Study for the Development of Photocatalytic *Sprayable* Aqueous Formulations for Application in Asphalt Pavements

J. Fermoso[1], M. Gomez[1], A. Costa[2], J. Loma[2], E. Martínez[3], G. Recio[3], J.M. Baena[3], V. Carrera[4], V. Contreras[4],
CARTIF[1], Valladolid, Spain. ELSAN[2], Madrid, Spain, Madrid City Council[3], Madrid, Spain, REPSOL[4], Madrid, Spain.
josdom@cartif.es

SPEA 9
JUNE 13 - 17, 2016
STRASBOURG - FRANCE

INTRODUCTION

Presently, **urban environments** are facing serious problems concerning air quality, mainly due to exhaust gases from traffic and burning fuels in industries, leading to a major environmental issue on a global scale. Air pollutants can be classified according to their origin as primary or secondary pollutants. Primary pollutants are those that are emitted directly by the sources to the atmosphere, like carbon monoxide (CO), sulfur dioxide (SO_2), **nitrogen oxides (NO_X)** and particles (PM10 and PM2.5).

Secondary pollutants are formed from chemical reactions occurring in atmosphere, such as tropospheric ozone (O_3), nitric acid (HNO_3) and sulfuric acid (H_2SO_4). Nitrogen oxides will be the focus of this study.

A promising approach for decreasing high levels of nitrogen oxides NO_X in urban environments is their ability to be photochemically converted to nitrates by heterogeneous photocatalytic oxidation with TiO_2. Photocatalytic paint surfaces have been shown to be an effective sink of NO, NO_2 and HONO, precursors of harmful secondary products, like PAN or O_3 [1].

In this study we have study some aspects in order to formulate an **aqueous suspension with TiO_2** easily applied on asphalt pavements. We have evaluated type and load of organic binder and type of catalyst presentation and its concentration.

EXPERIMENTAL

To get started let go to select the main **materials** we need:

- **Water**, the majority component. This component serves as a vehicle for application in large areas and to stabilize the suspension.
- **Resin** as TiO_2 binder to the asphalt. There are several possible compounds (silicate [2,3], siloxane-based [2], acrylic [3], styrene-acrylic, vinyl, EVA among others) **compatible with catalyst**. Another important property for the resin is its **adhesiveness** on asphalt
- **TiO_2**, active component. Concentration and type are the main factors influencing product cost.
- **pH modification additive**. We employed NaOH to basify the suspension in order to increase solution stability and to avoid photocatalytic formation of HONO[1].
- **Other additives** are strongly recommended, as an anti-foaming agent, for industrial fabrication. This study aims to be only an approach at lab scale, so we have not included any additional additive.

A chemiluminescence instrument (eco physics cld 770al) was used in this study to follow NO/NO_2 and **ISO 22197-1:2007** was used as standard test method. A FTIR (Varian 670) equipped with an attenuated total reflection tool was used to study evolution of the material with UV exposition.

Among the many affecting factors to photoactivity, type (powder PC500 Cristal, slurry PC-S7 Cristal and 50% of them, S/L) and concentration (10, 25 and 50 g/L, CAT) of TiO_2 and type (Acrylic, EVA and Silicate, AES) and concentration (1, 2,5 and 5%, RES) of resin were chosen as control factors based on references and previous studies. We selected a orthogonal array L9 (table 1) to carry out the experimental plan.

***Table 1**. L9 Orthogonal array.*

	RES	S/L	CAT	AES
Run 1	1,0%	S	10 g/L	Acrylic
Run 2	1,0%	50%	25 g/L	EVA
Run 3	1,0%	L	50 g/L	Silicate
Run 4	2,5%	S	25 g/L	Silicate
Run 5	2,5%	50%	50 g/L	Acrylic
Run 6	2,5%	L	10 g/L	EVA
Run 7	5,0%	S	50 g/L	EVA
Run 8	5,0%	50%	10 g/L	Silicate
Run 9	5,0%	L	25 g/L	Acrylic

For tests we use aluminum plates as substrates and a formulation load of 0,3 L/m^2.

RESULTS

Photocatalysis removal of NO_X (reduced to 1 hour of test) of different runs are shown in table 2 (2 replicates). An analysis of variance (ANOVA) of the results has been made mixing contributions of no significant factors according to significance test of Fisher with a confidence level of 99%.

***Table 2**. % NO_X removal results.*

	Rep. 1	Rep. 2	CAT/RES	%NOX/CAT
1	4,15%	4,99%	1	0,5%
2	22,34%	17,07%	2,5	0,8%
3	30,96%	10,36%	5	0,4%
4	36,41%	25,65%	1	1,2%
5	60,32%	64,39%	2	1,2%
6	20,55%	8,73%	0,4	1,5%
7	54,23%	56,09%	1	1,1%
8	0,65%	5,53%	0,2	0,3%
9	5,11%	3,45%	0,5	0,2%

According to the results obtained by the analysis of variance, TiO_2 concentration ([TiO_2]) is the most significant factor with an influence of 58,42%. Resin concentration is the second one with an influence of 16,61% and the type of catalyst presentation the third one with a 12,08% (99% level of confidence). Type of resin has a very small influence on the photocatalytic performance.

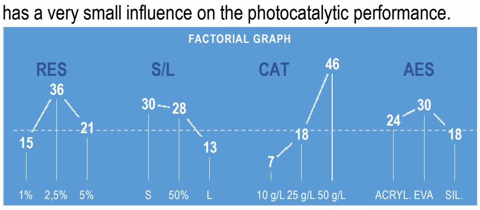

***Fig. 1**. Factorial Graph.*

Factorial Graph (fig.1) shows optimal levels of the factors (bigger the best). An interesting parameter in order to select catalyst and resin concentration is the relationship between %NO_X removal and [TiO_2].

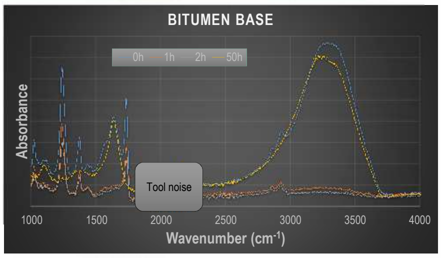

***Fig. 2**. FTIR of bitumen coated with formulation from Run7 before and after 2 and 50 hours aging.*

The FTIR spectra of bitumen coated with formulation from Run7 before and after UVA aging for 2 and 50 hours are shown in Fig.2. As it can be observed, peaks at 2.950, 2.880 (methylene -CH_2- in aliphatic chains) and 1.450 (asymmetric deformation in both CH_2 and CH_3 groups) cm^{-1} disappeared due to bitumen oxidation. Furthermore, peaks at 1.740, 1.240 and 1.020 cm^{-1} (Vinyl acetate bands) disappeared because TiO_2 oxidation.

TiO_2 shows a broad band between 3600 to 3000 cm^{-1} which is related to stretching hydroxyl (O-H), representing the water as moisture. Additionally, other peak at 1635 cm^{-1} indicates stretching of titanium carboxylate[5]. Both bands in these samples are associated to TiO_2 presence on the surface with photocatalytic properties. It is interesting to note that there is an initial period of aging UVA in which no TiO_2 is detected.

CONCLUSIONS & REFERENCES

When you think about designing a photocatalytic formulation to apply on asphalt pavement to remove NO_X in urban environments you have to take into account:

- The most important factor on photocatalytic activity is **TiO_2 concentration**.
- Then select binder concentration (lower than TiO_2 concentration).
- In addition, you should take into account other properties as **adhesiveness** (binder nature), formulation **stability** (TiO_2 powder load and pH), **color** (TiO_2 particle size or use colorants) and final **pavement superficial properties** in order to get an adequate industrial product.
- Optimal formulation should be defined from these advices and after deciding commercial products to use, photocatalytic performance of the product and formulation dosage to apply on the pavement. Of course, do not forget cost product (ideally less than 1 €/m^2).

FTIR studies show how formulation nature is modified by UVA aging. It is interesting to note that there is an initial period of aging UVA in which no TiO_2 is detected. It is needed an initial UVA aging to show maximum presence of TiO_2 in the surface.

REFERENCES

[1] S. Laufs, G. Burgeth, W. Duttlinger, R. Kurtenbach, M. Maban, C. Thomas, P. Wiesen, J. Kleffmann. *Atmospheric Environment* 44 (2010) 2341.
[2] C. Pirola, D.C. Boffito, S. Vitali, C.L. Bianchi. *J. Coat. Technol. Res.* 9 (4) (2012) 453.
[3] T. Maggos, J.G. Bartzis, P. Leva, D. Kotzias. *Appl. Phys. A* 89 (2007) 81.
[4] M. Gallus, et al. *Environ. Sci. Pollut. Res.* 22 (2015) 18185.
[5] M.M. Ba-Abbad, et al. *Int. J. Electrochem. Sci.*, 7 (2012) 4871.

Acknowledgements
The authors gratefully acknowledge the support of this work by the LIFE+ Program under the responsibility of the Directorate General for the Environment of the European Commission through the agreement LIFE12 ENV/ES/000749 EQUINOX project.

LIFE EQUINOX
@LifeEquinox
info@life-equinox.eu
www.life-equinox.eu

Surface Treatment for Asphalt pavements to Nitrogen oxides removal in Urban Environments
LIFE12 ENV/ES/000749