# Study of the applicability of $TiO_2$ as a decontaminating agent over treated metal surfaces

## Estudio de la aplicabilidad del $TiO_2$ en su faceta descontaminante sobre superficies metálicas tratadas.

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**Resumen**
La evolución trae consigo la contaminación, pero en el siglo XXI la sociedad ha sido consciente la importancia del control y minimización de las emisiones contaminantes de origen antrópico. Por esta razón, la investigación y aplicación de productos fotocatalíticos con fines descontaminantes ha aumentado exponencialmente en estos últimos años. El objetivo de este artículo es desarrollar la investigación y estudio de la utilización de vehículos no como agentes contaminantes, sino como elementos descontaminantes utilizando como metodología la aplicación directa sobre la carrocería de un producto con base de Dióxido de Titanio, cuya efectividad ya ha sido demostrada sobre en pavimentos asfálticos, así como el estudio de los resultados. Los resultados obtenidos muestran unos valores con una efectividad media, superior a la de productos que en la actualidad están siendo comercializados y aplicados en distintos medios. Una vez finalizados los estudios se abren numerosas líneas de investigación para obtener un producto más eficiente y cuya aplicación resulte favorable en el parque automovilístico mundial.

**Palabras Clave**: Fotocatálisis; Tratamiento, Contaminación; Dióxido de Titanio, Vehículo.

**Abstract**
The progressive deterioration we cause to the environment by exhalation of pollutants into our atmosphere is not sustainable. The degradation of air quality and pollution, caused by human activity, is endangering the very life of our species and the planet. For this reason, research and application of photocatalytic products with decontamination purposes has exponentially increased in recent years. In this article, the aim of this paper is to develop research and study of the use of vehicles is to develop not as pollutants, but as decontaminating substances through direct application to the bodywork of a product holding a Titanium Dioxide base, whose effectiveness has been demonstrated over asphalt pavements, and the study results. The results show values with a proven effectiveness, higher than products currently being marketed and used in different means. Once completed the analysis, several lines of research are initiated to improve the uses proposed.

**Keywords:** Photocatalysis; Treatment, Pollution; Titanium Dioxide, Vehicle.

## Description of the problem

Air pollution is an aggravating factor in the health of people as it can lead to premature death, as well as pulmonary and cardiovascular diseases (Ballester, 2005). Degradation of air quality is the result of phenomena whose origin lies in the natural supply and human activity (Ministerio de Agricultura, Alimentación y Medio Ambiente, 2014). Apart from traffic, another cause of atmospheric pollution is the gases produced in the industry. Contaminants pose a greatest impact on our health are nitrogen oxides (NOx), particulate matter (PM) and tropospheric ozone (O3) (Aránguez et al., 1999), (Alonso, Rubio, Velasco & California, 2007).

The main source of anthropogenic emission both nitric oxide (NO) and nitrogen dioxide (NO2) - generally, known as nitrogen oxides (NOx) - is the burning of fossil fuels. These oxides negatively influence directly in the water and land quality they contribute to the formation of acid rain and favor the formation of O3 and particularized aerosols. The aim of this paper is to take advantage of photocatalytic oxidation (Vallée et al., 2004) in order to reduce NOx and other pollutants (Fujishima, Zhang & Tryk, 2007b) and sulfur oxides (SOX), volatile organic compounds and even carbon monoxide (CO) by fixing TiO2 with resins to the vehicle bodywork.

Photocatalysis process starts from the nature's principle of decontamination and is produced by a photochemical reaction that converts the energy from sunlight into chemical energy in the surface of a catalyst, being this a semiconductor material, thus accelerating the speed reaction. The catalyst is the compound which causes the reaction acceleration. The photocatalysis phenomenon was discovered in 1971 (Fujishima & Honda, 1971) and, since then, has attracted huge interest, but its application in everyday life has not taken place until the last decade. Photocatalytic oxidation of NOx to nitrates NO3- (Ballari, Yu & Brouwers, 2011) produces a series of reaction products in the form of NO3- in low concentrations which can be removed from the surface on which they are formed through the rainwater (Asociación Ibérica de Fotocatálisis, 2014).

There are multiple semiconductors with photocatalytic function such as ZnO, Fe2O3, CdSe, CdS and TiO2, among others. (Li, Zhu, & Li, 2012). The photocatalyst that has been chosen is titanium dioxide (TiO2) due to its greater availability and efficiency under sunlight. The TiO2 is a clean, photostable product, and do not pose a negative impact on environment. It presents three polymorphic forms under atmospheric pressure: rutile, anatase, and brookite. The rutile phase is the only one stable, whereas the anatase and brookite phases are metastable and irreversibly change into rutile by heating. The crystalline structure of TiO2, that shows a higher photocatalytic activity, is anatase, which is used routinely for environmental decontamination applications. Because of the differences in their network structures, rutile and anatase have different mass densities and electronic band structures (Balaguru & Chong, 2006a).

TiO2 photocatalytic properties are based on their optoelectronic properties. Since it is a semiconductor, it is capable of absorbing photons having enough energy to transfer electrons from the valence band to the conduction band (De Lasa, Serrano & Salaises, 2005). Absorbable photons are in the surrounding ultraviolet region of the electromagnetic spectrum corresponding to a band-gap of 3.2 eV. (Maury & De Belie, 2010). TiO2 is a semiconductor that absorbs radiation in the UV-Visible range (315-380 nm UV and visible 380-780 nm). According to different authors, the anatase crystalline phase of TiO2 is in a band-gap of 3.2 eV corresponding to a wavelength of approximately 380 nm; while the rutile crystalline phase has a band-gap of 3.0 eV corresponding to a wavelength of 413 nm. UV absorption creates electron-hole pairs that are responsible for the formation of radicals and generated species on the surface of TiO2 (Maury & De Belie, 2010). Thus, after this process, the TiO2 acquires an oxidizing profile which is able to degrade the organic molecules deposited on its surface. A reference to the oxidizing potential of the species formed convey us the proof that hydroxyl radicals are the highest oxidizers after fluorides radicals. The reactions that occur during this process are (Bordes, Moreno, Bou, & Sanz, 2007):

$$TiO_2 \xrightarrow{hv} TiO_2(h_{vb}^+ + e_{eb}^-) \quad (1)$$
$$h_{vb}^+ + OH^- \rightarrow HO^+ \quad (2)$$
$$e_{eb}^- + O_2 \rightarrow O_2^- \quad (3)$$
$$2O_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (4)$$
$$H_2O_2 + e_{eb}^- \rightarrow HO^{\cdot} + OH^- \quad (5)$$

Where: $e_{eb}^-$ is an electron in the valence band; $h_{vb}^+$ is a hole in the valence band.

In the references section, we may find works about the application of TiO2 in cementitious materials and glass, and paving stones. Currently, we can find several materials being marketed and protected under patent using TiO2 photocatalytic properties of different materials; although their use is not yet widespread, photocatalytic products incorporate various sectors (construction, automotive, environment, energy and the field of medicine) their applications are still under investigation process or at a prototype development stage.

The TiO2 nanoparticles can be introduced in materials, mainly under anatase form, to obtain multifunctional self-cleaning properties and to prevent microbiological growth within the same properties, maintaining fungi and molds away from its surface as they exhibit a highly hydrophilic behavior. Over the evolution phase, we find additives, sealants, paints, and chemical solvents into construction materials, restoration and repair, but these practices are not sufficient due to the state of art of the effects of environmental pollutants and micro-organisms (Marinoni, Birelli, Rostagno, & Pavese, 2003); (Gaylarde & Gaylarde, 2005). The photocatalytic materials are also applied on the glass in self-cleaning treatments, self-fogging and anti-reflecting.

Current studies also indicate that the use of photocatalytic materials used in external environments, being exposed to sunlight, can easily oxidize pollutants absorbed on their own surfaces. Especially VOCs, CO, industrial emissions and, more specifically NOx. These contaminants represent a more direct hazard to our health. Therefore, the application of photocatalytic materials (heterogeneous oxidation) to solve pollution problems caused by NOx, by photochemical conversion thereof to nitrates (soluble compounds that can be carried by water from rain or irrigation (Guerrini, 2012) is a priority. It is noteworthy that the concentrations of NOx, usually low enough, even with high levels of conversion to nitrate, in order not to be a problem in the treatment in wastewater treatment plants of wastewater (WWTP) (Vallée et al., 2004).

The aim of this paper is to disclose the findings of research conducted about binding through resins applied to the outer bodywork of a vehicle, using thus this type of photocatalytic materials. The company currently markets the product Italcementi TxActive®, a photocatalytic active ingredient used in cement products that has the ability to reduce the level of organic and inorganic pollutants in the air, in addition to self-cleaning properties, creating a new dimension and contribution to construction industry, such as the ability to decontaminate the outer surfaces of buildings or pavements (Italcementi, 2009).

Moreover, the EUROVIA company is applying a product called Noxer® as a wall, flooring, and pavements coating whose primary function is the photocatalytic degradation of NOx gases using TiO2 as a photocatalytic principle for the degradation of these pollutants. This product is being applied mainly in France. These materials have in common that the active layer having the catalyst, possess a reduced thickness, so that the catalyst amount of is small too. This is the most expensive component that the final product will contain. Currently, the cost of the active photocatalytic TiO2 is high because it is produced mainly for research and development purposes. However, the enormous amount of research groups are working on the issue and the numerous publications listed annually on their applications, suggests that in the future the demand for these products will grow considerably and significantly shrink its price.

In the references section, articles dealing with the application of TiO2 in cement, mortar and/or concrete have been reviewed (Diebold, 2003); (Lackhoff, Prieto, Nestle, Dehn, & Niessner, 2003); (Mills & Lee, 2002), indoor and outdoor paving stones (Lackhoff et al., 2003); glasses (Lackhoff et al., 2003); (Puzenat & Pichat, 2003) and plastics and/or glass fibers (Pozzo, Baltanás & Cassano, 1997); (Choi, Ko, Park & Chung, 2001); (Mills & Lee, 2002); (Diebold, 2003). Moreover, none of them make reference to the study about the incompatibility of carrier material with the use of TiO2 as photocatalytic material. It should be noted that the commercial production of TiO2 has mainly focused so far in Japan. However this position is changing because of the interest in self-cleaning materials based on the technique of photocatalysis, large companies in the production of crystals in the United States, United Kingdom, and Europe. The addition of TiO2 in paints and cementitious materials placed at strategic locations where pollution has a significant presence, can contribute significantly to its reduction thereof (Balaguru & Chong, 2006).

## Methodology

Photocatalytic coatings of 600 nm-1μm show high activity, that is, in order to make photocatalytic oxidation reactions efficient, we need concentrations of TiO2 relatively low (Olabarrieta et al., 2012). To maintain a good photocatalytic efficiency of these materials, it is necessary that the following requirements are met:

- Relatively high concentration of NOx,
- Important daylight irradiation or an acceptable amount of UV radiation.
- To guarantee a minimum absorption of dirt and dust; either by applying the photocatalytic material so that a low surface roughness is obtained, or by regularly washing the surface to remove dust, nitrates, etc.

All these aspects are shown on the outside of a vehicle, and this is the main reason why the binding process to the vehicle's body has been suggested. Therefore, and after its study, we may validate or reject this application.

## Materials

For this study we have used EP14380020 patent: "Surface treatment of asphalt road pavements with a photocatalytic composition for the abatement of atmospheric pollutants" assuming that, being this as a water suspension, TiO2, and resin, greater effectiveness is achieved, as its application leads to water evaporation. Suspension is neutral because this way the components do not modify the added water pH at the time the water and the catalyst is dispersed. The pH of the dispersion of TiO2 in distilled water will be between 6-7 values depending on the concentration, when encountering the pH of the dispersion of the resin in distilled water between 7 and 8, the final pH of the mixture is between 6-8 depending on the concentration and water. The resin to be bound to the catalyst, a small amount of the content decreases the adhesion of the catalyst but an excessive content thereof makes their excess reducing partially or entirely cover the exposed surface and, thus, its effectiveness.

**Table 1.** Amount of $NO_x$ reduction depending on the concentration of $TiO_2$ and resin present in the mixture. Patent EP14380020, 2014

| $TiO_2$ (%w) | Resin (%w) | NOx reduced (%) |
|---|---|---|
| 0.8 | 1.0 | 14.3 |
| 1.6 | 2.5 | 10.2 |
| 3.2 | 5.0 | 8.2 |

**Application**

Two samples have been used for research purposes; the first one, after being treated with the product, was confined in a vacuum chamber for three months to prevent contact thereof with light and air. This sample is referred to below as Cover 3. The second sample (Cover 1), after being subjected to the application of the product, was again placed in the vehicle and has been circulating exposed to both light and water, and pollution, checking the effectiveness of the product under normal conditions in the city of Madrid. The car even has undergone industrial equipment washing three times. Initially, the direct application of the product was performed with a brush over the tops of the fuel tank of a vehicle Opel Combo (See Figure 1). As shown in Figure 1a, adherence of the product to fuel covers at first vehicle was negligible. This was due to the surface treatment of the wax-based vehicles. After completing the withdrawal by using a detergent cleaning pad, the result was satisfactory.

**Figure 1. a**) Direct application of the product over the covers of the fuel, b) Cover 1 placed on the vehicle after applying the photocatalytic material. Own Research, 2014

a b

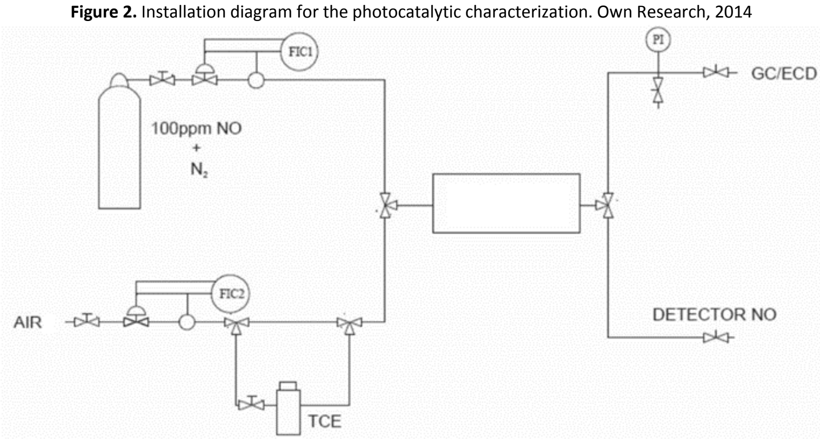
After applying photocatalytic composition and drying the Cover 1, it was placed back into the car and started to drive with through the streets of Madrid see Figure 1.b.

## Metodology

**Photocatalytic Reactor**

As for the experimental facility for conducting the tests, it has been followed the UNE-ISO 22197 policy; using the chamber in which the sample is placed, and a series of devices shown in Figure 2 in which photocatalytic tests have been carried out. The supply of NO to the equipment is done by using pressurized bottles with NO in N2. NO is unstable in air atmospheres and bottles would be stable for only a few days. Therefore, the flow coming from the bottle is mixed with an air stream which also provides a certain concentration of trichlorethylene as a model compound of volatile organic compounds.

**Figure 2.** Installation diagram for the photocatalytic characterization. Own Research, 2014



Samples were sent to laboratories Cartif located in Valladolid (Spain), testing according to the standard (although this indicates that the samples have to be subjected to ultraviolet radiation for at least 5 hours to decompose the residual organic material of the sample to be treated; Cartif laboratories have developed a similar test with a shorter duration, with proven similar results). The Cartif equipment is as shown below:

- Air mass flow controllers: Brokhorst EL-FLOW0-10NL/min.
- Mass flow controller of $N_2$+NO: Brokhorst EL-FLOW0-250NmL/min.
- Analyst NOX: ECOPHISICS CLD 700 AL.
- UV Lamp: PHILIPS TL-K 40W/05.
- UV Radiometer and Probe: HAMAMATSU C6080-03.

***Calculation of $NO_x$ reduction***

According to the UNE-ISO 22197 policy, the calculation of NOx gas reduction is performed according to the following formulation:

$$n_{NO_X} = n_{ads} + n_{NO} - n_{NO_2} - n_{des} \qquad (6)$$

Where: $n_{NO_X}$ is the amount of absorbed NOx (µmol); $n_{ads}$ is the amount of NOx absorbed by the sample (µmol); $n_{NO}$ is the amount of NOx reduced by the sample (µmol); $n_{NO_2}$ is the amount of NO2 generated by the sample (µmol); $n_{des}$ is the amount of NOx desorbed by the sample (µmol)

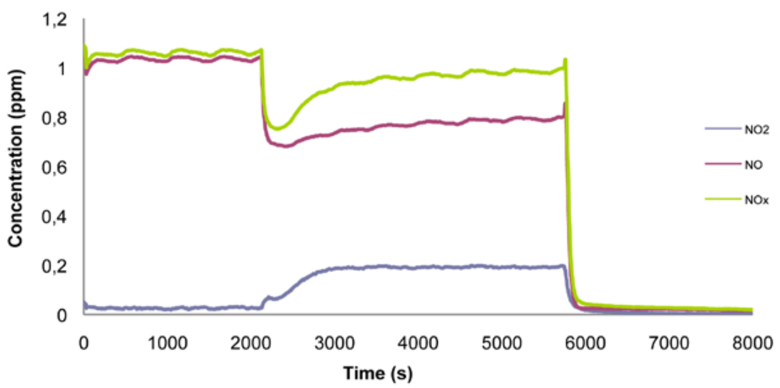
## Results

As shown in Table 2, NOx reduction in the Cover 1 sample is 6.3%. In Figures 3 and 4, we can observe the photocatalytic reaction graph in the Cover 1 as well as the full test graphically shown.

**Table 2.** $NO_x$ reduction in Cover 1. Cartif, 2014

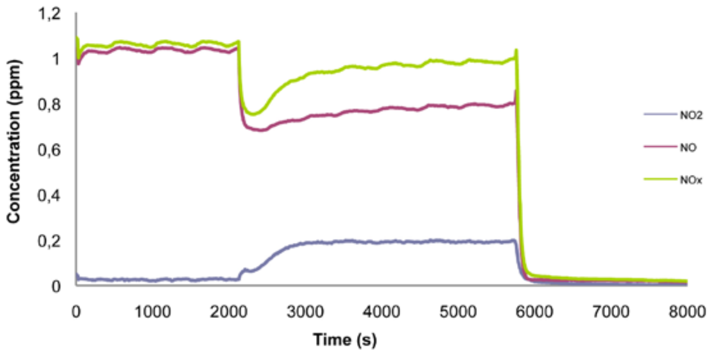
| Duration (min) | $NO_2$ (ppm) | NO (ppm) | $NO_x$ (ppm) | $NO_x$ reduced |
|---|---|---|---|---|
| 0 | 0,050 | 1,039 | 1,090 | |
| 5 | 0,027 | 1,025 | 1,052 | |
| 25 | 0,023 | 1,026 | 1,049 | |
| 30 | 0,030 | 1,037 | 1,068 | |
| 35 | 0,025 | 1,042 | 1,067 | 0,1% |
| 80 | 0,193 | 0,790 | 0,984 | 6,2% |
| 85 | 0,191 | 0,791 | 0,982 | 6,4% |
| 90 | 0,189 | 0,792 | 0,982 | 6,4% |
| Average | 0.191 | 0.791 | 0.983 | 0.063 |

**Figure 3**. Graph of the photocatalytic reaction in Cover 1. Cartif, 2014




After performing tests, and after Cover 1 sample manual cleaning, these showed almost identical results to those found in Cover 3 sample or pattern.

**Figure 4.** Graph of the complete photocatalytic reaction test in Cover 1. Cartif, 2014




Cover 3, that had been kept in a vacuum chamber away from external agents, has also been subjected to direct exposure of NOX and placed into the photocatalytic system, and as shown in Table 3, the results of NOX reduction obtained are close to 20%.

**Table 3.** $NO_x$ reduction in Cover 3. Cartif, 2014

| Duration (min) | $NO_2$ (ppm) | NO (ppm) | $NO_x$ (ppm) | $NO_x$ reduced |
|---|---|---|---|---|
| 0 | 0,037 | 0,995 | 1,033 | |
| 5 | 0,027 | 1,004 | 1,032 | |
| 25 | 0,027 | 1,010 | 1,038 | |
| 30 | 0,025 | 0,992 | 1,017 | |
| 35 | 0,043 | 0,828 | 0,872 | 14,3% |
| 80 | 0,182 | 0,645 | 0,828 | 20,2% |
| 85 | 0,199 | 0,643 | 0,842 | 18,9% |
| 90 | 0,202 | 0,638 | 0,841 | 19,0% |
| Average | 0,194 | 0,642 | 0,837 | 0,194 |

**Figure 5**. Graph of the photocatalytic reaction in Cover 3. Cartif, 2014

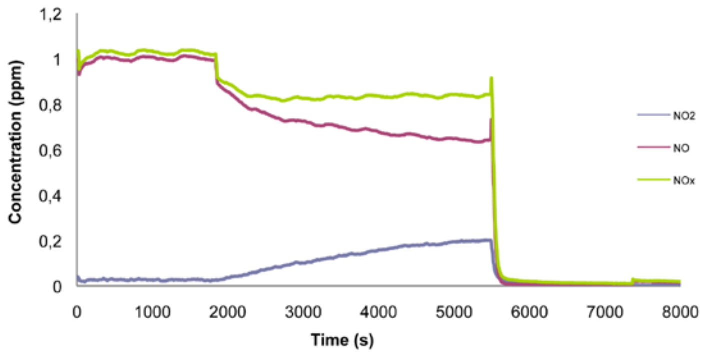
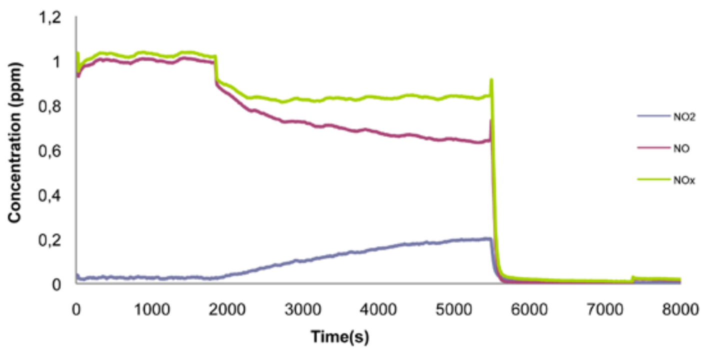



**Figure 6.** Graph of the complete photocatalytic reaction test in Cover 3. Cartif, 2014



In Figures 5 and 6, we can observe the photocatalytic reaction graph in Cover 3 as well as the full test graphically shown.

## Conclusions

The patent used is projected to be applied on bituminous pavements, and the resin that contains and binds the titanium dioxide to the pavement is the most suitable for this type of surfaces. While having very good results in this application, it might be useful to analyze whether there is even any other more appropriate. Because there is good adhesion between the product and waxes applied to the vehicle bodies, it is required to proceed, beforehand, to their removal by cleaning. The product used does not involve significant losses after simulating normal conditions of use.

Considering the numerical value, the NOx reduction lowest data exceeds the standard value of currently marketed products (6% of decontamination efficiency ceramic tiles and some paints). This nearly triples by eliminating aesthetic treatments (waxes) incorporated by carwash tunnels. In any event, although these waxes significantly reduce the effectiveness of the product, it may be possible to apply the photocatalytic product at larger scale, on the rooftops of city buses adapting washing machines equipment to this constraint. It would be desirable to study the reactivity of the product with the most common cleaning products on the market, in order to detect any sort of incompatibility.

It is being studied the color of the paint on which we apply the product, due to the crucial importance of light irradiation in the photocatalytic process and the fact that dark colors favor the absorption of light irradiation under which they are exposed.

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