Durability of a photocatalytic coating on a bituminous pavement

M. Palacios [(1)], L. Núñez [(1)], M. Pujadas [(1)], S. Suárez [(1)], B. Sánchez [(1)], M. B. Gómez-Mancebo [(1)], J. Fernández-Pampillón [(2)], A. Mazarío-Fernández [(3)], A. Moral [(4)] and J. Pérez [(4)]

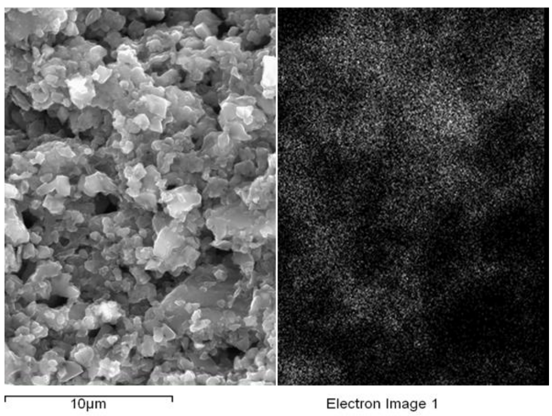
[(1)] CIEMAT (Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas).
+34- 91 346 65 41, e-mail: magdalena.palacios@ciemat.es

[(2)] UNED (Universidad Nacional de Educación a Distancia).
[(3)] CNME (Centro Nacional de Microscopía Electrónica).
[(4)] CEDEX (Centro de Estudios y Experimentación de Obras Públicas).

1. Introduction – The use of titanium dioxide (TiO_2) as coating for concrete pavement has received considerable attention in recent years. In particular, applying TiO_2-modified coatings onto the external covering of roads might be a supplement to conventional technologies for mitigating NO_x air pollution. In spite of the promising benefits of some photocatalytic materials and although their air-purifying activity have been deeply studied in laboratory, the durability and resistance to wear of this technology in pavement application needs to be evaluated before large-scale implementation is undertaken [1].
In the framework of the LIFE MINO$_x$-STREET European project, co-financed by the EU, a variety of commercial photocatalytic coatings, designed for use in bituminous mixtures, has been subjected to rigorous essays, testing both their depolluting capability as the operation-induced changes and durability.
Here, we present the effects of wearing on a TiO_2 surface layer and NO removal efficiency for one photocatalytic coating applied on a close-graded bituminous pavement at a test track.

2. Experimental – The objective of the experimental protocol was to measure and compare the photocatalytic performance of the TiO_2 coating before and after large scale-simulated abrasion and wearing and study the structural changes induced by traffic rolling and their relationship to NO removal capacity observed. For this purpose, the CEDEX Accelerated Test Track (ATT) facility was used to apply one selected photocatalytic coating on a close-graded bituminous mix similar to other mixes widely used in Spanish municipalities. The photocatalytic product was applied by rolling following manufacturer instructions. A coring of asphalt mix of two test sections (side and center) was carried out and the samples obtained were cut into 99 mm x 49 mm x 5 mm specimens.
The photocatalytic activity of photocatalytic concrete samples was then essayed under ISO 22197-1:2007 [2]. In bed flow photo-reactor experiments, like the one used in this work, a test gas mixture flow (NO, air, H_2O) (50% relative humidity) is passed over the flat rectangular sample of typically 5 cm x 10 cm and is irradiated by UV-A light (10 W m^{-2} irradiance) through a UV transparent window with a distance to the sample of 5 mm. Under the conditions applied, a laminar-plugged flow is assumed and very short reaction times of only a few seconds are obtained. This set-up is comparable to a classical flow tube approach often used in heterogeneous chemistry. Before and after accelerated pavement testing (35000 and 80000 cycles), samples were obtained to quantify the removal of nitric oxide by using the ISO essay data.
Additionally, the distribution of Ti on the coating surface before and after durability testing was investigated by means of scanning electron microscopy (SEM) and X-ray energy-dispersive spectroscopy (XEDS).
Scanning electron microscopy (SEM) was carried out in a JEOL 6400-JSM scanning electron microscope (Image 1) [3] . This microscope is especially suitable for observing the surface of materials in which, moreover, it is possible to

Image 1. SEM image and XEDS map showing surface structure and Ti distribution, respectively, of a sample.



collect semiquantitative analysis regarding the composition of the sample.

SEM images were recorded working at an acceleration voltage of 20 kV at different magnifications, in most cases at X3000. The cationic composition was analyzed by X-ray energy-dispersive spectroscopy (XEDS) with an OXFORD INCA analyzer system attached to this microscope by working at an acceleration voltage of 20 KV.

The preparation of the sample analyzed by XEDS involves placing specimens of approximately 10 mm x 10 mm x 10 mm on a carbon tape in the sample holder. Three specimens were meticulously cut for every kind of sample for which the resistance to wearing was studied: two from the extremes and one from the center. Subsequently, graphite is deposited on the surface of the sample to ensure the conduction of electrons and prevent the collection of charged images.

The surface of every sample was scanned, the area of interest was selected and the spectrum image was collected. Therefore, two images were collected per every sample: the corresponding scanning microscopy image in which the morphology of the sample surface can be seen and the spectrum image in which the brightest areas correspond to those areas of the sample having Ti (titanium).

After that, images were processed by means of a utility of the CorelDraw software designed to generate an image histogram, that is, a type of histogram that acts as a graphical representation of the tonal distribution in a digital image. It plots the number of pixels for each tonal value. A sample with no photocatalytic coating was taken as a reference and quantity of Ti computed as a function of the number of pixels within a pre-evaluated and selected tonal range.

In addition, TiO_2-modified coating was extracted from an aliquot of each sample and the powder was ground to a particle size lower than 63 µm for crystalline characterization. The crystal structures determination was performed from powder X-ray diffraction (XRD) measurements using a CuKα radiation source from a PANalytical X´Pert PRO diffractometer operating with Bragg-Brentano geometry. The data was collected from 20 -120º (2θ). Additionally, an aliquot of each sample was analysed for major and minor elements determination by wavelength dispersive X-ray fluorescence spectrometry (XRF) using a PANAlytical, AXIOS automated XRF spectrometer.

Further, a study of the photocatalytic material stability to wearing has been assessed throughout the course of the test track by means of image processing technique as well. In order to obtain digital images of section surfaces, a system composed of a tripod, Canon EOS 400 digital camera, photo-shooting tent and lights was formed. CEDEX Accelerated Test Track (ATT) is provided of six test sections. This study was performed over one of these sections, where the photocatalytic product was applied. In this section, the no tracking area and wheel path surfaces were photographed by the help of the set-up and the digital camera. Also the called control section, where no product was applied, was photographed. The obtained section images were processed and luminance was determined against barium sulphate standard by NI-Vision Assistant V8.6 program of National Instrument.

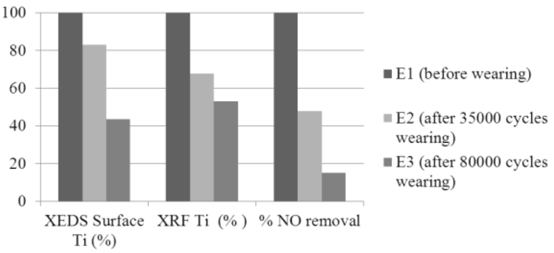
Table 1. Estimates of Ti content by means of image histogram processing from XEDS data (referred to non-coated sample).

Type of sample	Sample	Relative Ti content	Average	Standard Deviation
Non-road (center)	M13c	43,39	30.83	11.32
	$M13e_1$	21,41		
	$M13e_2$	27,7		
Non-road (side)	M14 c	32,38	34.40	3.15
	$M14e_1$	38,03		
	$M14e_2$	32,8		
After 35000 cycles (center)	M15	29,78	30.14	0.46
	$M15e_1$	29,97		
	$M15e_2$	30,66		
After 35000 cycles (side)	M16c	20,95	23.94	2.61
	$M16e_1$	25,73		
	$M16e_2$	25,15		
After 80000 cycles (center)	M20	5,32	14.22	8.13
	$M20e_1$	16,07		
	$M20e_2$	21,26		

3. Results and Discussion – The experimental method used for testing the NO photocatalytic efficiency, based on a bed flow photo-reactor, has revealed different values of air-purification performance depending on the wearing time to which the photocatalytic pavement was subjected. The NO removal capacity (as χ, or %NO removal, $(NO_{input}-NO_{output})/NO_{input}*100$) varied from 46% to 22% after 35000 load cycles and to 7% after 80000 load cycles. So, results from the ISO essay reveal a sharp decrease in the NO removal capability of the photocatalytic material under test (around 52 % and 85% after 35000 and 80000 cycles of wearing, respectively) as a reflect of the a substantial lessening in the amount of Ti distributed at the surface of the samples (XEDS) and within the samples (XRF) as the wearing progresses (Image 2).

Image histograms from XEDS digital images allowed a comparative semi-cuantitative estimation of the quantity of Ti presented in every sample (Table 1). A significant variability not only inter-sample but also intra-sample was observed mainly due to the consubstantial non-homogeneous structure of the bituminous mixtures and the manner in which the photocatalytic product is fixed over them. This circumstance forces to a deep characterization of the samples by means of the analysis of a huge quantity of samples by using different techniques to obtain representative data and conclusions.

Image 2. Effect of wearing by different analysis techniques (data normalized to values before wearing).



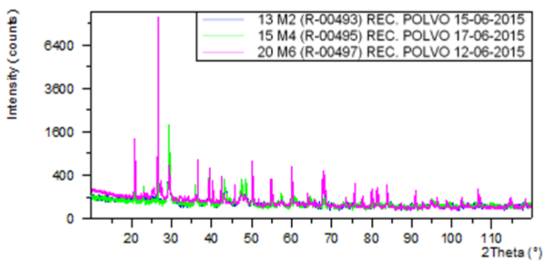
The wearing affects mainly the surface so that the loss of TiO_2 is clearly dependent on the abrasion intensity and duration, more aggressive at the surface. In order to be effective, the TiO_2 active centers need to be exposed to gaseous pollutants that diffuse to them. So, efficient oxidation process takes place mainly at the surface and, although the decrease in the total amount of TiO_2 contained in the asphalt mix, given by XRF, is significant due to wearing (Image 2), it is the missing at surface of photoactive concrete which leads to a relevant decrease in $deNO_x$ capacity as the damage by abrasion of the photocatalytic coating progresses.

The samples characterized by XRD (M13, M15, M20) were obtained by scratching a part of the original samples surface. The results of the crystalline characterization, by XRD technique, show a similar composition in the three samples (Table 2).

Table 2. Crystalline phases in some analyzed samples.

Compounds	Abundance in samples		
	M13	M15	M20
SiO_2 (Quartz)	↑↑↑	↑↑	↑↑↑
$Ca(CO)_3$ (Calcite)	↑↑↑	↑↑↑	↑↑
$Al_4Si_2CaO_{10}(OH)_2$ (Margarite)	↑↑	↑↑	↑↑
TiO_2 (Titanium oxide)	↑	↑	below the limit of quantification
$Ca_2(Fe_{0.17}Al_{0.83})Al(Si_3O_{10})(OH)_2$ (Prehnite)	-	-	↑

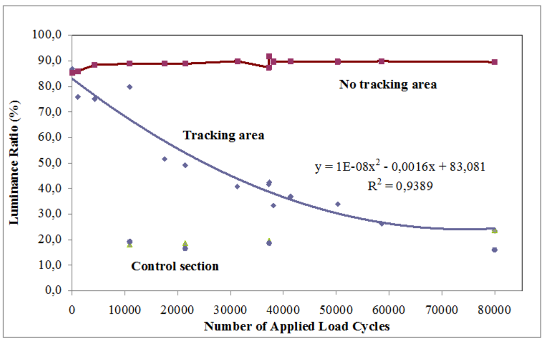
Image 3: XRD spectrum of the samples M13, M15 and M20



In Image 3 the XRD spectra are featured. The most abundant crystalline phases in the three samples are quartz and calcite but distributed in different proportions as it is shown in Table 2. TiO_2 coating is composed of rutile-type crystalline phase, present in other photocatalytic coatings [4], with no TiO_2 phase changes after wearing. The semicuantitative analysis shows that TiO_2 coating amount decreases after wearing. While in sample M13 the concentration is 5 %, in sample M15 this amount is reduced to 4 % and in sample 20 it is below the limit of quantification.

Image 4 shows the results obtained from luminance experiment. In the no tracking surface, this variable was found to be independent of the time by which the load cycles were applied. In the wheel path surface, a high correlation between both variables was found (R^2= 93.9%), showing that the product was removed by the contact with the wheel. The luminance reduction was more intense in the first 30000 applied load cycles, stabilizing afterwards. The closed bituminous mixture on which the photocatalytic coating was applied provides a high number of contact points between the product and the tire which facilitates entrainment thereof by the tire. These results are coherent with data analysis from the other techniques presented and can be useful to study the photolytic

Image 4. Luminance ratio dependence on number of applied load cycles for tracking and non tracking airea.



product behaviour against traffic road weathering. The results from image analysis show a nearly 94% correlation between the luminance and the load cycles.

4. Conclusions – A commercial titanium product, in rutile form, applied on a close-graded mixture, was investigated in efforts to prove its durability and resistance when road traffic passes over it. A methodology, based on different techniques and essays, has been set up in order to characterize the changes induced by wearing over the photocatalytic coating and the corresponding potential decrease of photocatalytic activity.

The study showed that both the surface distribution as the total amount of Ti decreased over time and, coherently, the NO removal efficiency. The structural analysis carried out highlights the heavy dependence of the efficiency of removal of NO exposure time rolling. In fact, effects on wearing on the NO removal efficiency are dramatic in the studied operating conditions. Consequently, it is highly recommended to investigate the operation-induced changes and durability of photocatalytic coatings before their implementation at real scale.

Further research is recommended to consider factors such as type of photocatalytic product applied on the concrete, type of concrete, coating composition, coating application method and variation of the NO removal efficiency with ambient air conditions, specially radiation and humidity.

5. References

[1] M.M. Hassan, H. Dylla, L.N. Mohammad and T. Rupnow, *Constr. Build. Mater.*, ***24***, (2010) p. 1456.

[2] International standard ISO 22197-1:2007, Geneve, 2007.

[3] http://www.cnme.es/

[4] J.O Carneiro, S. Azevedo, V. Teixeira, F. Fernandes, E. Freitas, H. Silva and J. Oliveira, *Constr. Buil. Mater.*, ***38***, (2013) p. 594.