

# Photocatalytic Performance of White Cement Mortars Exposed in Urban Atmosphere

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## Abstract

The objective of this study was evaluation of the photocatalytic performance of the addition of n-TiO<sub>2</sub> in white cement mortars in terms of the light reflection (evaluated by CIE L\*a\*b\* scale) and reflectance of the mortar surfaces exposed to solar radiation in an urban environment. Are produced specimens of 1.2m × 1.2m with n-TiO<sub>2</sub> additions of 1

**Index terms**— photocatalysis, self-cleaning, solar radiation, the difference of color, urban warming

## 1 Introduction

Corrective maintenance is typically carried out on facades as a result of changes in their visual appearance. Is expected that a self-cleaning surface maintains its original appearance and reflectance under exposure to solar radiation to more time than the conventional coatings used in the facades of buildings.

There has been an increase in the use of facade coatings with high solar reflectance characteristics, in addition to retro-reflective materials, which reflect direct solar radiation towards the sky and not in the direction of other buildings [1][2][3][4][5][6]. An increase in the light and thermal reflectance of building facades could be an effective strategy for the reduction of urban warming, to improve indoor thermal comfort and the energy consumption of heating, ventilation, and air conditioning (HVAC) systems [7][8][9][10], which results in the mitigation of the urban heat island effect [11]. However, the constant contact between coatings and environmental degradation agents, the incidence of ultraviolet radiation [12], and the coating roughness [13] tend to decrease the reflectance and induce changes in color over time. The role of nano titanium dioxide (n-TiO<sub>2</sub>) in the decontamination of water and the oxidation of several organic atmospheric pollutants as a result of photocatalytic activity well established. Moreover, although the photocatalysis not considered a reliable technology for breaking down large quantities of dirt, it can be applied to prevent accumulation [14,15]. The process is an alternative for the maintenance of surface cleanliness and clarity, in addition to constant solar reflectance, which ensures the proper operation of cooling properties [16].

Because of the large band gap and high photocatalytic activity, the n-TiO<sub>2</sub>, it is commonly used in the photocatalysis processes. Several researchers [17][18][19][20][21][22][23][24][25] have investigated the addition of n-TiO<sub>2</sub> in its anatase mineralogical form to cement coatings, with the objective to evaluates self-cleaning surfaces upon exposure to solar radiation. Also, self-cleaning and photocatalytic materials can add market value to buildings because of the improved maintenance of the optical performance of their facades.

Krishnan et al. [26] revealed that the photocatalytic activity is significantly degraded by the presence of calcium and sulfur from the substrate, which may accumulate on the surface of the coating and penetrate the n-TiO<sub>2</sub> lattice, thus weakening the photocatalytic effect. The surface finish should maintain its properties over time; so, it should resist the action of environmental agents that lead to gradual erosion [14], which reduce the performance of buildings concerning the reflectance under exposure to solar radiation and the aesthetic.

So, the maintenance of color and reflectance is critical to the useful life of the buildings, and this study offers other insight into the effectiveness of photocatalytic coatings when evaluated at a long time.

The tests were carried out on specimens with dimensions of 1.2m × 1.2m under exposure to an urban environment for 41 months in the city of São Paulo produced specimens of 1.2m × 1.2m with n-TiO<sub>2</sub> additions of (Latitude: 23° 33' 15" S; Longitude: 46° 44' 1" W) in the northwest direction, to maximize exposure to sunlight,

as shown in Fig. 1. A slope of 33° used concerning to the ground, to obtain, (i) a higher solar radiation index; and The mortars were applied by a mason, with a maximum thickness of 1 cm and with the absolute minimum roughness to obtain a high reflectance. The substrate was finished with cement paste to achieve regularisation, the homogenization of water absorption, enhanced adhesion, and to prevent an increase in the consumption of the mortars. The reflectance under exposure to solar radiation measured for 36 months at monthly intervals. A measurement was then carried out after washing the mortars, following 41 months of exposure, to verify the restoration of the photocatalytic activity. The color measured at the beginning of the exposure time period and after 41 months of exposure, for a comparison of the initial and final color conditions. Moreover, unexposed specimens are used as references for the initial color.

### 2 a) Materials

All the mortar compositions were formulated agent based on sodium lauryl sulfate molecules; and water-retaining agents based on cellulosic ether molecules. The n-TiO<sub>2</sub> used in this study was 100% anatase (ACTiVTM PC105 Ultrafine), recommended by the manufacturer for applications in the photocatalysis processes. Twenty specimens produced, fifteen exposed to the urban atmosphere, and five used as references of the initial color. The samples were classified into five types (A, B, C, D, and E) and divided into four groups (1, 2, 3, and 4).

The mortars classified as A and B represent compositions formulated without n-TiO<sub>2</sub> and as a benchmark. Type-B mortars are painted, whereas type-A mortars were unpainted. The type-C, type-D, and type-E mortars were unpainted, and they represent the compositions formulated with the direct addition of the terminology and exposure conditions of the specimens. using white Portland cement (WHITE CEM I 52.5R EN 197-1); dolomites #20, #40, and #80; an air-entraining different n-TiO<sub>2</sub> contents to the mixture. Table 1 presents (ii) to prevent the stagnation of rainwater on the specimen surfaces, thus limiting the proliferation of microorganisms.

### 3 Methods a) Measuring reflectance indices

The reflectance values were determined in accordance with the methods given in the ASTM and ASHRAE standards [28,29]. All measurements were carried out from 11h00 to 13h00 because of the highest surfaces. The measurements were carried using two pyranometers, with measuring ranges of 305-2800 nm and maximum measuring ranges of up to 2000 W/m<sup>2</sup>, with an output signal of 0-50 mV and sensitivity of 10-35?V/W/m<sup>2</sup>. A data acquisition system was employed using a datalogger with a 6. 5

### 4 Raw Material Characteristics

Table 2 shows the characteristics of the raw materials, in accordance with a study by Dantas et al. [27]. For determination of the specific surface area (SSA), the Brunauer-Emmett-Teller(BET) method was employed, and the real density analysis was determined using the He pycnometer method. The particle size distribution of finer particles was determined using laser granulometry, and the dolomite particle size distribution was determined using a dynamic image analyzer.

The mineralogical compositions of the white Portland cement (WPC) and n-TiO<sub>2</sub> were determined by X-ray diffraction using the Rietveld analysis method, and the chemical composition of the cement determined by the Brazilian Association of Technical Standards (ABNT) and ASTM standards.

ii.

### 5 Mortar specimens composition

Each composition was prepared with a different n-TiO<sub>2</sub> (1%, 5%, and 10%) and water contents to ensure of the mason during the mixing. This procedure was adopted to conduct an in-situ experiment. Table 3 shows the consumption of each raw material.

### 6 White Portland Cement

Water and Loh [12]. Fig. 3 presents the measurement procedure.

the same workability for all, as defined by the experience incidence of global solar radiation on the specimens

### 7 b) Measurement of color

The evaluation of the color differences and yellowing index (YE) was carried out by the ASTM standard [30], using a Spectro-Guide Sphere d/8° spin spectrophotometer with geometric dimensions of 45 circ./0, d/8. A measurement area within the range of 400-700nm, the spectral resolution of 20 nm, photometric area of 0-100% (0.01), and standard observer D65 with an aperture angle of 10° were employed. The measuring procedure was carried out as previously described by Dantas, Vittorino, and Loh [12].

### 8 c) Optical microscopy analyses

IV.

## 9 Results and Discussion

Observation of the samples over the exposure period revealed a direct relationship between the solar and luminous reflectance, rainfall incidence, and roughness of the samples. An increase in the roughness of the mortars over the exposure time period was observed, which allowed for an increase in the accumulation of dirt on the specimens. In combination with the low rainfall during the first year of exposure, this resulted in a higher impregnation of the samples by dirt. Surface samples were obtained from the specimens and stored in plastic bags. No preparation process was carried out on the samples before, to ensure the maintenance of the as-exposed state. The surface textures of the mortars and the surface n-TiO<sub>2</sub> dispersions were observed using an Eclipse electronic microscope with a 40-fold increase, a fibre optic illuminator, and a digital camera with a resolution of 3.2 megapixels.

Visual inspection using an optical microscope revealed an increase in the roughness of the specimens surfaces. The images revealed that the type-B specimens exhibited a lower roughness than those of the other specimens in the early stages of the exposure time period. Also, a lower rugosity can prevent impregnation and to ease the removal of dirt by rainfall, resulting in an increased reflectance under exposure to solar and luminous radiation. However, this is not observed after 24 months of exposure, when the acrylic film exhibited degradation, allowing for increased accumulation of dirt on the surfaces of type-B specimens. Fig. 4 presents the surfaces of the mortars. The mortars exhibited similar behaviors with respect to solar radiation reflectance. Therefore, the results for each mortar evaluated can be presented concerning to the mean reflectance, as suggested by Dantas, Vittorino, and Loh [12] and Dantas; Vittorino [31]. After 12 months, type-E mortars exhibited a decrease in the reflectance under exposure to solar radiation when compared with the other mortars. This exposure. However, with longer exposure time, an important difference in the behavior of the mortars was the reflectance results of the other mortars groups, which could be considered to have equal values. For type-A mortar, a decrease in the reflectance was expected as a result of the natural aging process, which results from the accumulation of dirt. For types C, D, and E, their initial reflectance values were expected to remain stable for a longer time period. Also, the small differences observed between their reflectance values were due to the different n-TiO<sub>2</sub> contents. However, this behavior was not noticed after one year of exposure because of the lack of rainfall and high impregnation of the specimens surfaces by dirt. difference remained significant until the 16 th month of observed. The increase in reflectance from September (2015) to October (2015) was directly related to the high rainfall that occurred during this period (Fig. ??) and the increase in solar radiation (Fig. ??) associated to the beginning of the spring season. This two factors sand the increase in the photocatalytic activity during this period.

In the third year (2017), a significant decrease was observed in the values of reflectance under exposure to solar radiation in all the specimens. Over all the mortars exhibited a higher impregnation by dirt, which limited the photocatalytic activity. After that, the samples were cleaned using a washing machine, to reproduce the process commonly employed for cleaning building facades. Fig. ?? presents some examples before and after the washing. of exposure, a reflectance measurement was carried out. The main objective was to verify the restoration of the photocatalytic activity and the initial color. The final measurement, after the washing, revealed that the reflectance of type-B specimens under exposure to solar radiation are not restored. This loss of reflectance under exposure to solar radiation can be attributed to the degradation of the paint film, which resulted in the exposure of the mortar to a higher impregnation by dirt. Nevertheless, after washing, all the other mortars exhibited a restoration concerning their reflectance under exposure to solar radiation.

The addition of different n-TiO<sub>2</sub> contents to the mortars did not result in statistical differences between the characteristics of reflectance under exposure to solar radiation after washing. These results reveal that the effectiveness of the photocatalytic process of the mortars is not dependent on the added n-TiO<sub>2</sub> content.

## 10 b) Color change results

For evaluation of the white color, the CIE L\*a\*b\* components ( $\hat{L}^*/\hat{a}^*/\hat{b}^*$ ) to be individually considered for a better perception of the changes in the shades of the mortars. The components were calculated using simple arithmetic differences, and Fig. ?? presents the initial values and the differences between the colors at the beginning of exposure and after 41 months of exposure, following the washing of the specimens. contributed to the cleaning of the specimens surface From October (2015) to January (2016), the seasonal changes caused reflectance changes on the mortars surface. At the beginning of the summer season, there was an increase in the incidence of solar radiation and a decrease in rainfall. Because of this, different effects occurred on the mortars surfaces, that can be attributed to the variation of precipitation, the surfaces roughness, and their levels of dirt impregnation.

specimens. From February (2016) to February (2017), the mortars exhibited a continuous and significant decrease in reflectance. This behavior can be attributed to the low rainfall over these two years, which resulted in the impregnation of the specimens surfaces by dirt. the three years of exposure, apart from type-B samples, After washing (4 st month) and a short period of After 41 months of exposure and washing, is not observed significant differences between the luminance ( $\hat{L}^*$ ) values of type-B and type-C mortars. Type-A, type-D and type-E mortars exhibited more noticeable differences in color concerning to luminance ( $\hat{L}^*$ ). This behavior is expected for type-A mortars, which were not subject to pre-treatment (e.g., painting or water repellent), thus allowing for a higher deposition of dirt on the surface. For the type-D and type-E mortars, the photocatalytic activity was expected to be more effective because of the higher levels of n-TiO<sub>2</sub> contents used in the mixtures. However, no differences observed between the mortars concerning luminance ( $\hat{L}^*$ ), which indicates that an

increase in the added n-TiO<sub>2</sub> content does not influence the photocatalytic activity. Besides, the incidence of solar radiation and the amount of rainfall on the specimens has an impact on the photocatalytic activity. As previously highlighted, the ineffectiveness of the photocatalytic activity can connect to: (i) the increased accumulation of dirt on the specimens surfaces; (ii) increases in the surface roughness of the mortars, and (iii) the impact of n-TiO<sub>2</sub> non-dispersion that resulted in the formation of agglomerates, as shown in Fig. 10.

From the evaluation of the  $\hat{I}^*a$  component (green and red), no noticeable color differences were observed between the all mortars. These results indicated that with respect to this chromatic component, there were no significant differences between type-B specimens and the other mortars. The  $\hat{I}^*b$  component (blue and yellow) exhibited the most significant color differences. Is observed marked differences in type-B specimens, which was in good agreement with the measurements of the reflectance under exposure to solar radiation, as a result of the degradation of the acrylic resin in the paint composition.

In general, type-A mortars exhibited the least significant difference concerning to chrominance. This behavior is associated with the high deterioration of specimen A1, which led to the displacement of the mortar, thus altering the general data. a) Type-A mortars exhibited more significant color perception differences concerning to luminance ( $\hat{I}^*L$ ), and lower chrominance ( $\hat{I}^*a$  and  $\hat{I}^*b$ ). b) Type-B specimens exhibited less significant color perception differences concerning to luminance ( $\hat{I}^*L$ ) and more significant color perception differences concerning to the chrominance component  $\hat{I}^*b$ . Moreover, no observes significant color perception differences concerning to the chrominance component  $\hat{I}^*a$ . c) Type-C mortars exhibited less significant color perception differences than type-B specimens concerning to luminance ( $\hat{I}^*L$ ). Moreover, observed a less significant color difference in the chrominance component  $\hat{I}^*b$  with those of type-D and type-E mortars. No observes significant color differences in the chrominance component  $\hat{I}^*a$ . d) Type-D and type-E mortars exhibited more significant color perception differences concerning to the luminance ( $\hat{I}^*L$ ) and the chrominance component  $\hat{I}^*b$ . However, no observes significant color difference in the chrominance component  $\hat{I}^*a$ .

The yellowing index (YE) determined by the spectrophotometer (see Fig. 11) was higher for type-B specimens than it was for the other. The yellowing of the specimens was also observable using the naked eye when compared with other white-color surfaces. This change was due to the degradation of the acrylic film of the paint over the long-term exposure. From the evaluation of the luminance ( $\hat{I}^*L$ ), observes a significant color difference between type-B and type-A (unpainted and without n-TiO<sub>2</sub>), type-D, and type-E mortars (higher n-TiO<sub>2</sub> content). When compared with type-C mortar (low n-TiO<sub>2</sub> content), no observes marked color differences. Moreover, concerning to the chrominance components ( $\hat{I}^*a$  and  $\hat{I}^*b$ ), color differences were observed in all mortars.

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Among the mortars with the added n-TiO<sub>2</sub> contents, type-C mortar exhibited the least significant color difference; where as type-D and type-E mortars exhibited the same degree of color difference, which was more significant than that of type-C mortar.

Thus, concerning to the difference of color (measured according to CIE L\*a\*b\* scale), differences in the chromatic components of the mortars were observed upon evaluation after 41 months of exposure, following the washing, as shown in Fig. ???. It is reasonable to use  $\hat{I}^*E$  as a measure of the difference between the visual appearances of two given colors. Although the results indicated by  $\hat{I}^*E$  can be used to determine color differentiation, this should only be considered as a general guide, as it is possible to obtain a  $\hat{I}^*E$  value of less than 1.0 for two colors that appear different.

The definition of  $\hat{I}^*E$  differs slightly depending on the formula used, which indicates that it may not always be a reliable measure. Hence, observations made by the human eye may be required to verify the final answer, and more significantly, to provide a delimitation of the acceptable minimum and maximum limits for a specific application.

Considering that human eyes are more sensitive to luminance than chrominance, it may appear as though a surface has lost luminance ( $\hat{I}^*L$ ), when it has instead lost chrominance ( $\hat{I}^*a$  and  $\hat{I}^*b$ ), which ranges from green to red or blue to yellow colors, resulting from the presence of fungi or soot. After washing all the specimens exhibited white color surfaces, in the observation by the naked eye. However, in comparison with the colors in the beginning, different shades were observed for the specimens. Considering that the perception of color change is intrinsically subjective and dependent on the personal judgment of each observer, the perception of the white color is exclusively dependent on the type of lighting in which the surfaces are evaluated, in addition to the intensity of the light. The specimens exposed into an urban environment, which implies that there were variations in the visual perception of the observer concerning the time of day, degree of occurrence, and amount of rainfall during the surface evaluation. However, the spectrophotometer indicates the same color, independent of the weather conditions. Fig. 12 presents the differences in the color perceptions of the mortars at the beginning (t = 1 st month) and end (t = 41 st month) of the exposure time period. This differentiation is associated with two factors, as follows. a) The chromatic components ( $\hat{I}^*a$  and  $\hat{I}^*b$ ), which contributed significantly to the results obtained using the spectrophotometer, as the loss of the initial white color.

V.

## 12 Conclusions

The results obtained in this study therefore revealed the following. The use of specimens with larger sizes ( $1.2\text{m} \times 1.2\text{m}$ ) facilitated the analysis of the photocatalytic effect possible to observe the influences that are generally unobservable when small specimens are employed; such as the influence of the mason during application, the in-situ mixing process, the pollution in the accumulation of dirt, and the heterogeneity of the specimens, which typically occurs during the application of mortars. a) After three years, the mortars with higher n-TiO<sub>2</sub> contents exhibited a reflectance statistically effectiveness of the photocatalytic mortars is not dependent on the added n-TiO<sub>2</sub> content. b) Concerning to the color differences (measured according to the CIE L\*a\*b\* scale), there was a significant difference between the luminance ( $\hat{I}^*L$ ) of type-B specimens (painted and without n-TiO<sub>2</sub>) and those of type-A (unpainted and without n-TiO<sub>2</sub>), type-D, and type-E (higher n-TiO<sub>2</sub> content) mortars.

Concerning to type-C mortars (low n-TiO<sub>2</sub> content), no observes significant color differences. However, observes increase color differences in all specimens about the chrominance components ( $\hat{I}^*a$  and  $\hat{I}^*b$ ). c) The rugosity of the surfaces and the rainfall indices influenced the self-cleaning effect throughout the study. d) A vital thing observed is that the evaluations carried out within a short period of exposure to an urban environment did not reveal the effectiveness of the added n-TiO<sub>2</sub>. So, higher exposure time to be necessary to determine the differences concerning the maintenance of the initial conditions of the mortars with added n-TiO<sub>2</sub> contents, when compared with the painted mortars.

spectrophotometer, this phenomenon was not detected using the equipment.  
with n-TiO<sub>2</sub>, as well as the color differences. It was Year 2019



Figure 1: Fig. 1 :



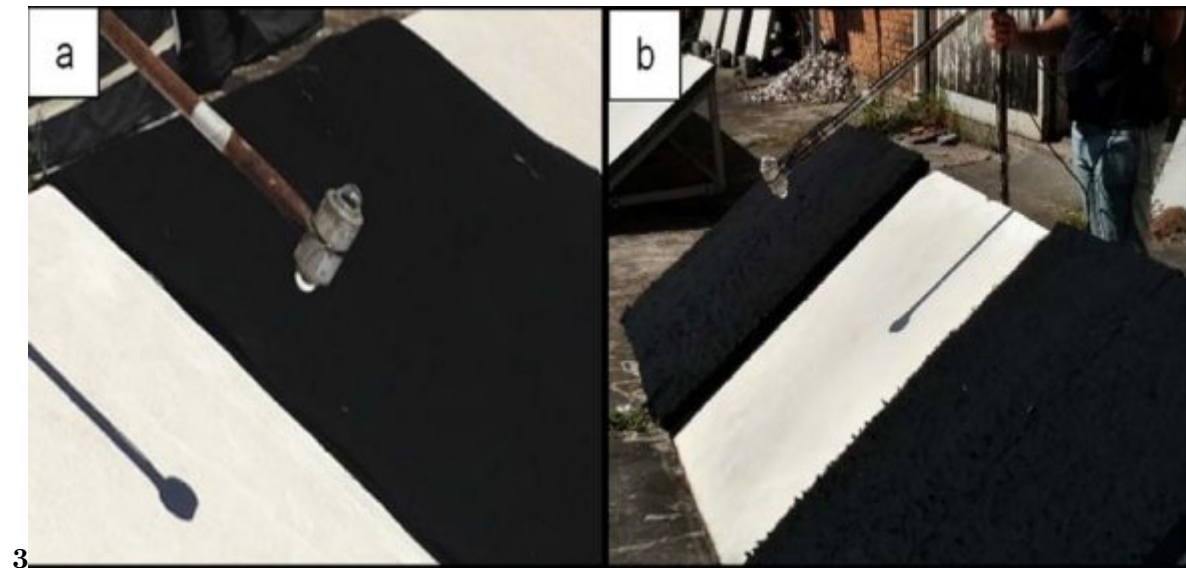


Figure 2: Fig. 3 :

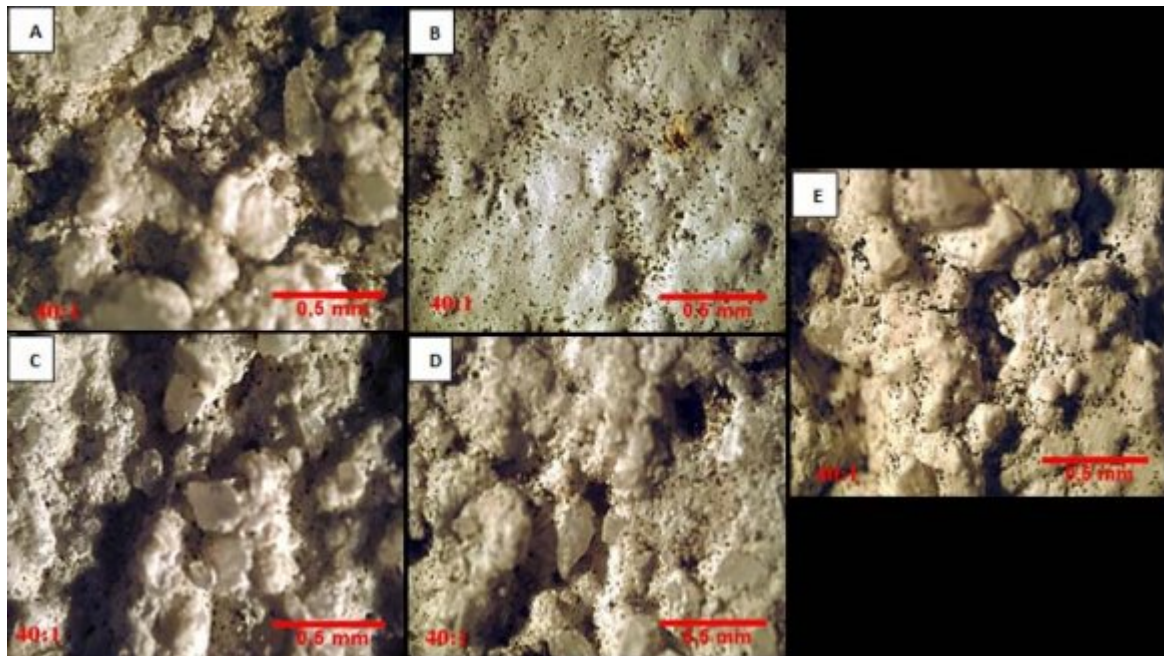


Figure 3: C



4

Figure 4: Fig. 4 :



567

Figure 5: Fig. 5 :Fig. 6 :Fig. 7 :



Figure 6:



89

Figure 7: Fig. 8 :Fig. 9 :



Figure 8: C

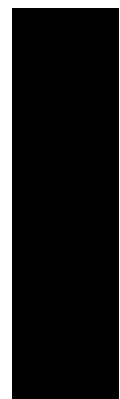


Figure 9:



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11

Figure 10: Fig. 11 :

Figure 11: C



12

Figure 12: Fig. 12 :

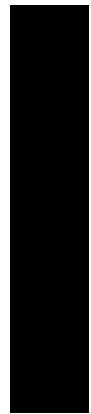


Figure 13: C



Figure 14:

1

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Groups	Mortars A (unpainted) 0%TiO <sub>2</sub>	Mortars B (painted) 0%TiO <sub>2</sub>	Mortars C (unpainted) 1%TiO <sub>2</sub>	Mortars D (unpainted) 5%TiO <sub>2</sub>	Mortars E (unpainted) 10%TiO <sub>2</sub>	Exposure
1	A1	B1	C1	D1	E1	
2	A2	B2	C2	D2	E2	Exposed
3	A3	B3	C3	D3	E3	
4	A4	B4	C4	D4	E4	Unexposed

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[Note: CPhotocatalytic Performance of White Cement Mortars Exposed In Urban Atmosphere]

Figure 15: Table 1 :

2

Materials	Diameter (?m)			Specific surface area (m <sup>2</sup> /g)	Average Density (cm <sup>3</sup> )
	d 10	d 50	d 90		
White Portland cement	2.6	17.7	19.5	0.86	3.05
Dolomite #20	975.1	1242.1	1620.5	0.16	2.90
Dolomite #40	24.3	230.0	739.6	0.56	2.94
Dolomite #80	4.5	38.3	133.9	0.80	2.81
n-TiO <sub>2</sub>	0.66	1.50	4.59	79.8	3.62

Figure 16: Table 2 :

3

III.

Figure 17: Table 3 :

i.

Materials	Mortars A (un- painted) 0%TiO 2	Mortars B (painted) 0%TiO 2	Mortars 1%TiO 2	C (unpainted)	Mortars D (un- painted) 5%TiO 2	Mortars E (un- painted) 10%TiO 2
	117.6	117.6	116.1		106.9	99.2
Dolomite # 20	68.7 386.6	68.7 386.6	67.9 5.4	381.8 105.0	1.5 0.2	322.1 62.5 58.0
Dolomite # 40	106.4 0.2	1.5 319.0	106.4 1.5	0.2	322.1 1.4	0.1 379.2
Dolomite # 80	—	319.0 —				355.9 46.3 25.0
Water retained						
Air- entrainment						
n-TiO 2						

conversion rate (maximum) of 10 measurements per second, with an RS232

-digit display and

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Figure 18:

## .1 Acknowledgements

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## 12 CONCLUSIONS

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