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Jian Lu
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Introduction

The Third International Conference on Smart Materials and Nanotechnology was successfully held 5–8 December in Shenzhen. This unique conference offered many opportunities to communicate with colleagues from a variety of disciplines in universities, companies, factories, and governments from all over the world. As a premier event, this conference promised great excitement, inspiration, and benefits. The conference is the first in what we hope will be a series that encompasses and bridges the rapidly evolving smart materials and the cutting edge nanotechnology for varied applications.

In the last decade, a wide range of novel smart materials have been produced for aerospace, transportation, telecommunications, and domestic applications. Meanwhile, nanotechnology is rapidly developing, permitting control of matter at the level of atoms and molecules that would form the building blocks of smart materials. Thus the combination of these two fields provides many advantages, realizes novel designs that could not be achieved in traditional engineering, and offers greater opportunities as well as challenges.

The conference deals with the integration of smart materials and nanotechnology for applications ranging from bioengineering to photonics, with emphasis on the application in aerospace engineering. It also addresses and predicts novel developments in this field. Discussed were various topics including shape-memory alloys and polymers; electro-active polymers; (EAPs); piezo-materials; electro- and magneto-restrictive materials and fluids; fiber optic sensors; MEMS; sensors and actuators; thermo-electric materials; electro-chromic, photo-chromic, fluorescent, and phosphorescent materials; nanocomposites, and others.

We received about 450 abstracts in response to the call for submissions. Of these we invited authors of 260 abstracts to submit full papers. Eight plenary speakers and 32 keynote speakers were selected to inform and inspire the attendees. A total of 160 papers were presented in 32 oral sessions and 100 papers were presented in poster session.

We would like to take this opportunity to thank the organizing committee, the cooperating organizations, the international scientific committee and every attendee whose support, dedication, and cooperation make this event more exciting, inspiring, and fruitful. This SPIE volume would not have been possible without the support of many colleagues. First and foremost, we wish to express our appreciation for SPIE staff for giving us the opportunity to organize the proceedings with SPIE. Next we thank the reviewers who spent hours reviewing papers in the editorial process.

We hope all the participants benefited from this conference and it should be very interesting to see how the smart materials and nanotechnology field will be further developed at the Fourth International Conference on Smart Materials and Nanotechnology in Engineering in 2013.

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Experimental evaluation of the durability of innovative cementitious coatings: photocatalytic activity and colour

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ABSTRACT

Today, in a world context characterized by high pollution levels and increasingly limited natural resources, even in the building sector, focusing on environmental issues, through energy saving and a more rational use of these resources, both during construction and management, is fundamental. An important contribution in this direction is given by the knowledge of the durability of products and building components, especially when innovative products are applied and no information are available on the reliability and service life. The research concerns the evaluation of the durability of cement-based photocatalytic coatings ("rasanti" in the Italian diction), containing different types of pigments, used for the external finishing of the buildings envelope and applied in low thicknesses on different supports. These products were prepared using photocatalytic cements by Italcementi (TX Active®) The investigated aspects are: the photocatalytic properties, conferring self-cleaning attitude and reduced maintenance to the treated surfaces, and the colorimetric ones, meaning the conservation of colour and giving aesthetic quality to the building envelope. The paper presents some results carried out on TX Active® cement-based coatings, performed according to the ISO 15686 methodology, aimed at defining the Reference Service Life, through accelerated ageing tests in climatic chamber and the corresponding monitoring of photocatalytic and colorimetric properties. The photocatalytic tests were carried out according to the UNI 11247-2010, in terms of NOx abatement capability, and the colour measurements were taken on the CIELAB colour space.

Keywords: Sustainability, durability, photocatalysis, cementitious coatings, color.

1. INTRODUCTION

Recent studies and several applications confirm that photocatalytic prducts can provide a contribution to the solution of environmental issues, in a context of sustainable development.

Innovative technologies based on photo-active nanomaterials ensure a considerable reduction of harmful substances in the various areas of application: reduction of air pollutants, water and air purification[1, 2, 3, 4].

These materials, nanometer and/or micrometer-sized semiconductors, available on a large scale and at low cost, base their efficiency on the absorption of UV light energy, resulting in oxidation of harmful substances.

Within the solid semiconductors, the most efficient for applications in the construction industry is titanium dioxide (TiO_2) due to its wide availability on the market, its high photo-activity, photo-stability and low cost.

Surface coatings' experimental research led to the definition of products with distinct capability of air pollutants, organic and inorganic reduction and self-cleaning properties.

The application of these products, recently introduced in the market, requires special attention for issues related to durability, particularly according to the Regulation No 305/2011 of the European Parliament, laying down harmonised conditions for the marketing of construction products and repealing Council Directive 89/106/EEC[5]. The Regulation increases the sustainability aspects of the basic requirements and introduces a new requirement, the seventh, called "Sustainable use of natural resources" which requires, among other aspects, the durability of constructions.

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The knowledge of the durability of building products and components, especially for innovative products, for which there is no historical information on the reliability and service life, becomes, therefore, essential.

2. RESEARCH METHODOLOGY AND TESTED MATERIALS

The methodological approach, descibed by the ISO 15686 "Service Life Planning" and used in this study, provides a comparison of data derived by accelerated aging tests inside climatic chamber and tests of natural aging, in order to derive useful correlations to determine the durability of the materials tested.

Cement-based finishing plasters, *rasanti* in the Italian diction, with photo-catalytic properties. Tested plasters used were added with three different inorganic pigments - black, yellow and salmon - (Fig. 1), in two formulations, different only in the presence of the photocatalytic principle, i.e. the TX Active® cement dispersed in the matrix.

Figure 1. The three different color samples

The aim of the research, therefore, was to evaluate the behaviour in time of photocatalytic activity, through the standardized procedure described by the UNI 11247, in the Italcementi laboratories of Brindisi, and colorimetric characteristics through colorimetric coordinates measurements, in accordance with the procedures of the UNI 8941.

Premixed plasters were applied on a brick support whose thickness was equal to 1 cm and dimensions were 23 x 30 cm, after the drafting of a 15 mm thickness plaster, natural hyadraulic lime based. The thickness applied of decorative plaster, in accordance with the data sheets of products, was equal to 2-3 mm. According to the minimum dimensions required by the UNI 11247, from each 23 x 30 cm sample were obtained six 8 x 8 cm test units (Fig. 2), through dry cutting of the sample.

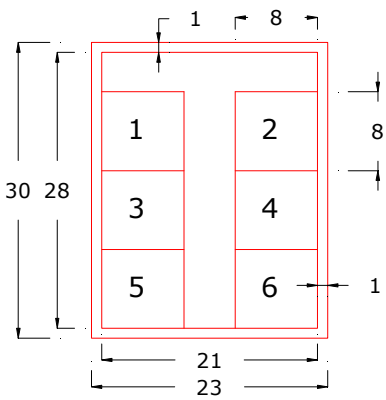


Figure 2. The schematic drawing of the test units taken on the sample

The samples were coated with a cementitious waterproofing adhesive, 1 cm width all along the edge of the test surface, on the sides throughout the thickness of the sample and on the back over the entire surface of the brick. Overall, 36 test samples were made, 24 of which were set in the climatic chamber and 12 set outdoors on the terrace of the Faculty of Engineering, exposed to the South orientation, with an inclination of 65° from the horizontal (Fig. 3).

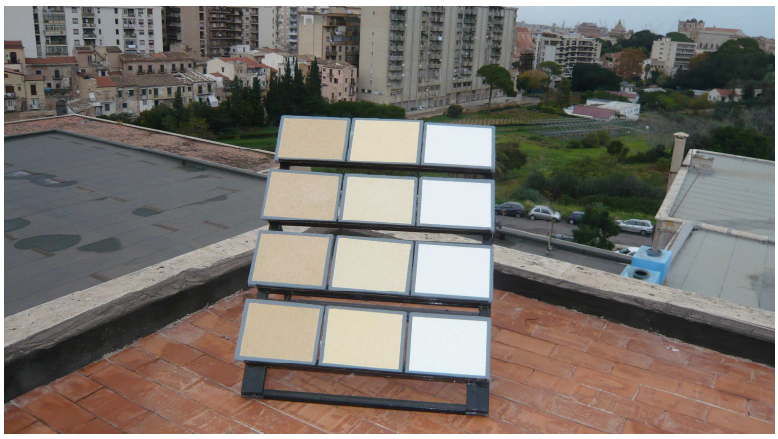


Figure 3. The samples exposed outdoors on the terrace of building 8 of the Faculty of Engineering

3. ACCELERATED AGING OF SAMPLES

The aging cycle was developed considering the weather and climate context of Palermo[6], characterized by very hot summers and mild winters, as well as the studies carried out by the Italian Durability Group, for over 15 years[7, 8, 9, 10], in order to obtain a close representation of the alternation of the seasons (Table 1).

Table 1. The aging cycle

PHASE A	Actual cycle (Minutes)	Temperature (C°)	Relative Humidity (%)	Theoretic cycle (Minutes)	Duration (%)
Rain (autumn season)	75	20	95	75	30
Transition	8				
Cold (winter season)	32	2	50	40	10
Transition	8				
Hot-humid (spring season)	107	35	87	115	40
Transition	6				
Hot-dry (summer season)	64	70	56	70	20
Total	**300**			**300**	**100**
PHASE B					
Hot-humid + UV radiation	**120**	35	87	**120**	

Each step of accelerate aging was set by the repetition for 48 times of the two phases, A and B, alternating 24 repetitions of the two stages for a total of 336 hours (14 days).

- phase A, 300 min long = 5 h x 24 repetitions = 120 h = 5 d
- phase B, 120 min long = 2 h x 24 repetitions = 48 h = 2 d
- phase A, 300 min long = 5 h x 24 repetitions = 120 h = 5 d
- phase B, 120 min long = 2 h x 24 repetitions = 48 h = 2 d

Total step di accelerated aging = 14 d

The research foresaw the evaluation of the chosen parameters after each step until the completion of the 6th step, being 2016 hours (84 days) of total duration of the accelerated aging period. For each step of the research, a couple of 8 x 8 cm test units were sampled from each 23 x 30 cm sample to evaluate the photocatalytic activity.

4. ANALYSIS AND INTERPRETATION OF EXPERIMENTAL RESULTS

At the end of each step of accelerated aging, the two parameters measured were: photocatalytic activity and color.

4.1 Photocatalytic activity

The evaluation of photocatalytic activity, through the procedure described by the UNI 11247, in continuous mode, was carryed on for the entire test units, both those added with the photocatalytic principle and those without. The results available show at time-zero, before setting into the climatic chamber, high photocatalytic activity detected by the dimensionless parameter A_c representing the percentage of nitrogen oxides reduction after 30 minutes by the UV lamp on.

$$A_c = 100x\frac{(C_B - C_L)}{C_B} x \frac{I_n}{I} x \frac{S_n}{S} \quad [\%]$$

Where:

C_B = measured concentration of NOx with UV lamp off	[ppb]
C_L = measured concentration of NOx with UV lamp on	[ppb]
I_n = measured Irradiance	[W mq^{-1}]
I = nominal Irradiance	[20 W mq^{-1}]
S_n = measured area of the sample	[cm^2]
S = nominal area of the sample	[64 cm^2]

The medium value of the percentage of NOx reduction for the white samples was equal to 40%, for the yellow ones was equal to 32% and for the salmon ones was equal to 18%.

The graph in Fig. 4 reports the values of the photocatalytic activity at time-zero and after six steps of artificial ageing test of the photocatalytic plaster. The results show a good photocatalytic activity up to the third step, equal to about 150 cycles of accelerated aging. Beyond this limit the performance of the products decreases significantly. The white samples, despite an eccellent initial value, were those who suffer a faster decrease of the NO_x reduction. It is evident that the salmon samples maintain a more uniform value in time, up to the third step of accelerated aging, where the best value is measured among the three different colored samples.

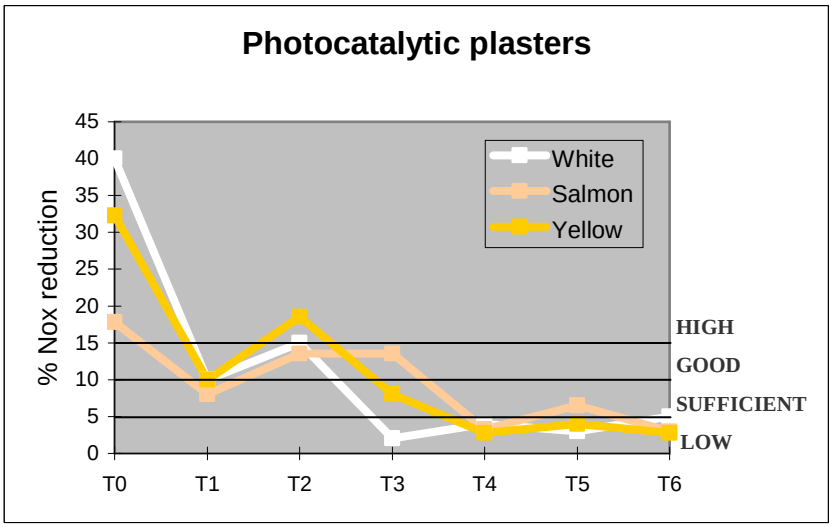


Figure 4. The evolution of photocatalytic activity in terms of nitrogen oxides reduction, after six steps of accelerated aging

The capability to develop photocatalytic activity by samples free from photocatalytic principle was negligible, therefore the capability to reduce nitrogen oxides depends exclusively on the presence of the photocatalytic principle.

4.2 Color

Colorimetric coordinates measured in the color space L*a*b* (well-known as CIELAB)[11], through the use of a spectrophotometer and a colorimeter, showed significant changes since the first step of aging, more evident for the non photocatalytic samples than the photocatalytic ones. Using the coordinate colorimetric and brightness measuments, the more significant colorimetric parameters were calculated: the color difference *ΔE*ab* and the chroma difference *ΔC*ab*, representative of the aging process of color on the surface of the samples. Particularly, the color difference *ΔE*ab* represents in the three-dimensional CIELAB color space, the measure of the distance between two points, expressed by a positive number, using the following formula:

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

The chroma difference *ΔC*ab* represents the measure of the difference of the intensity of a color and chroma is also known as saturation. The chroma difference can be represented in the two-dimensional chromaticity diagram, a* in the x-axis and b* in the y-axis. The measure of the radial distance between two points is expressed by a positive or negative number, depending on the point 1 if it has a radial distance higher or lower than the point 2, meaning the color of point 1 is more brilliant than the color of point 2. The following formula is used to measure the chroma difference:

$$\Delta C^*_{ab} = \sqrt{a_1^{*2} + b_1^{*2}} - \sqrt{a_2^{*2} + b_2^{*2}}$$

In the graph of Fig. 5 the results of the monitoring of color difference for both samples, photocatalytic and not, are reported, after six steps of aging, taking as reference the color at time-zero, equal for all samples of the same color, with or without the photocatalytic principle.

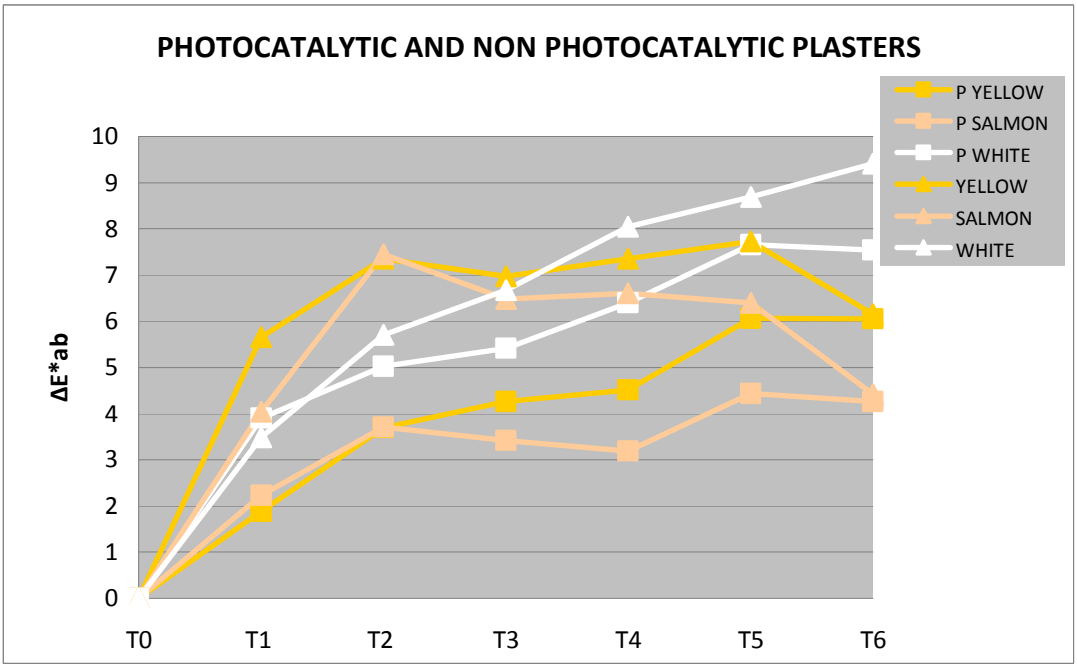


Figure 5. The evolution of the color difference of the photocatalytic (P) and not photocatalytic samples in terms of ΔE*ab

The photocatalytic plaster samples showed a tendency towards color variation that is about 2 points average lower than non-photocatalytic ones, demonstrating a greater capacity to keep the color over time.

The color difference had an almost linear trend up to 2nd step of aging, remaining fairly constant until the 6th step (up to 4.5 points for photocatalytic samples and 7.3 points for non photocatalytic ones), for both the two different types

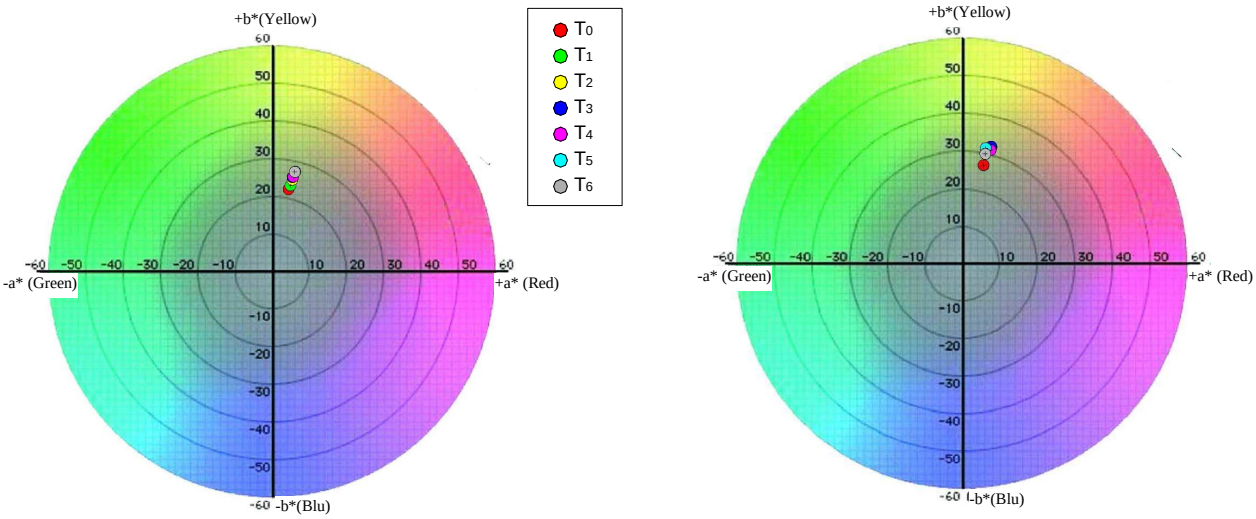
of samples.

The salmon-colored samples tended to better maintain the color over time, compared to yellow and white ones.

In general, the white photocatalytic plaster underwent, during the six steps, the greatest change in color, with ΔE*ab values always greater than those of the other colors. Values were lower for the white non photocatalytic plaster until the the third step and then passing through the other colors.

The chromaticity diagrams, a*-b*, showed a tendency to the b* increasing for both the photocatalytic yellow samples, in Fig 6, and non photocatalytic, in Fig 7, with progressive increase of the coordinate b* in the positive y-axis.

The tendency to the b* increasing (yellowing) is higher in samples characterized by the absence of the photocatalytic principle for which the increase of the coordinate b* reached the value of 32, after six steps of aging, while the photocatalytic ones showed the b* value equal to 28.



Figg. 6-7. Chromaticity diagram a*-b* for the yellow photocatalytic samples (left) and non photocatalytic ones (right)

Similar results were observed for the white and salmon samples.

For the white samples, the tendency to yellowing is greater in those without the photocatalytic principle, the increase of b* reached the value of 13, while the photocatalytic ones showed the b* value of 11.

For samples of salmon color, the increase of b* reached the value of 24 for non- photocatalytic ones and 23 for the others.

The diagrams correlating the chroma difference, ΔC*ab, and the lightness difference, ΔL*, are useful to estimate the evolution of color in terms of visual perception, as they provide qualitative information easy to understand.

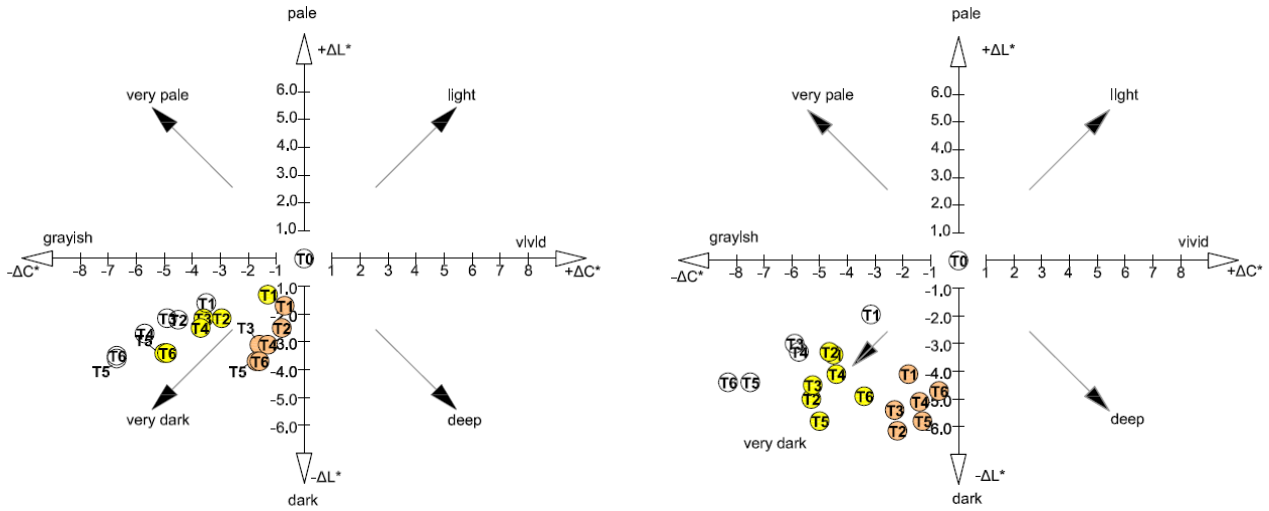
The chroma-lightness diagrams Figs. 8-9, relative to white samples, showed ΔC*ab and ΔL* values higher of around 1 point, in favor of non-photocatalytic samples.

The photocatalytic samples had a lower tendency to become greyish than non-photocatalytic ones.

For the yellow samples, compared to non-aged sample, at T_0, the chroma difference is almost the same for both types of samples, with values around -5 to -6, while a significant difference is related to the lightness difference: for photocatalytic samples was approximately -3, while for non-photocatalytic ones was about -6.

The photocatalytic samples showed, therefore, a tendency to become darker lower than non-photocatalytic ones.

The salmon-colored samples show very close final values for the chroma difference, around -1, while the photocatalytic samples showed lightness greater than 1 point, at the end of the six cycles of accelerated aging.



Figg. 8-9. ΔC*ab - ΔL* diagrams for per photocatalytic samples (left) e non (right)

4.2.1 Color monitoring of the naturally aged samples

The samples set outdoors underwent the weather conditions of Palermo, the data refer to a period of 12 months of outdoor exposure, since November 2010. Fig. 10 shows the monitoring of the color difference for both the tested samples.

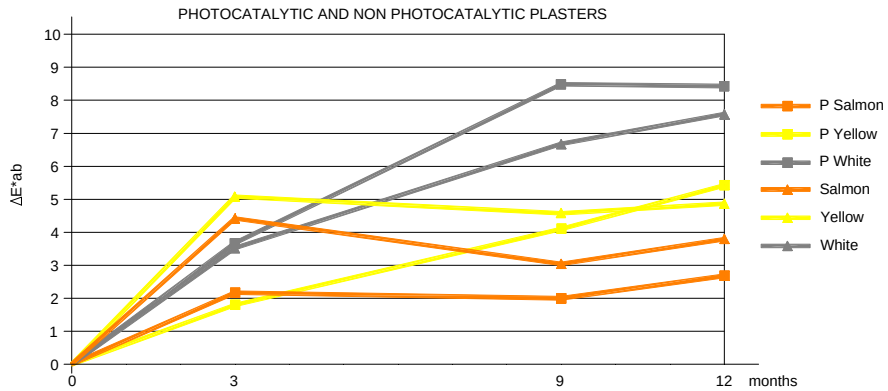


Figure 10. The evolution of the color difference of the naturally aged photocatalytic (P) and non photocatalytic samples

From these results, an initial increase of the color difference on exposure during the winter months (November-January) was experienced, the higher for the non photocatalytic colored plaster (salmon and yellow) and similar for both the white ones. In the following months, it was observed the maintenance of the values for photocatalytic and non photocatalytic yellow and salmon samples, while for the white samples, the color difference increased, reaching values close to 8 points, after 12 months of natural aging. The salmon-colored samples were the most efficient in maintaining of the color and the maximum color difference measured was equal to 2.73 points for photocatalytic plaster and 3.81 for non-photocatalytic one. The procedure of time rescaling, as codified in the ISO 15686 and UNI 11156, is the comparison of the laboratory accelerated aging data with the measured data on the same materials naturally aged, in the reference climatic context. The comparative analysis of the colorimetric data of natural and accelerated aging allows to determine a time-rescaling factor as the evolution of color is the same after 12 months as one step of accelerated aging, equal to 48 cycles for the salmon samples and the yellow ones. Similar evolution was registered for the other samples. The results show that after 12 months of natural aging color variations were different depending on the pigment and the presence of the photocatalytic principle. The results of photocatalytic activity of samples derived from the external monitoring are not yet available, so the time rescaling is related only to the color and not to the photocatalytic activity.

4. CONCLUSIONS

The photocatalytic activity of plaster samples is very high at time-zero, gradually reducing and maintaining significant values up to the 3rd step, which corresponds to 150 cycles of accelerated aging, beyond which there is a loss of efficiency. The white color stands out, despite of its initial highest value, it shows the faster decrease.

The salmon plaster remains quite uniform over time up to the 3rd step of aging when it reachs the highest value in comparison to the other colored plasters.

The photocatalytic plaster, at the same aging, undergoes color changes of about 2 points average lower than non-photocatalytic one of the same color, demonstrating a greater capability to maintain the color over time.

Also for maintaing the color, the salmon samples maintain higher efficiency, compared with the yellow and white ones.

The time rescaling procedure, related only to color attitude, shows that 12 months of natural aging produce different color variations depending on the pigment and the presence of the photocatalytic principle and on average, one step of accelerated aging corresponds to 12 months of natural aging.

The photocatalytic darker plasters (salmon and yellow) develop more constant photocatalytic activity in time[12] and keep the color better than the white one, more subject to phenomena of yellowing.

In general, for the same composition, the presence of the photocatalytic principle increases the durability of the color of the plaster. Durability is greater for darker colors.

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