

# **Nanotechnology and Advanced Materials II**

Edited by  
Guohui Yang

# **Nanotechnology and Advanced Materials II**

Selected, peer reviewed papers from the  
2013 2<sup>nd</sup> International Conference on  
Nanotechnology Technology and Advanced Materials  
(ICNTAM 2013),  
August 4-5, 2013, Los Angeles, CA, USA

*Edited by*

**Guohui Yang**



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# Preface

2013 2nd International Conference on Nanotechnology Technology and Advanced Materials (ICNTAM 2013) will be held on August 4-5, 2013, Los Angeles, CA, USA. ICNTAM 2013 serves as good platforms for academics, researchers, and engineers to meet and exchange innovative ideas and information on all aspects of nanotechnology and material technologies.

Nanotechnology is the study of manipulating matter on an atomic and molecular scale. Nanotechnology entails the application of fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, microfabrication, etc. There is much debate on the future implications of nanotechnology. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials and energy production. On the other hand, nanotechnology raises many of the same issues as any new technology, including concerns about the toxicity and environmental impact of nanomaterials, and their potential effects on global economics, as well as speculation about various doomsday scenarios. These concerns have led to a debate among advocacy groups and governments on whether special regulation of nanotechnology is warranted.

Materials science is an interdisciplinary field applying the properties of matter to various areas of science and engineering. This scientific field investigates the relationship between the structure of materials at atomic or molecular scales and their macroscopic properties. It incorporates elements of applied physics and chemistry. With significant media attention focused on nanoscience and nanotechnology in recent years, materials science has been propelled to the forefront at many universities. It is also an important part of forensic engineering and failure analysis. Materials science also deals with fundamental properties and characteristics of materials.

The selected, peer reviewed paper from ICNTAM 2013 focus on four topics: (1) Material Science and Engineering, (2) Nanotechnology Technology, (3) Manufacturing and Mechanical Engineering, and (4) Information Technologies and Computational Procedures in Engineering Researches and Design. We expect that the conference and its publications will be a trigger for further related research and technology improvements in this importance subject.

The Organizing Committee thanks the sponsors, government agencies and sponsors that contributed definitely to the conference success. We hope that ICNTAM 2013 will be successful and enjoyable to all participants. We look forward to seeing all of you next year at the ICNTAM.

Guohui Yang

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# Table of Contents

<b>Preface</b>	v
<b>Organizing Committee</b>	vi

## Chapter 1: Material Science and Chemical Engineering

<b>The Influence of Sulfurization Time and H<sub>2</sub>S Concentration on the Properties of Cu<sub>2</sub>ZnSnS<sub>4</sub> Thin Films</b>	
M. Xie, D.M. Zhuang, M. Zhao, B.J. Li and J. Song.....	3
<b>Research of Superplasticity Deformation Behavior about Coarse-Grain Ti-22Al-25Nb Alloy</b>	
Y.Z. Li, Z.K. Yao, W. Zhou, C. Qin, H.Z. Guo and X.B. Liang.....	9
<b>Friction Stir Processing: An Operational Method to Improve Ductility in Pure Copper</b>	
V. Rezazadeh, A. Sharbatzadeh, A. Hosseinzadeh, A. Safari and S. Salahi .....	14
<b>Microstructure Analysis for Emulsified Asphalt Cement Concrete</b>	
J. Fu, Z.M. Shi, D.R. Dai and J.B. Huang.....	20
<b>Use of Cement Hydration Stabilizer Admixture at Ready Mix Concrete to Avoid Material Waste</b>	
A.N. Haddad, B.G.F.R. Cortes and A.C.J. Evangelista.....	24
<b>Experimental and Numerical Study of Ballistic Impact Performance on UHMWPE Composites</b>	
Y.K. Wen, C. Xu, A.J. Chen and S. Wang .....	30
<b>Spectroscopic Characterization Technical High Resolution of Gold from a Memory Card RAM</b>	
M.A. Cortes, M.L.D. Patiño, A.R. Martínez, R.G. Tapia and R.M.M. Alemán.....	37
<b>Preparation of Castor Oil-Based Waterborne Polyurethane and its Application in Electrostatic Copy Paper Surface Enhancing</b>	
H.M. Fan, C. Zhang, Y.Q. Ma and J.A. Liu .....	42
<b>Carbon Fiber Reinforcing Frame Joint with Shear Failure of Core Area</b>	
J. Hu and Z.Y. Yang .....	48
<b>Synthesis and Characterization of Reactive Michler's Ketones</b>	
Q.H. Huang, X.Q. Dou, X.X. Bai, Z.Y. Hu and C.J. Cheng.....	54
<b>Simulating the Effect of Current Pulse on Plasticity of the Pure Aluminum 1A99</b>	
S.H. Peng, J.J. Yang and Y. Li.....	58
<b>Study of Gypsum Dehydration Time in CaCl<sub>2</sub> Solution</b>	
K. Dvořák.....	64
<b>Slag-Sulphate Binder Preparation</b>	
D. Gazdič .....	68
<b>Crystal Field Analysis of the Magnetization Curves of HoFe<sub>11</sub>Ti under High Pressure</b>	
G. Su.....	72

<b>Analysis of Two Surfaces under Viscoelastic Contact</b> M. Mongkolwongrojn, J. Panichakorn, S. Supawanich and S. Chutima.....	77
<b>Effect of Silver Content on Bulk Properties and Interfacial Morphology of Sn-xAg-Cu Solders</b> P. Li, X.L. Gu, X.G. Liu and H.F. Zhong.....	83
<b>The Structural Characteristics of CIS Thin Films Prepared by Electro-Deposited Method</b> K. Liu, J.S. Yang, R. Li, W. Peng and S. Pan.....	88
<b>Modeling of BOF Steelmaking Based on the Data-Driven Approach</b> J.N. Li, Y. Li, F. Liu, S.P. Bie, C.C. Tang and X.L. Zhang.....	92
<b>Service Life of Cementitious Photocatalytic Paints Newly Formulated</b> D. Enea, G. Alaimo, L. Bottalico and T. de Marco .....	98
<b>On the Influence to Social Life of the Artistic Features in the Reuse of Materials</b> Z.Y. Li, W.P. Hu, Y. Liu, J. Li and T.F. Wang .....	104

## Chapter 2: Nanotechnology

<b>Using the Superficial Resonant Peak and PCA for Determining the Gold Nanoparticle Diameter</b> J.C. Martínez-Espinosa, T. Cordova-Fraga, A. Reyes-Pablo and M. Vargas-Luna .....	111
<b>Pull-in Voltage Analysis of Carbon Nanotube Based Electrostatic Actuators by Using the ANSYS Software</b> P.A.G. Sankar and K. Udhayakumar .....	117
<b>Variation of Concrete Strength with the Insertion of Carbon Nanotubes</b> A.N. Haddad, J.F. de Moraes and A.C.J. Evangelista.....	124
<b>Nonlinear Optical Studies of SWCNT+Coproporphyrin III Hybrid Systems</b> I.M. Kislyakov, N.R. Arutyunyan, E.D. Obraztsova, I.S. Sheiko, S.A. Povarov, A.V. Venediktova and C.S. Yelleswarapu.....	132
<b>Localized Surface Plasmon Resonance of Single Silver Nano-Hemisphere</b> R. Li, K. Liu, S. Pan and J.H. Ding.....	137
<b>Laser Driven Paraffin Microsphere Transportation on a Single Carbon Nanocoil</b> Y.M. Sun, Y.L. Liu, H. Ma and L.J. Pan .....	141

## Chapter 3: Management, Analysis and Engineering Research

<b>Research on Emergency Management System Based on Cloud Computing</b> Y.X. Chen and C.B. Xie.....	147
<b>Measurement and Testing of the NSRRC Power Supply for Conduction EMI</b> C.Y. Liu and K.B. Liu.....	153
<b>The Field Current Research on Paratactic Structure Hybrid Excitation Synchronous Generators for Wind Power Generation</b> C.H. Zhao, J.C. Li, J.L. Sun and X. Hu .....	159

<b>Operating Mode Analysis on Paratactic Structure Hybrid Excitation Synchronous Generators for Wind Power Generation</b>	
C.H. Zhao, J.L. Sun, J.C. Li and X. Hu .....	166
<b>The Research and Application of Configuration Management Based on Equipment of PDM</b>	
Z. Cheng, C. Xu and K. Cao .....	172
<b>Analysis of Stress in Half-Space Using Jacobian of Transformation and Gauss Numerical Integration</b>	
R. Cajka.....	178
<b>Theoretical and Experimental Investigation of Machining of AISI H13 Steel</b>	
T. Márton and F.B. Zsolt.....	187
<b>Analysis of Machinery Manufacture and Production from the Metal Mechanics Perspective</b>	
Y. Xia.....	193
<b>Horizontal Friction Parameters in Soil – Structure Interaction Tasks</b>	
R. Cajka.....	197
<b>Chapter 4: Control, Automation and Detection Technologies</b>	
<b>Path Programming and Motion Controlling of AMR</b>	
J.H. Luo, Y. Zhang and X.H. Wang.....	209
<b>Research on Voltage Oriented Control Strategy of Grid-Connected Inverter of Wind Power Generation</b>	
Y. Yang, G.M. Lan, Z.Q. Sun, J. Guo and Z.Q. Zhang .....	212
<b>Intelligent Fault Diagnosis of Gear Box Based on BSS and SVM</b>	
W.J. Ma, R.X. Yu, J.Y. Wang and X.F. Wan .....	218
<b>A Novel Key Management Strategy for Heterogeneous Wireless Sensor Networks</b>	
Y.Q. Zhang.....	224
<b>Solving Secure Problems for Wireless Sensor Networks Using Clustering and OKS</b>	
Y.Q. Zhang.....	230
<b>The Select Device of Weight Coefficient in the Vehicle-Use Engine Performance Optimization Process</b>	
J.H. Luo, X.H. Wang and Y. Zhang.....	237
<b>Comparison and Application of Two Mathematical Models in Predicting and Determining the State of Deposition and Slagging of Coal Burning Boiler</b>	
X.Q. Wen .....	240
<b>Predicting the Characteristics of Biofouling Mass Based on RBF Network</b>	
X.Q. Wen .....	246
<b>Keyword Index</b> .....	251
<b>Author Index</b> .....	255



## Service Life of Cementitious Photocatalytic Paints Newly Formulated

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**Keywords:** Durability, Photocatalytic paint, Color, NOx

**Abstract.** The use of photocatalytic products for surface coating of buildings contributes to the sustainability of building interventions, due to the reduction of some atmospheric pollutants and self-cleaning attitude. The world market produces a wide range of coatings, applied in limited thickness, transparent and opaque, high initial performance, although data on their durability are still missing. The knowledge of the performance over time of such innovative products is necessary according to the new EU Regulation No. 305/2011, which introduced for construction works, the seventh requirement on their sustainability and particularly their durability. The study concerns the evaluation of the durability of white photocatalytic paint, TX Active® cement-based. The methodology is based on ISO 15686 and consists in monitoring the most significant selected parameters, during laboratory accelerated aging tests and natural environment exposure. Measured performance were the morphological appearance of the surface, the photocatalytic activity and the color. The results obtained demonstrate the efficiency in time and the maintenance of performance of the photocatalytic paint, above limits defined by standards and conservation of color.

### Introduction

In the past two decades, photocatalytic products (plasters, coatings, painting, paving, flooring, tiles) attracted a broad market segment because of their contribution to the mitigation of environmental issues. The use of photosensitive nano-materials, mixed with the basic formulations of building products, provides significant reduction of harmful substances: air pollutants, purification of water and air [1, 2, 3]. The principle of activation of these nanometric and/or micrometric semiconductors is based on the absorption of light and consequent oxidation of harmful substances. Titanium dioxide (TiO<sub>2</sub>) is the most efficient among the solid semiconductors and the most used in the construction industry for its wide availability, low cost, high photo-activity and self-cleaning properties [4]. The durability aspect, especially for innovative materials and products, is still less known, although of significant interest, because of the recent Regulation EU No. 305/2011, repealing the Directive 89/106/EEC [5]. This new regulation introduced the requirement of “the sustainable use of natural resources”, in the design and realization of constructions, and in particular of the durability. This paper presents a study on the durability of a photocatalytic paint, formulated at the laboratories of CTG Italcementi group, according to the method specified by ISO 15686.

### The research methodology, the parameters investigated and the materials used

The research is part of national and international studies on the evaluation of the durability of building products and components, according to the methodology of ISO 15686 and UNI 11156, based on the assessment of the service life of the component through correlations (time rescaling) between accelerated aging tests in laboratory and outdoor natural aging. The surface coating product tested is classified among “the paints” (UNI 8752:1985) and was applied in limited thickness, about 300 microns. It is a new formulation of photocatalytic paint, TX Active® cement-based with titanium dioxide, which ensures, for outdoor applications, that the product has remarkable self-cleaning attitude and reduction of harmful substances, particularly of nitrogen oxides. The photocatalytic activity measurements, in terms of NOx reduction, were performed

according to the UNI 11247. The paint, white in color, was applied on substrates in tile, thickness of 4 cm, whose dimensions were 20x20 cm, parts not subject of observations were waterproofed. For the test of outdoor natural aging, samples were exposed to the South with inclination of 65° to the horizontal. To evaluate the photocatalytic activity, from each tile, 4 samples, 8x8 cm dimensions, were obtained by dry cutting. The measurement of surface color was made, according to the UNI 8941, by means of spectrophotometer with numerical gloss control. The observations were made with the Standard Illuminant D<sub>65</sub>, with an inclination angle of 10°. The chosen color space was the CIELAB [6] based on the brightness, L\*, and the two chromaticity coordinates, a\* and b\*. Starting from the colorimetric coordinate values measured at time zero, it can be measured the difference of color,  $\Delta E^*_{ab}$ , and the difference of chroma,  $\Delta C^*_{ab}$ , over time. Each color measurement<sup>1</sup> was the average of five.

### The artificial aging

The aging cycle for the tests in climatic chamber was developed taking into account the weather and climate of Palermo [7], typical of the Mediterranean area, as well as the studies conducted by the Durability Group, active in Italy for over 15 years [8, 9], and is reported in table 1. In addition to the climatic chamber (Fig. 1 and 2), tests were also conducted in dry corrosion test cabinet to assess the influence on the paint on marine environment.

Table 1. Values of the parameters of the aging cycle

PHASE 1	Real cycle (Minutes)	T (C°)	RH (%)	Theoretical cycle (Minutes)	Percentage (%)
Rain (Autumn season)	75	20	95	75	30
Transition	8				
Cold (Winter season)	32	2	-	40	10
Transition	8				
Humid hot (Spring season)	107	35	87	115	40
Transition	6				
Dry hot (Summer season)	64	70	56	70	20
<b>Total</b>	<b>300</b>			<b>300</b>	<b>100</b>
<b>PHASE 2</b>					
UV light (Spring season)	<b>120</b>	35	87	120	

Each step of aging consists in the repetition of 48 phases 1 + 2, in alternation, for a total of 336 hours (14 days). This is artificial aging cycle A.

- Phase 1 (300 min): 5 h x 24 repetitions = 120 h = 5 d
- Phase 2 (120 min): 2 h x 24 repetitions = 48 h = 2 d
- Phase 1 (300 min): 5 h x 24 repetitions = 120 h = 5 d
- Phase 2 (120 min): 2 h x 24 repetitions = 48 h = 2 d

Totale duration of single step = 14 d

For each step and for half of the samples, two cycles of the Phase 1 were replaced with two cycles in dry corrosion test cabinet (Fig. 3), at T=35°C and RH=87%. This is artificial aging cycle A+B. The accelerated aging, produced inside climatic chamber was concluded with the 6th step, for a total of 2,016 hours (84 days). For each step of the research a couple of 8x8 cm samples was taken for the evaluation of photocatalytic activity. These artificial aging cycles were designed to evaluate the performance of the paint to outdoor weather conditions.

<sup>1</sup> The experimental work was conducted at the Laboratorio di Edilizia, UniNetLab, of the University of Palermo.

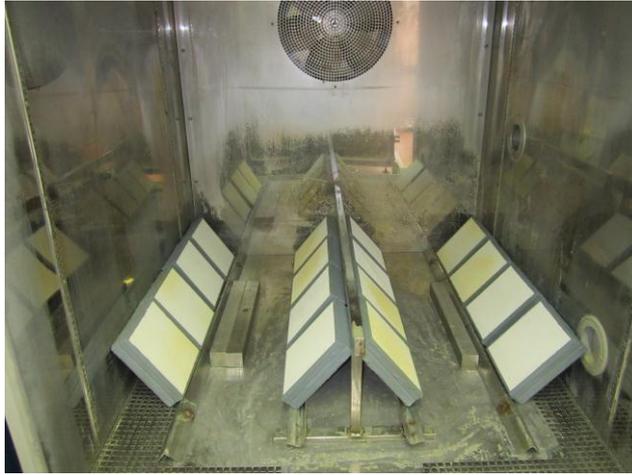


Fig. 1. The samples set in the climate chamber, for phase 1 of artificial aging. Some samples derive their yellowing to a treatment with ferric oxide

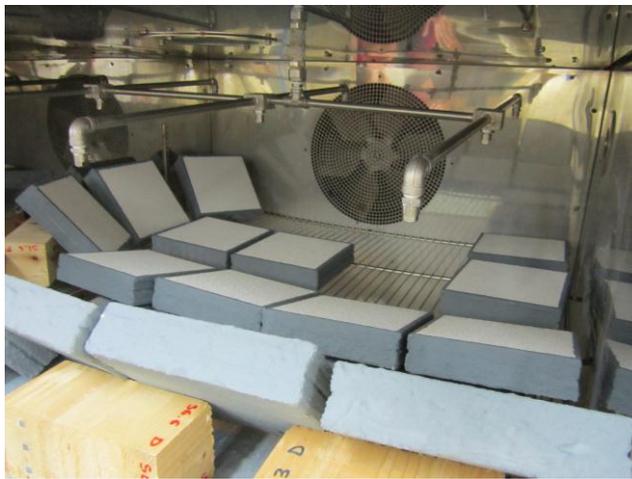


Fig. 2. The samples set in the climatic chamber for phase 2. The radial arrangement allows a measured intensity of the luminous flow constant, equal to  $5 \text{ Wm}^{-2}$



Fig. 3. The samples set in the dry corrosion test cabinet.

### Results and conclusions

The parameters measured, at the end of each step of artificial aging, were:

- photocatalytic activity;
- color;
- morphological appearance.

### Photocatalytic activity

The photocatalytic activity was evaluated according to the UNI 11247, in continuous mode. The results at time zero show high photocatalytic activity identified by the dimensionless parameter,  $A_c$ , which represents the percentage of nitrogen oxides abatement after 30 minutes from the UV lamp on.

$$A_c = 100 \frac{(C_B - C_L) I_n S_n}{C_B I S} \quad [\%] \quad (1)$$

where:

$C_B$ = concentration of $\text{NO}_x$ in dark conditions, at equilibrium	$[\mu\text{g m}^{-3}]$
$C_L$ = concentration of $\text{NO}_x$ in light conditions, at equilibrium	$[\mu\text{g m}^{-3}]$
$I$ = measured intensity of the luminous flow	$[\text{W m}^{-2}]$
$I_n$ = nominal intensity of the luminous flow	$[20 \text{ W m}^{-2}]$
$S$ = geometrical surface area of the sample	$[\text{cm}^2]$
$S_n$ = nominal surface area of the sample	$[64 \text{ cm}^2]$

The value of  $\text{NO}_x$  abatement at time zero is about 40%. In Figure 4 the results of monitoring the photocatalytic activity of the samples under artificial aging is reported, pointing out the different artificial aging of the samples.

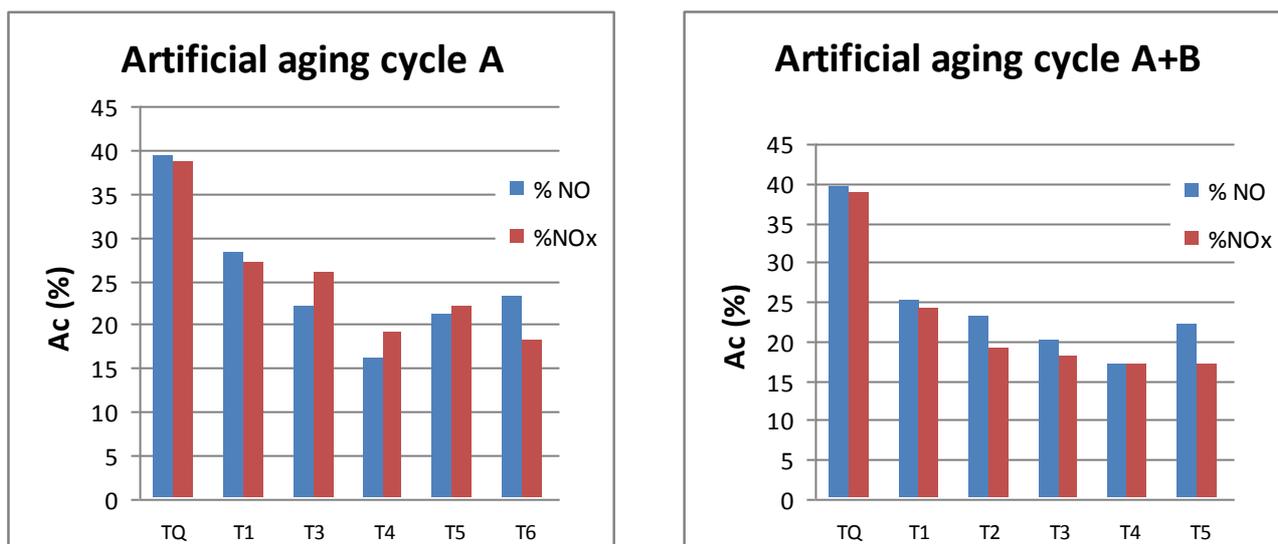


Fig. 4. The evolution of the photocatalytic activity (UNI 11247:2010) of the samples artificially aged

The results show significant photocatalytic activity up to the 6th step of aging, equal to about 300 cycles, with maximum reduction of 30%. Figure 5 shows the artificial aging with salt spray do not significantly influence the decrease in photoactivity.

### Color

Using the colorimetric coordinates, that showed marginal changes, the color difference,  $\Delta E^*_{ab}$ , and the chroma difference,  $\Delta C^*_{ab}$ , were calculated. The color difference,  $\Delta E^*_{ab}$ , represents the distance between two points in space  $L^* a^* b^*$ , according to the following formula:

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

Fig. 5 shows the results of monitoring the color difference of the photocatalytic samples, after 5 step of artificial aging.

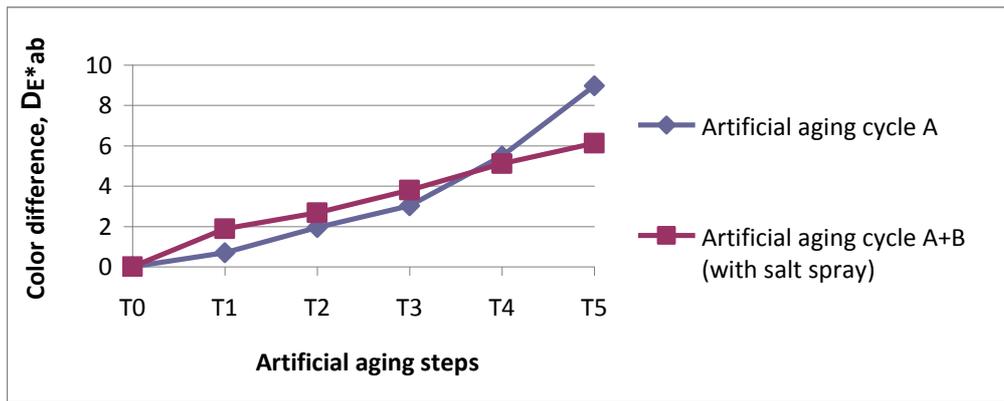


Fig. 5. The evolution of the color difference of samples artificially aged

The color difference shows a trend almost linear up to the 4th step of aging, with similar increases for the samples aged with the standard cycle (A) and the cycle with salt spray (A+B) and a measured color difference in favor of the standard cycle of approximately 1.5 points. After the 4th step, the trend is reversed and the color difference is higher for the samples under the standard cycle, compared to the others, with a difference of about 2.5 points.

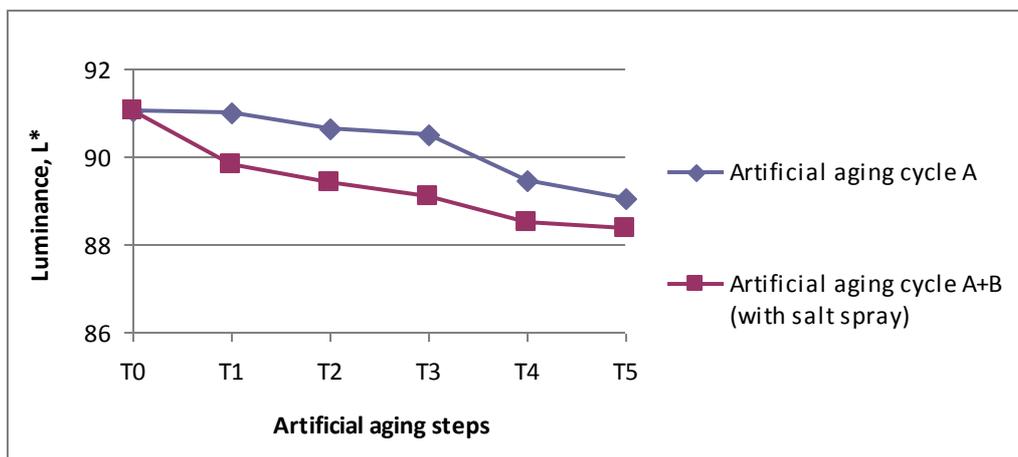


Fig. 6. The evolution of Luminance of samples artificially aged

Data show that the coordinate  $b^*$  increases progressively towards yellow, while the coordinate  $a^*$  is kept constant. Luminance,  $L^*$ , in Fig. 6 has low decrease and no significant difference is evident between the two different aging cycles. The natural aging of the samples in outdoor conditions refers to the weather conditions of Palermo and the exposure period was of 12 months, since November 2010. From these preliminary results, it was observed an initial increase of the color difference on exposure in early winter (November-January). In subsequent months, it was observed that color difference was maintained around 1 point. The procedure of the time rescaling, as codified by ISO 15686 and UNI 11156, was followed, representing the comparison of data derived by artificial aging, with the measured data in outdoor conditions. The evolution of the color of the samples after one year of natural aging is comparable with that of the samples artificially aged after 1 step (48 cycles), according to the two artificial aging tests, standard and salt spray. These evaluations may be more detailed after at least another year of natural exposure.

#### *Morphological aspect*

The monitoring with scanning electron microscope (Fig. 7) shows unperceivable differences in the surface morphology and chemical analysis shows after 6 step of aging, a very compact surface with diameter of micro-cavities between 3  $\mu\text{m}$  and 5  $\mu\text{m}$ . The surface chemical composition shows high amount of calcium (33.43%) and small amount of Titanium (0.46%) almost constant after aging.

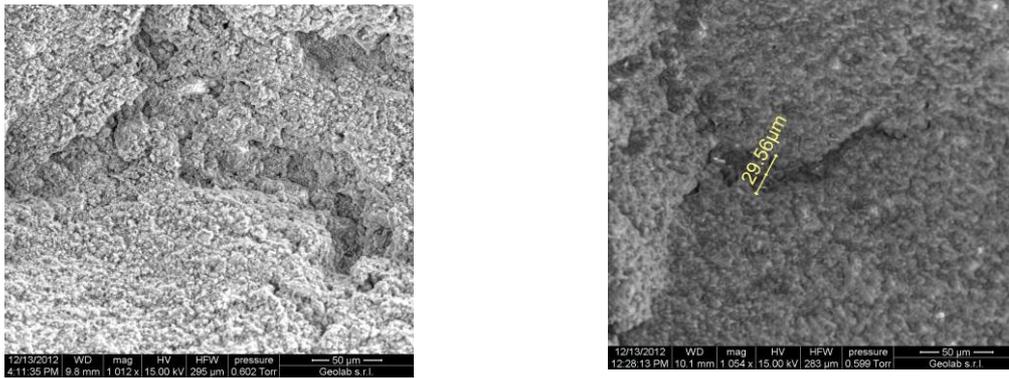


Fig 7. SEM images at 2000x for non-aged samples (left) and after the 6th step of accelerated aging (right)

## Conclusions

The experimental work shows the photocatalytic activity of paint is very high at time zero [10], remaining acceptable until the 6th step with maximum around 30%. Regarding the maintenance of color, only over the 5th step, there is a significant yellowing of the surface. The results of time rescaling indicate natural aging for the first 12 months corresponds to one step of artificial aging (48 cycles 1+2). The data of photocatalytic activity to one year of natural aging are not yet available. The surface of the samples is virtually the same after aging. Additional data may clarify the decay characteristics of the product.

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