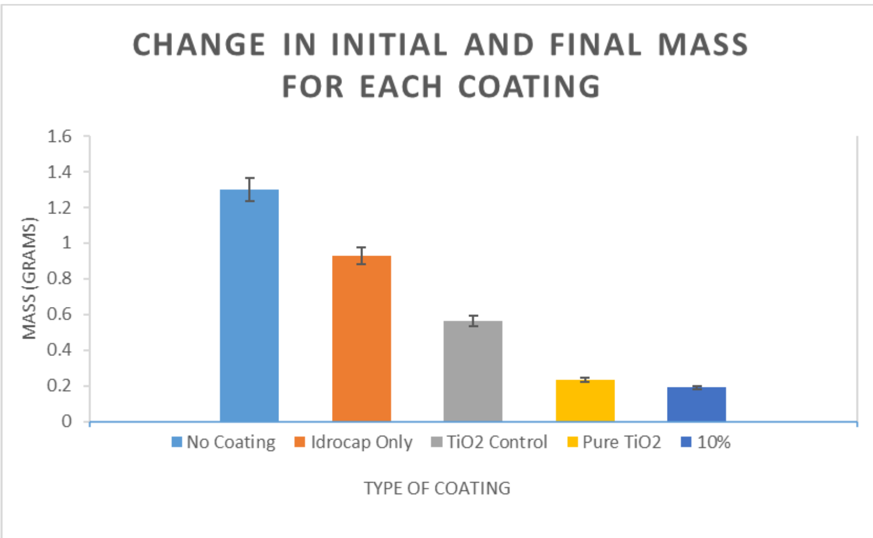


Figure 7. Change in total mass for each coating

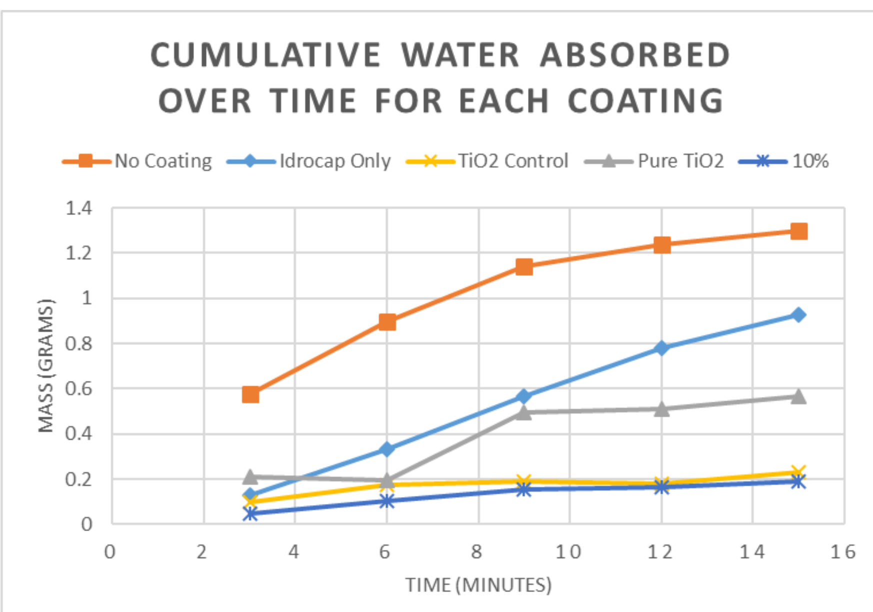


Figure 8. Water absorbed over time for each coating.

Discussion

In order to assess which coating was the most effective, static contact angle tests were conducted. The contact angle is the angle a liquid creates when in contact with a solid surface or capillary walls of a porous material. It can be influenced by various properties of both the liquid and solid being tested on, the interaction and repulsion forces between the solid and liquid, and the three phase interface properties (gas, liquid, and solid). This angle can be used to assess the wettability of each coated surface. If the contact angle is small, it implies that the cohesive forces are weaker than adhesive forces. This will cause liquid molecules to interact with solid molecules more than other liquid molecules. Taking no other factors into account, a low contact angle can be interpreted that the surface is hydrophilic. With a hydrophilic surface, the liquid does wet the surface. On the other hand, a large contact angle implies that the cohesive forces are stronger than the adhesive forces. This, therefore, causes the liquid molecules to interact more with each other than with the solid molecules. With no other factors coming into play, a large contact angle implies that the surface is hydrophobic. A hydrophobic surface states that the liquid does not wet the surface.

Water absorption tests were also conducted to analyze the water transfer properties of each coating. Since water is a preeminent factor of the stone decay, one of the main conservation needs is the protection against water penetration from the stone surface. These tests can also help identify if the presence of titanium dioxide has any influence on the performance of the Idrocap 993PF polymer. Water absorption is used to determine the amount of water absorbed under specified conditions. Factors affecting water absorption include: type of plastic, additives used, temperature and length of exposure. The data sheds light on the performance of the materials in water or humid environments. Due to water playing such a large part in the stone decay process, the best protection of the surface is when the coating on the surface is able to limit the entrance of liquid water from outside. TiO2's superhydrophilicity is an unwanted aspect in heritage preservation coatings. Idrocap Only tiles display a relatively poor barrier effect against the water transfer. While it is hydrophilic, the polymer is not far from displaying hydrophobic properties (90o contact angle) with its 73o contact angle. Idrocap is hydrophobic while TiO2 is superhydrophillic. However due to the larger proportion of Idrocap in the coating, this explains why the contact angle is not exactly 0^o.

It has been discussed in previous studies [5-7] that contact angle measurements could be poorly correlated with the degree of protection of the treatments applied to the stones due to the surface roughness and heterogeneity of the substrate influencing both measurements. In addition, static contact angle measurements are only representative of short time intervals, a sharp contrast to the long-term measurements of the water absorption tests. Moreover, a variety of different dynamic factors influences each time of measurement, hindering their ability to be accurately correlated against one another.

Conclusion

The functionalization of the building stone surface with self-cleaning and depolluting properties by the application of photocatalytic TiO2 coatings can provide protection of the building facades against the deposition of organic pollutants that leads to the darkening of the urban stone surfaces, as well as benefits to the polluted environments. However, the hydrophilicity of the TiO2 photocatalytic coatings can limit their use when hydrophobic properties are desired for stone preservation applications. Therefore, multiple coatings, which combined the photocatalytic ability of the TiO2 and the water repellency of a polyurethane carbonate, were created by adding various concentrations of TiO2 and Er and Yb to a commercial polymer, Idrocap993 PF.

In this experiment, data concluded that certain concentrations of pure TiO2 and the polymer affect the performance of the coating. By finding the optimal concentrations can the self-cleaning and water penetration properties be fully utilized. With these optimal concentrations can stones keep their aesthetic beauty and appeal.

TiO2 was found to affect the hydrophilic properties of the Idrocap993 PF by in fact showing better ability to penetrate water transfer into the tile. Coatings that had the presence of TiO2 showed a significantly smaller water of water absorption than those tiles with Idrocap only. When rare earth metal ions were present, the amount of water absorbed had decreased significantly as well. When TiO2 nanoparticles were present, the coating on the stone surface exhibited more hydrophobic behavior. This is sharp contast to the large amount of water absorbed in the TiO2 Control tiles.

In this study, a possible approach has been followed in order to obtain multifunctional products addressing building stone protection. A double component solution was developed by mixing the TiO2 nanoparticles with polymeric materials, which are already well-established as water repellent products for stone and suitably chosen in order to maximize the properties of both the components while minimizing the unwater aspects. This combination could also improve the retention of TiO2 nanoparticles on the stone surface. This aspect deserves attention due to the possible release of the nanoparticles to the environment.

Tourism largely depends on these architecture marvels which attract millions of people every year. There is a sector of the economy devoted to tourism and millions of jobs are dependent on the success of this industry. People relax while visiting these breathtaking buildings and this improves the positivity of life. These buildings symbolize the culture and traditions of past generations. It is important to invest and keep them intact as they are vital for the country's economy and cultural heritage. The return on investment is high and governments and private companies should invest more to preserve these monuments.

Polycarbonate urethane/TiO_2 coatings are appropriate to be used on stone preservation applications. This experiment contributes to current knowledge on potential methods for heritage preservation. By developing new coatings we can enhance the preservation of stones worldwide and keep the culture, traditions, and beliefs of the standing in the future generations to come. By combining innovative new polymers to traditional cultural heritage preservation compounds can a more efficient and effective solution be reached.

Steps toward this solution could be taken by repeating the current steps in hopes of gaining more accurate results. The time period allotted for this project did not allow for the dye degradation tests' results to be interpreted. Therefore, in future applications the results will be taken into consideration. In addition, although limestone was used in the purposes of this project, many common building materials that have limestone foundations, such as concrete, could also be tested on. Moreover, outdoor exposure of the coated tiles could potentially provide more realistic and elaborative results.

References

1. Colangiuli, 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. http://dx.doi.org/10.1016/j.conbuildmat.2015.05.100
2. D'Orazio, L. & Grippo, A. (2015). A water dispersed Titanium dioxide/poly(carbonate urethane) nanocomposite for protecting cultural heritage: Preparation and properties. *Progress In Organic Coatings*, *79*, 1-7. http://dx.doi.org/10.1016/j.porgcoat.2014.09.017
3. 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*(1), 186-191. http://dx.doi.org/10.1016/j.porgcoat.2011.12.008
4. Toniolo, L. (2016). *Conservation and monitoring of historical architecture: new materials and technologies* (1st ed., pp. 1-32). Milan: Politecnico di Milano. Retrieved from http://events.arch.tuc.gr/fileadmin/users_data/arch/_uploads/Conservation_and_monitoring_historical_architecture_Toniolo_2016_01.pdf
5. Licchelli, M., Malagodi, M., Weththimuni, M., & Zanchi, C. (2013). Water-repellent properties of fluoroelastomers on a very porous stone: Effect of the application procedure. *Progress In Organic Coatings*, *76*(2-3), 495-503. http://dx.doi.org/10.1016/j.porgcoat.2012.11.005

6. Tsakalof, A., Manoudis, P., Karapanagiotis, I., Chryssoulakis, I., & Panayiotou, C. (2007). Assessment of synthetic polymeric coatings for the protection and preservation of stone monuments. *Journal Of Cultural Heritage*, *8*(1), 69-72. http://dx.doi.org/10.1016/j.culher.2006.06.007

7. Brugnara, M., Degasperi, E., Volpe, C., Maniglio, D., Penati, A., & Siboni, S. et al. (2004). The application of the contact angle in monument protection: new materials and methods. *Colloids And Surfaces A: Physicochemical And Engineering Aspects*, *241*(1-3), 299-312. http://dx.doi.org/10.1016/j.colsurfa.2004.04.035