Arab J Sci Eng (2016) 41:4827–4833
DOI 10.1007/s13369-016-2168-5

RESEARCH ARTICLE - CIVIL ENGINEERING

Durability of NO Oxidation Effectiveness of Pavement Surfaces Treated with Photocatalytic Titanium Dioxide

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Received: 16 December 2015 / Accepted: 15 April 2016 / Published online: 12 May 2016

Abstract Nowadays, photocatalysis has demonstrated to be a reliable solution in order to purify the atmosphere from the pollutants originated by vehicular traffic. Owing to the primary importance of this problem, the potential of innovative photocatalytic techniques, dealing with the immobilization of titanium dioxide TiO_2 on the surface of the asphalt pavement, has been investigated. In particular, three different products, two bituminous emulsions and a cement mortar, were applied on the right lane and on the emergency lane of a highway section in Italy. The effectiveness of the photocatalytic treatments and its evolution with time were evaluated on cores taken after 1, 17, 46, 88, 218, and 527 days from the application of the products. Two tests were carried out on the cores: The NO degradation was evaluated through continuous flow tests, and the size of the treated areas was quantified by means of digital image analysis methods. The research showed interesting results, as all the techniques, in particular the bituminous emulsion-based products, proved to have a good effectiveness in air de-polluting, even if a decay of performance was noted, depending of traffic and weather conditions.

Keywords Photocatalysis · Titanium Dioxide · Asphalt pavement · Bituminous emulsion · Cement mortar

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1 Introduction

In the last years the use of photocatalytic techniques, with the aim to de-pollute air from traffic emissions, has aroused lively interest in many administrations [1]. In photocatalytic reactions, Titanium Dioxide TiO_2 in its anatase phase (atomic network is composed by titanium octahedrons connected by vertexes) acts as a photocatalyst allowing air purification from many polluting particles, including nitrogen oxides NO_x [2,3].

According to [4], the mechanism of photocatalytic degradation of NO_x (NO and NO_2) happens in three stages:

- Adsorption of the gas reactants by the photocatalyst surface;
- Generation/recombination of electron/hole pairs;
- Oxidation of NO and water reduction.

From the chemical point of view, NO_x oxidation can be described by the following reactions [5,6]:

$$NO + OH^{\cdot} \rightarrow NO_2 + H^+$$
$$NO_2 + OH^{\cdot} \rightarrow NO_3^- + H^+$$

The $OH^{\cdot}$ act as a strong oxidant and oxidize NO to NO_2 in the first step. The formed NO_2 is then oxidized to nitrate ions (NO_3^-).

Since the beneficial effects of photocatalysis has been assessed, researchers have focused on the type of support where titanium dioxide can be fixed, following precise requirements [7]:

- The TiO_2 fixing process should not inhibit the photocatalytic effect;
- TiO_2 particles must have good adhesion to the support;
- The support has to be chemically inert;

– Since photocatalysis is a surface reaction, the support should have a large specific surface area;
– The support should be compatible with the environmental use.

In the last years, a wide range of solutions have been identified and tested [8]. One of these consists in the application of titanium dioxide particles directly on the road pavement, as the photocatalytic effect is facilitated by the proximity to the pollution source [9] and the ability of the pavement to deposit the accumulating byproducts [10]. Since the first experiment carried out in Japan in 1999 [11], several trial projects were conducted around the world investigating the application on TiO_2 on concrete pavements [12–14], on asphalt pavements [15–17] or on porous asphalt mixes filled with cement mortars [18,19].

Despite the promising benefits of the various solutions, only few recent studies aimed to investigate the loss of efficiency of the photocatalytic pavements in NO degradation [20,21]. In particular, the research by Osborn [20] aimed to quantify the short-term durability (over 5 months) of a TiO_2 spray application on concrete and asphalt pavements. By interpolating the results with a regression curve, the complete loss of photocatalytic efficiency was expected after 6–11 and 10–16 months for the concrete and the asphalt pavement, respectively.

The present investigation has been developed with the aim to compare, in terms of photocatalytic potential and medium/long-term durability of the de-polluting effectiveness (over 18 months), two different techniques to introduce titanium dioxide particles in the road pavement, as described in the following section.

2 Experimental Program

This paper deals with the real scale application of different photocatalytic products on an important Italian highway. The trial was organized in a section of the Highway A14, in a suburban area close to the city of Loreto (Ancona), during the works for the widening of the road from four to six lanes (Fig. 1).

The objective of the study was to investigate the effectiveness of various solutions for air de-polluting. In particular, three different photocatalytic products, two bituminous emulsions (products A and B) and a cement mortar (product C), were applied on the right lane and, for a smaller width, on the emergency lane of a straight section. The final goal of the project was identify the best product in terms of photocatalytic efficiency and durability, in anticipation of the future application on the tunnel pavements, where the concentration of traffic-emitted pollutants is higher.

The effectiveness of the photocatalytic treatments and its evolution with time were evaluated on cores taken from the trial sections after 1, 17, 46, 88, 218, and 527 days from the application of the products. Each core was named with a letter, related the type of product (A, B, or C), and a number.

Two tests were carried out on the cores: The NO degradation was evaluated through continuous flow tests, according to the Italian Standard 11247 [22]; in addition the size of the treated areas was quantified by means of digital image analysis methods, that allowed to identify the number of white pixels which denote the presence of TiO_2.

In order to investigate the effect of traffic on the photocatalytic properties of the different products, cores were also taken from the emergency lane of the Highway (not interested

Fig. 1 Location of the trial section

Table 1 Experimental program

Sampling area	Main lane	Emergency lane
Products applied	A, B and C	A, B and C
Sampling time	1, 17, 46, 88, 218 and 527 days	218 days
No. of cores	3	3
Experimental analysis	NO_x degradation and white pixel percentage analysis	NO_x degradation
No. of repetitions	4 for each test	4

by traffic) after 218 days from the treatment and subjected to continuous flow tests.

Table 1 summarizes the experimental program.

3 Test Procedures

3.1 NO Degradation

The nitrogen oxides degradation rate measurements have been carried out in a continuous gas flow reactor equipped with a chemiluminescence analyzer, according to the Italian Standard 11247 [22].

The photocatalytic reactor consists of a glass chamber where the specimen can be located on the bottom part, supported by a proper sample holder. The specimen surface exposed to the air flow is 69.4 cm^2. The gas inlet tube allows the air/NO mixture to flow directly onto the specimen upper surface and exit through the gas outlet tube positioned on the opposite side. A specific lamp emitted the ultraviolet radiation with wavelength between 300 and 400 nm and produced an average irradiance of 25 ± 1 W/m^2 on the specimen surface. A schematic diagram of the photocatalytic reactor equipped with the UV lamp is illustrated in Fig. 2.

During the test, the specimen is put in the reactor with the light off to determine the steady concentration (C_0). When the light is turned on, the photocatalysis process begins and the NO concentration equilibrium value (C_1) is recorded. The nitrogen oxides degradation rate is calculated with Eq. (1)

$$\eta_{NO} = 100 \times \frac{C_0 - C_1}{C_0} \quad (1)$$

where η_{NO} is the percentage of NO degraded, C_0 and C_1 are the NO concentration in ppb with the light off and on, respectively.

Equation (2) allows to convert the degradation rate in the photocatalyst-related parameter λ.

$$\lambda = \frac{\eta_{NO} \times \alpha}{100} \quad (2)$$

where λ is the amount of NO degraded per time and surface unit in mg/m^2 h and α is a constant equal to 10.4 mg/m^2 h at the given pollutant concentration and irradiance.

3.2 White Pixel Percentage Analysis

The white pixel percentage analysis is an indirect method to evaluate the capability of the road surface to degrade air pollutants. By photographing the upper surface of a core and using a digital image analysis software, it is possible to identify the number of white pixels, which denote the presence of Titanium Dioxide (Fig. 3).

The evolution of the white pixel percentage with time allows to quantify the amount of TiO_2 pigments that can resist the polishing effect caused by traffic and meteorological phenomena and keep being in contact with the air, permitting the photocatalytic reaction to take place.

4 Materials

4.1 Asphalt Concrete

The upper layer of the pavement consisted in a porous asphalt concrete (PAC) containing 4.8 % of polymer modified bitumen by mixture weight. The aggregate gradation of the mix, compared with the envelope provided by Italian specifications [23], is shown in Fig. 4, while the volumetric properties are reported in Table 2.

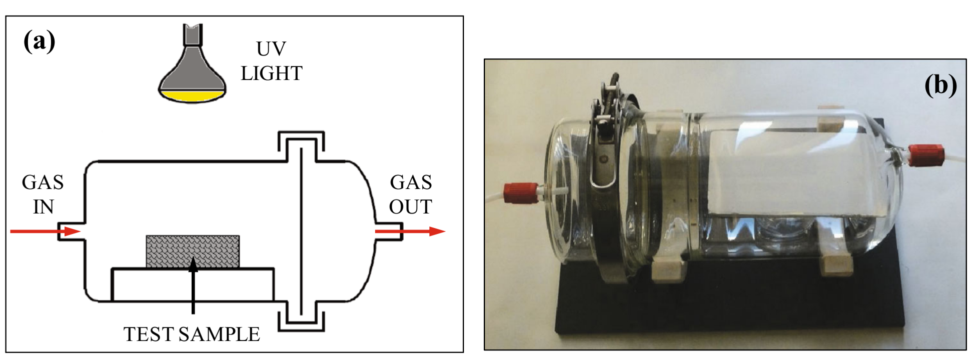

Fig. 2 Photocatalytic reactor for NO oxidation

Fig. 3 Core pictures for white pixel percentage analysis

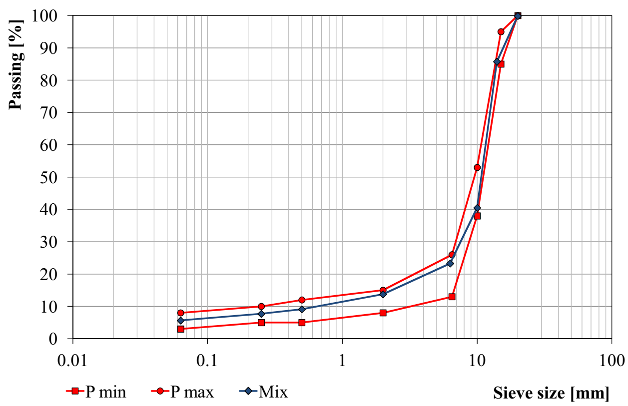

Fig. 4 Gradation of the PAC

Table 2 Volumetric properties of the PAC

Property	Method	Value
Maximum density (Mg/m^3)	EN 12697-5	2.524
Bulk density (Mg/m^3)	EN 12697-6	1.889
Air voids content (%)	EN 12697-8	25.1
Void in the mineral aggregate (%)	EN 12697-8	33.9
Void filled with bitumen (%)	EN 12697-8	25.9

4.2 Photocatalytic Treatments

In order to treat road pavements with photocatalytic products, two techniques were adopted, involving the use of bituminous emulsions or cement mortars.

The first solution regarded the cold spraying of a water-based cationic bituminous emulsion containing TiO_2 on the surface of the PAC. The emulsion dosage was 0.067 kg/m^2 (1 kg of emulsion on 15 m^2) and the cost of this treatment was about 6.50 € (7.20 \$) per m^2, including both raw material and application. The same type of product can be also used on ordinary asphalt concrete mixtures for wearing courses (not only on PAC); in that case the emulsion dosage should be reduced to 0.05 kg/m^2 (1 kg of emulsion on 20 m^2).

The second solution dealt with the use of a cement mortar made of sand, cement, fluidifying additive, non-shrink additive and TiO_2. The product was supplied in form of powder, so that only the water was added on the construction site. The application consisted in pouring the fluid mortar in the voids of the PAC layer. As the photocatalytic reactions take place only on the surface of the mortar, which is in contact with the air, it was not necessary to fill the whole thickness of the wearing course. Indeed, the mortar penetration was limited to the upper 15–20 mm of the layer, in order to reduce the amount of mortar needed, with clear economical benefits, but still having a good anchorage to the asphalt concrete. In particular, about 1.0 kg of powdered product was used to obtain necessary amount of mortar to fill 1 m^2 of pavement. The cost of this intervention is about 20 € (22 \$) per m^2, including raw material and application.

5 Environmental and Traffic Conditions

The effectiveness of the photocatalytic treatments is affected by several external factors including vehicle traffic and weather conditions, that directly influence the road surface polishing hence the removal of the photocatalytic particles [19].

Therefore, traffic has been observed and data were analyzed in order to determine the number of vehicles which passed on the treated lanes in the examined time period. As a result, the daily number of vehicle was about 19,300, for a total number of traffic passages equal to 10 millions in the 18 months considered. As the traffic flux was quite homogeneous, it can be affirmed that the surface polishing had been approximately constant during the entire testing period.

In addition, in order to evaluate the influence of the meteorological conditions, the number of rainy days was identified between each core sampling (Table 3). The mean temperature in every sampling interval was also recorded. The interval most interested by meteorological events resulted to be the No. 3 (between the third and the fourth sampling), with a rainy weather in the 69 % of the days and a mean temperature of 7.4 °C.

Table 3 Meteorological data

Interval no.	No. of rainy days	% of rainy days (%)	Mean temp. (°C)
1 (between 1st and 2nd sampling)	7 on 17	41	16.4
2 (between 2nd and 3rd sampling)	16 on 29	55	13.3
3 (between 3rd and 4th sampling)	29 on 42	69	7.4
4 (between 4th and 5th sampling)	47 on 130	36	9.3
5 (between 5th and 6th sampling)	78 on 309	25	14.7

6 Result Analysis

Table 4 shows the nitrogen oxides degradation rate measured through the continuous flow test. Results showed a good performance for all the products after 24 h from the application. In particular, the bituminous emulsions (products A and B) proved to have a slightly higher effectiveness, with degradation rate values about 40 %, than the cement mortar (product C) which showed a degradation rate of about 25 %. However, the decline of the performance was significant in the first weeks, until low final values have been reached after 200 days (Fig. 5). In particular, the cement mortar experienced a quick fall of the de-polluting activity just after 2 weeks.

Comparing the evolution of the photocatalytic properties with the meteorological conditions, it was noted that for products A and B the most important performance decay, identified with a bump in the curves in Fig. 5, corresponded to the time interval between the third and the fourth sampling, characterized by the coldest temperatures and the higher percentage of rainy days. This leaded to assume that for the bituminous emulsions the decay of the photocatalytic activity is noticeably affected by climatic conditions. On the other hand, traffic-related surface polishing, which determines the removal of the TiO_2 pigments, seemed less relevant for this kind of photocatalytic treatments. This can be related to the fact that, as the bituminous emulsion was sprayed on a PAC, many TiO_2 particles stuck inside the pores, avoiding the direct contact with the vehicle tires.

A different situation was observed for the product C: NO degradation, which was lower ever since the first day of application, almost entirely decayed after 17 days, i.e., at the second sampling. Moreover, the cores showed a sort of surface film, probably due to vehicular traffic. In such conditions, the de-polluting process seemed to be quickly inhibited or reduced, hindering the photoactivation of TiO_2 particles.

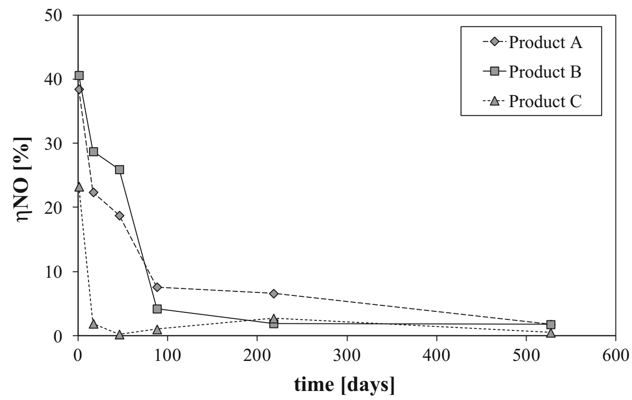

Fig. 5 Evolution of the degradation rate with time for the different products

Figure 6 depicts the percentage of white pixels in the surface of the cores as a function of time for the different treatments. It can be immediately noticed that the curves had a similar trend compared with the η_{NO} evolution shown in Fig. 5. In detail, the reduction of white pigments could be almost perfectly superimposed to the NO decay for bituminous emulsion products (A and B). Differently, for the clear cement mortar (product C) a certain amount of white pixels was always present and only a part of the core surface was interested by polishing, depending on traffic and climatic

Table 4 Degradation of nitrogen oxides

t (days)	Product A		Product B		Product C	
	η NO$_{mean}$ (%)	SD	η NO$_{mean}$ (%)	SD	η NO$_{mean}$ (%)	SD
1	38.44	2.92	40.61	3.35	23.27	2.53
17	22.38	2.45	28.72	2.66	1.90	0.16
46	18.76	1.70	25.93	3.13	0.44	0.15
88	7.60	0.49	4.21	0.54	1.01	0.21
218	6.59	0.30	1.91	0.08	2.72	0.29
527	1.77	0.11	1.76	0.11	0.49	0.09

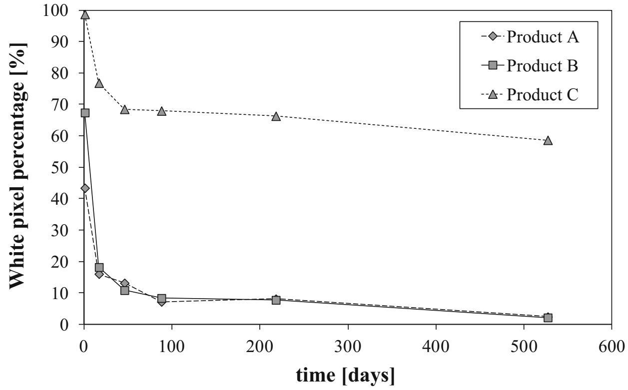

Fig. 6 Evolution of the white pixel percentage with time for the different products

conditions. However, as in the case of products A and B, also for product C the relationship between the decrease in the NO degradation potential and the reduction in the percentage of white pixels resulted evident. Simply, there was a shift of about 65 % but the trend appeared totally comparable.

The results showed similarities to those obtained by [20], which sprayed a TiO_2 coating on concrete and asphalt pavements. In fact, even if the techniques were different (PAC vs dense-graded asphalt mixture, PAC filled with a TiO_2-based cement mortar vs concrete pavement), both the studies registered an important decay of the photocatalytic efficiency in the first month and a higher durability when asphalt materials were used.

Figure 7 shows, for the different products, the results of the continuous flow tests performed on the cores taken from the emergency lane after 218 days from the treatment, compared with the nitrogen oxides degradation rate measured on the cores taken from the main lane. From the graph it can be noticed that products A and B presented the same NO degradation level both on main and emergency lane, confirming that the photocatalytic activity is mainly affected by

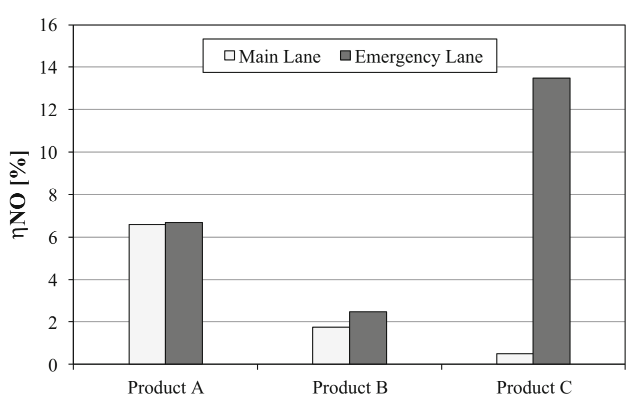

Fig. 7 Comparison of NO degradation between main lane and emergency lane after 218 days

the climatic conditions while traffic-related surface polishing is less relevant. On the contrary, the product C applied on the emergency lane proved to still have a certain de-pollutant effectiveness after 218 days, with η_{NO} values about halved than the ones measured the day after the treatment. This indicates that the photocatalytic activity of the cement mortar is partially affected by meteoric and atmospheric agents while is prevalently influenced by the polishing caused by vehicle traffic.

7 Conclusion

The present paper deals with the real scale application of different Titanium Dioxide based products on a Italian highway. In particular, three different photocatalytic products, two bituminous emulsions (products A and B) and a cement mortar (product C), were applied on the right lane and on the emergency lane of a straight section. The effectiveness of the photocatalytic treatments was evaluated on cores taken after 1, 17, 46, 88, 218, and 527 days from the application, through continuous flow tests for the measurement of the NO degradation and digital image analysis methods, that allowed to identify the number of white pixels which denote the presence of TiO_2.

Results showed a good performance for all the products after 24 h from the application. However, the decline of the performance was significant in the first weeks, particularly for the cement mortar treatment (product C), which experienced a quick fall of the photocatalytic activity.

Comparing the evolution of the photocatalytic properties with the meteorological conditions, it was noted that for products A and B the most important performance decay corresponded to the time interval characterized by the coldest temperatures and the higher percentage of rainy days. This leaded to assume that for the bituminous emulsions the decay of the photocatalytic activity is noticeably affected by climatic conditions. As the products A and B presented the same NO degradation level both on main and emergency lane, this assumption seems to be confirmed.

On the contrary, as the product C applied on the emergency lane proved to still have a certain de-pollutant activity after 218 days, it can be supposed that the photocatalytic performance of the cement mortar is prevalently influenced by the polishing caused by vehicle traffic.

In conclusion, the research showed interesting results, as the investigated techniques proved to have a good perspectives, even if a decay of performance was noted depending on traffic and weather conditions. Future developments will focus on solutions to better fix the TiO_2 on the pavement and consequently allow the photocatalysis to occur with profit in a longer period of time. Considering the possibility to purify the air inside tunnels, the use of the bituminous emulsion proved to be the most suitable solution. In particular, the emulsion-based products showed a higher durability with traffic (the effect of rain would be of course avoided), but also economic benefits, in terms of low price and capability to easily restore its efficiency by spraying some new one.

References

1. Chen, J.; Poon, C.S.: Photocatalytic activity of titanium dioxide modified concrete materials—influence of utilizing recycled glass cullets as aggregates. J. Environ. Manag. **90**(11), 3436–3442 (2009). doi:10.1016/j.jenvman.2009.05.029
2. Carp, O.; Huisman, C.L.; Reller, A.: Photoinduced reactivity of titanium dioxide. Prog. Solid State Chem. **32**, 33–177 (2004). doi:10.1016/j.progsolidstchem.2004.08.001
3. Riderelli, L.; Bocci, E.; Bocci, M.; Fava, G.: Airborne pollutant inside a highway tunnel coated with a photocatalytic mortar. Energy Environ. Eng. **3**(2), 23–31 (2015). doi:10.13189/eee.2015.030202
4. Yu, Q.L.; Ballari, M.M.; Brouwers, H.J.H.: Indoor air purification using heterogeneous photocatalytic oxidation. Part II: kinetic study. Appl. Catal. B Environ. **99**, 58–65 (2010). doi:10.1016/j.apcatb.2010.05.032
5. Hüsken, G.; Hunger, M.; Brouwers, H.J.H.: Experimental study of photocatalytic concrete products for air purification. Build. Environ. **44**(12), 2463–2474 (2009). doi:10.1016/j.buildenv.2009.04.010
6. Hassan, M.; Mohammad, L.N.; Asadi, S.; Dylla, H.; Cooper, S.: Sustainable photocatalytic asphalt pavements for mitigation of nitrogen oxide and sulfur dioxide vehicle emissions. J. Mater. Civ. Eng. **25**(3), 365–371 (2013). doi:10.1061/(ASCE)MT.1943-5533.0000613
7. Ângelo, J.; Andrade, L.; Madeira, L.M.; Mendes, A.: An overview of photocatalysis phenomena applied to NO_x abatement. J. Environ. Manag. **129**, 522–539 (2013). doi:10.1016/j.jenvman.2013.08.006
8. Bilmes, S.A.; Mandelbaum, P.; Alvarez, F.; Victoria, N.M.: Surface and electronic structure of titanium dioxide photocatalysts. J. Phys. Chem. **104**(42), 9851–9858 (2000). doi:10.1021/jp0010132
9. Beeldens, A.: An environmental friendly solution for air purification and self-cleaning effect: the application of TiO_2 as photocatalyst in concrete. In: Proceedings of Transport Research Arena, Europe-TRA, Göteborg, Belgian Road Research Centre (2006)
10. Martinez, T.; Berton, A.; Ringot, E.; Escadeillas, G.: Degradation of NO using photocatalytic coatings applied to different substrates. Build. Environ. **46**(9), 1808–1816 (2011). doi:10.1016/j.buildenv.2011.03.001
11. Murata, Y.; Tawara, H.; Obata, H.; Hirosi, T.: Air purifying pavement: development of photocatalytic concrete blocks. J. Adv. Oxid. Technol. **4**(2), 227–230 (1999)
12. Ballari, M.M.; Brouwers, H.J.H.: Full scale demonstration of air-purifying pavement. J. Hazard. Mater. **254**(255), 406–414 (2013). doi:10.1016/j.jhazmat.2013.02.012
13. Guo, M.Z.; Poon, C.S.: Photocatalytic NO removal of concrete surface layers intermixed with TiO_2. Build. Environ. **70**, 102–109 (2013). doi:10.1016/j.buildenv.2013.08.017
14. de Melo, J.V.S.; Trichês, G.; Gleize, P.J.P.; Villena, J.: Development and evaluation of the efficiency of photocatalytic pavement blocks in the laboratory and after one year in the field. Constr. Build. Mater. **37**, 310–319 (2012). doi:10.1016/j.conbuildmat.2012.07.073
15. Chen, M.; Liu, Y.: NO_x removal from vehicle emissions by functionality surface of asphalt road. J. Hazard. Mater. **174**, 375–379 (2010). doi:10.1016/j.jhazmat.2009.09.062
16. Carneiro, J.O.; Azevedo, S.; Teixeira, V.; Fernandes, F.; Freitas, E.; Silva, H.; Oliveira, J.: Development of photocatalytic asphalt mixtures by the deposition and volumetric incorporation of TiO_2 nanoparticles. Constr. Build. Mater. **38**, 594–601 (2013). doi:10.1016/j.conbuildmat.2012.09.005
17. Mohammad, L.N.; Hassan, M.; Cooper, S.: Mechanical characteristics of asphaltic mixtures containing titanium-dioxide photocatalyst. J. Test. Eval. **40**(6), 998–1005 (2012). doi:10.1520/JTE104607
18. Canestrari, F.; Bocci, M.; Ferrotti, G.; Pasquini, E.: Mechanical characterization of environmentally friendly mixtures. In: International Conference on Advanced Characterisation of Pavement and Soil Engineering Materials., vol. 2, pp. 1643–1652 (2007)
19. Bocci, M.; Cerni, G.; Colagrande, S.: Experimental investigation of the dynamic behaviour of asphalt concrete treated with photocatalytic mortars. In: Proceedings of the 3rd International Conference on Tranportation Infrastructure, pp. 95–102 (2014). doi:10.1201/b16730-16
20. Osborn, D.; Hassan, M.; Asadi, S.; White, J.R.: Durability quantification of TiO_2 surface coating on concrete and asphalt pavements. J. Mater. Civ. Eng. **26**(2), 331–337 (2014). doi:10.1061/(ASCE)MT.1943-5533.0000816
21. Liu, W.; Wang, S.Y.; Zhang, J.; Fan, J.F.: Photocatalytic degradation of vehicle exhausts on asphalt pavement by TiO_2/rubber composite structure. Constr. Build. Mater. **81**, 224–232 (2015). doi:10.1016/j.conbuildmat.2015.02.034
22. UNI 11247: Determination of the degradation of nitrogen oxides in air by photocatalytic inorganic materials: continuous flow test method. UNI Ente Nazionale Italiano di Unificazione, Milan (2010)
23. Autostrade per l'Italia: special specifications for highways, second part, civil works (in Italian), Rome (2008)