# Research, Design and Development of a Photocatalytic Asphalt Pavement

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ABSTRACT

The increasing attention to environmental problems and roads traffic lead research to improve tests on new materials that could reduce the concentration of polluting substances in the air.

Some varieties of titanium dioxide ($TiO_2$) are known for their ability to perform as photocatalytic agents in the oxidation reactions and atmospheric pollutants decay, such as nitrogen and sulfur oxides, ozone and atmospheric particles components.

In collaboration with prestigious research Institutes, a photocatalytic technology, based on a water emulsion added with titanium dioxide, has been developed. Sprayed onto asphalt pavement surfaces, this product obtains a reduction of the concentration polluting substances and, at the same time, guarantees the mechanical characteristics required for pavements.

This technology foresees the photocatalytic applying system onto wide-spread surfaces located in very polluted areas such as road (pavement) surfaces.

Particular attention was dedicated to the choice of the titanium dioxide type in order to obtain the highest effectiveness related to the use conditions, to the adhesive and antiskid characteristics of the dioxide dispersed matrix. This scope was achieved with the application of a very thin film that assures the original flexibility and mechanical resistance.

The tests were performed in laboratory and in real-scale fields with particular attention to the:

- percentages of $NO_x$ reduction in the air using pure TiO2 or photocatalytic mix;
- visual, environmental and health impacts of the products;
- determination of the best technology application;
- field tests in order to evaluate the products behavior on a real scale analysis;
- evaluation of the effective life of treated pavements compared to normal bituminous pavements.

The final products were then verified in order to determine the interaction between the emulsion and the bituminous mixture, to evaluate safety during application and life-cycle, to assess physical and mechanical characteristics and to check the technology of application and photocatalytic behavior in polluted environments.

Pavements Applications in the Milano hinterland have also been carried out and tested.

## 1. Introduction

Research has always been the basis of human evolution: starting from “how to obtain heat with fire”, how to “bring heavy loads with wheeled-vehicles”, how to “fight diseases with medicines”, until the use of electronics and new technologies for innovative materials production.

The same steps had been carried out in the development of road materials in order to improve the mechanical performances and maintain the aesthetic characteristics: from macadam to modified bituminous mixtures, sound-absorbing covers and colored pavements. “What’s next for the future?”

The industrialized World "is fighting" with a great set of environmental problems that are linked to the hazardous wastes remediation, contaminated groundwastes and noxious air contaminants.

In the last decade, technological progress, on one side, and increasing request of mobility, on the other side, brought to the necessity of finding out a solution to the environmental problems; the main target widely changed and enlarged: the environment became the reference points and the pollution the most urgent problem to be solved.

In light of these considerations, a new research has been develop in collaboration with important research Institute particularly with the "Politecnico di Milano" and the "Chemical Department of the Università "La Sapienza" di Roma".

## 2. Air Pollution

*Figure 1. ENVISAT*

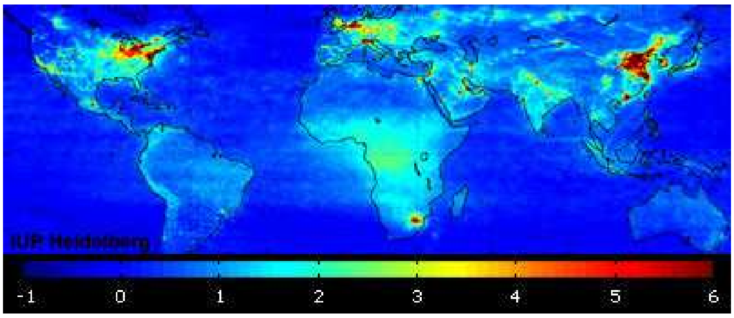


*Figure 2. World areas more polluted*

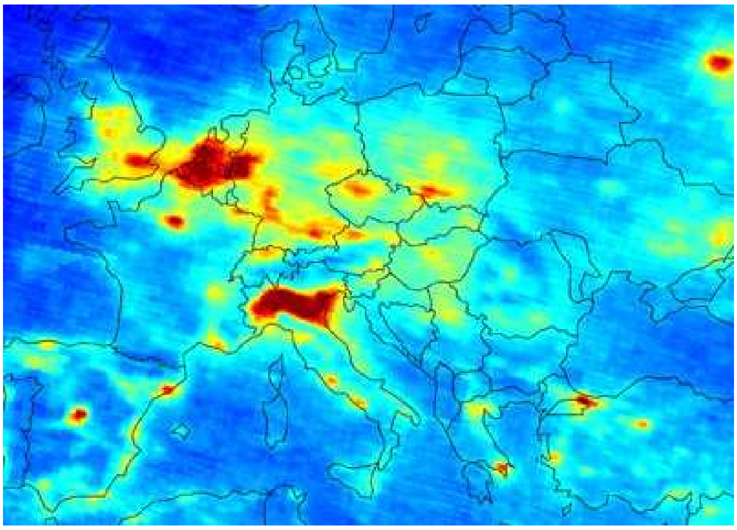

*Figure 3.European areas more polluted*

The European standards of pollutants emissions are almost never respected (Zampetti, 2006) and air pollutants have a negative effect on the respiratory and cardiovascular system.

Recently, a World Health Organization (WHO) research underlined that pollution is responsible for 100.000 deaths each year in the European area. Actually, atmospheric pollution represents the first factor of environmental risk in Europe and the eight total cause of death. The study result suggests that even a small reduction of the pollutants concentration in the air can have a relevant positive effect on health and mortality (Crebelli, 2003).

The air pollution situation on the Earth is monitored since 2002 by the ESA (European Space Agency). For this scope is used ENVISAT (Fig. 1) that is the world largest satellite for environmental monitoring and its "Scanning Imaging Absorption Spectrometer" onboard permits to record the sunlight spectrum shining through the atmosphere and, then, to control the spectral absorption of trace of gases in the air (ESA, 2009). The areas more polluted are underlined in red in the map (Fig. 2-3).

An air pollutant is a substance that can cause harm to humans and to environment. It's can be solid, liquid or gas.

Known as primary pollutants for their direct origin from combustion, the most common pollutants are the carbon monoxide and carbon dioxide, azote monoxide, sulfuric anhydride, dusts and unburned hydrocarbons. If subject to chemical-physical processes, these primary pollutants turn into secondary ones such as the azote dioxide, ozone, etc., which are more dangerous for the environment (Tab. 1).

The principal polluting sources are (Legambiente, 2001):

- vehicular traffic (NO; $NO_2$; CO; $CO_2$; PM10; H-CHO; NMHC);
- thermoelectric central and heating ($SO_2$);
- agriculture and breeding ($NH_3$, $CH_4$);
- solvents (VOC - volatile organic compounds).

***Table 1. Annual average production of $NO_2$, $CO_2$ and PM10 – (Zampetti, 2006)***

| STATE | % $CO_2$ EMISSION |
|---|---|
| USA | 19,0 |
| Cina | 11,9 |
| Giappone | 9,4 |
| Germania | 3,9 |
| India | 3,4 |
| Africa | 3,2 |
| Sud America | 2,7 |
| Regno Unito | 2,5 |
| Canada | 1,8 |
| Italia | 1,8 |
| Oceania | 1,3 |

| EUROPEAN CITY | EUROPEAN STATE | $NO_2$ - annual average [µg/m$^3$]* | PM10 - annual average [µg/m$^3$]** |
|---|---|---|---|
| Antwerp | Belgium | 47 | nd |
| Berlin | Germany | 62 | 36 |
| Brusells | Brusells | 87 | Nd |
| Copenhagen | Denmark | 52 | 41 |
| Stockholm | Sweden | 50 | 41 |
| London | U.K. | 110 | 43 |
| Madrid | Spain | 86 | 40 |
| Paris | France | 104 | 42 |
| Roma | Italy | 81 | 54 |

* World Health Organization allowed limit = 52 µg/m3

***** World Health Organization allowed limit = 90 µg/m$^3$***

# 3. Titanium Dioxide

## 3.1. Characteristic and application

The main ingredient for a photocatalytic product is the titanium dioxide, an element that is the fourth easy-to-find material in the earth's crust and it has got powerful oxidizing properties.

Titanium dioxide is the naturally occurred oxide of titanium and its chemical formula is $TiO_2$. The most common form is rutile, followed by anatase and brookite (this one is the less used).

Anatase is obtained heating the amorphous form until 300°C, while, Rutile is obtained heating the anatase above 800°C (Bessergenev, 2005). Although the crystalline symmetry is the same for both minerals (Fig. 4-5), there isn't relation between the interfacial angles of the two minerals. Rutile is not suitable for photocatalysis because of its high thermodynamic stability (Sandrolini, 2002), while Anatase is the most investigated titanium dioxide type due to its characteristics (high photochemical reactivity and stability in aqueous system).

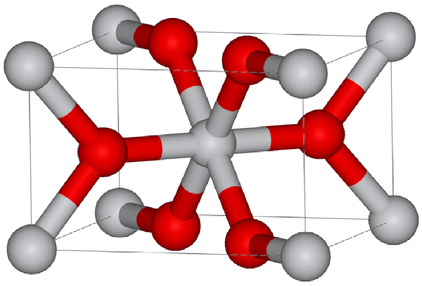

***Figure 4. Crystalline structure rutile***

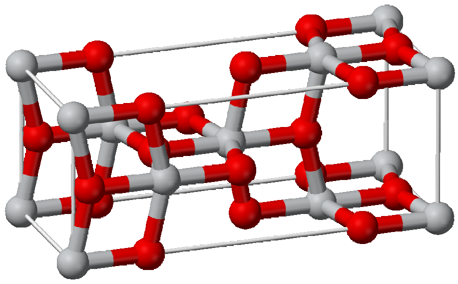

***Figure 5. Crystalline structure anatase***

Many variables influence this ability, especially the grains dimension and the presence of impurities .This implies the necessity of an accurate selection of the final product which is the basis of the research.

$TiO_2$ normally used has nanoparticles with a great specific surface (area to volume ratio) and diameter inferior to 100 nm.

The beginning of photocatalytic materials use was in the 1972: Fujishima and Honda photoinduced the decomposition of water on TiO2 electrodes.

$TiO_2$ is biologically inert on humans and animals and approximately 4 millions tons are consumed annually worldwide. The uses are manifold:

- for water and air purification (photo-assisted degradation of organic molecules and destruction of bacteria, viruses, photosplitting of polluted water and purification atmospheric odours and toxins (Hoffmann, 1995));
- for fixation of CO2, decomposition of NOx and chlorofluorocarbons (Masakazu, 2000);
- for medical use (photo-sensitizer for photodynamic therapy for endobronchial and esophageal cancers (Gurr, 2005), for slow or halt the development of tumor cells (Diebold, 2002) and for the destruction of nucleic acid molecules as well as proteins (Paspaltis, 2006)).
- as pigments in foodstuffs, paints, ceramics, cosmetics or pharmacology;
- as a corrosion resistant coating, self-cleaning coatings and anti-foggy on car windshield, protective coatings of marble and optical coating;
- in solar cells for the production of hydrogen and electric energy, in electronic devices and as gas sensor (Toma, 2008).

The most important aspect for vehicular traffic is that $TiO_2$ degrades air pollutants at ordinary temperature using ultraviolet light irradiation.

If titanium dioxide gets also in contact with an alkaline surface, another chemical reaction is induced and it produces salts (calcium nitrates, sodium carbonates, limestone) and water, decreasing consequently the polluting component.

An additional attention should be paid on the type of titanium dioxide used.

### 3.2. Photocatalytic process

The photocatalysis is comparable to the chlorophyll photosynthesis and denotes the acceleration of a photoreaction by catalyst action (Desrosiers; Pardon, 2002) for a substance chemical transformation. When the titanium dioxide gets in contact with an hydrocarbon, or any oxidable substance, it gains a new electron from this substance, which oxides. At the end of each catalytic cycle, the catalytic substance remain unchanged.

The $TiO_2$ propensity to absorb energy from the solar UV was discovered during the late 1970s for practical purposes: a self-cleaning surface.

To obtain a photocatalytic process, it is necessary to consider that the titanium dioxide should be directly exposed to the light source.

The Sun electromagnetic radiation spectrum can be divided into (Fig. 6):

- ultraviolet (UV) = 100 ÷ 400 nm:
  - ultraviolet Vacuum (UVV) = 100 ÷ 200 nm;
  - ultraviolet C (UVC) = 200 ÷ 280 nm;
  - ultraviolet B (UVB) = 280 ÷ 315 nm;
  - ultraviolet A (UVA) = 315 ÷ 400 nm;
- visible (light) = 400 ÷ 700 nm;
- infrared = 700 nm to 1000 nm.

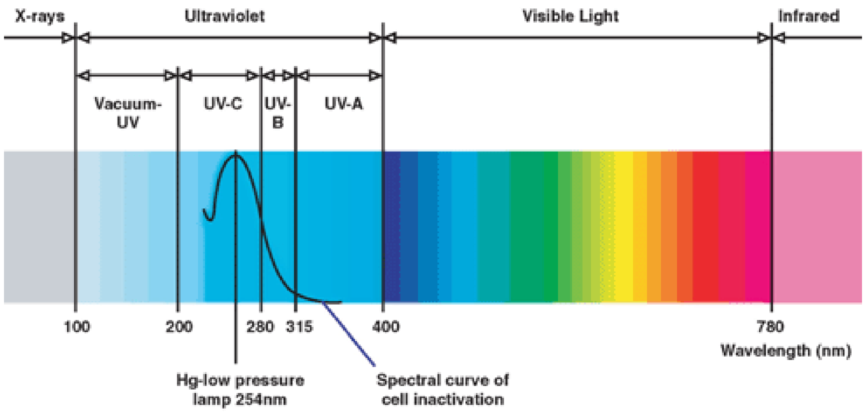


***Figure 6. Spectrum Solar***

Anatase is a semiconductor with a bang gap energy Eg = 3.2 eV, which is equivalent to a wavelength of 388 nm, that corresponds to the ultraviolet sunlight.

When $TiO_2$ is exposed to UV light of wavelength below 388 nanometers, in the presence of water vapour, two highly reactive substances are formed: hydroxyl radicals (OH-) and superoxide ion ($O_2$-) (Frazer, 2001). Particularly, when the $TiO_2$ is irradiated whit a energy > 3,2 eV (wavelength < 388 nm), the illuminated $TiO_2$ electron is excited from the valance band (VB) to the conduction band (CB), than two electrons (e-) and positive hole (h+) are formed, accordingly, the surface water is oxidized by positive hole, and $TiO_2$ can decompose and mineralise organic compounds by participating in a series of faster oxidation reactions leading to carbon dioxide (Huang, 1999):

$$TiO2 + hv \rightarrow h_{vb}^{+} + e_{cb}^{-}$$

The hole on TiO2 particle surface react whit adsorbed $H_2O$ or surface $OH^-$ group to form HO• radicals:

$$h_{vb}^{+} + H_2O\ (ads.) \rightarrow HO\bullet + H^{+} \quad \text{or} \quad h_{vb}^{+} + OH^{-}\ (sur.) \rightarrow HO\bullet$$

Than, superoxide ions are formed because excess electrons in the conduction band react whit molecular oxygen:

$$e_{cb}^{-} + O_2 \rightarrow O_2\bullet^{-}$$

and more HO• radicals are formed:

$$2O_2\bullet^{-} + 2H_2O \rightarrow 2HO\bullet + 2OH^{-} + O_2$$

Subsequently the photocatalysis "products" react. For example, approximately in presence of nitrogen dioxide, the reactions are (Giavarini, 2004):

$$NO_2 + HO\bullet \rightarrow HNO_3$$

$$2\ HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O$$

At the end of process (Fig. 7), a polluting product $(NO)_2$ has been transformed into a harmless and very soluble substance ($Ca(NO_3)_2$). The relative amount of soluble substance created is "ridiculous": the concentration for pavement unit is lower than a mineral water bottle.

At the moment there is a "second-generation titanium oxide photo catalysts" that has a ion-implanted (es. nitrogen ions); the main characteristic is that this catalysts are able to absorb visible light up to a wavelength of 400-700 nm.

The titanium dioxide efficiency can be verified with different testing methods:

- spectrophotometer (Mogyorosi, 2003);
- mass spectroscopy (Bessergenev, 2005);
- visible effect on a coating or treated mass (Guettai, 2005);
- crystalline structure (Toma, 2008);
- flow reaction system (Jinlong, 2002);
- degradation of formic acid diluted in water (Zhou, 2006);
- degradation of nitrogen dioxide (EN UNI 11247).

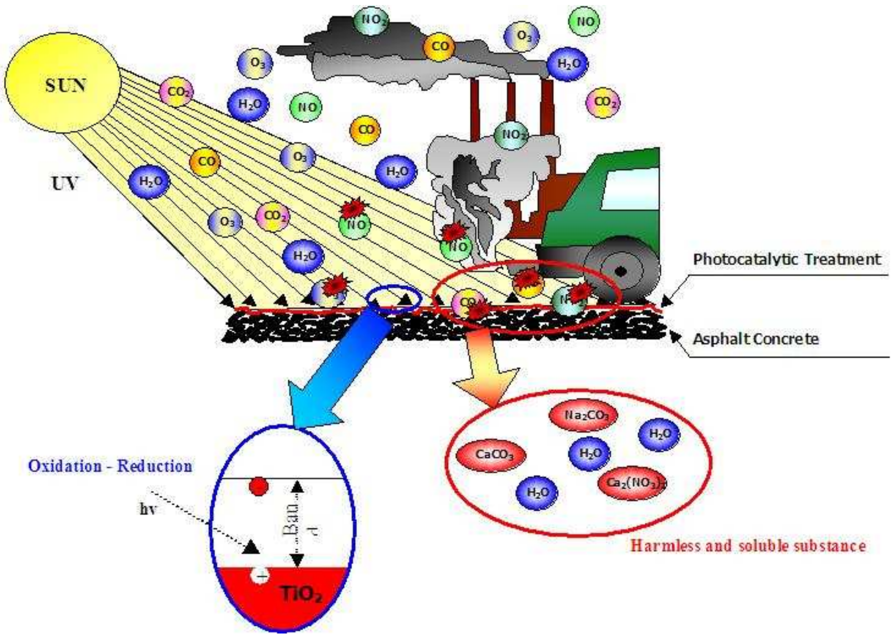


***Figure 7. Photocatalytic process***

# 4. Research for photocatalytic products for superficial asphalt surface treatments

## 4.1. Research protocol and tests

The main aim of the research on photocatalytic product was to develop a superficial treatment for asphalt concrete surfaces that could:

- decrease the concentration of atmospheric pollutants in the air;
- guarantee the adhesion between wheels and pavements in order to guarantee road-safety;
- maintain the functional and mechanical characteristics of original pavements (for example: permeability, colour and bearing capacity).

The research was developed following these principles and circumstances:

- the treatment should be applied onto asphalt concrete surfaces;
- the worst atmospheric conditions are in absence of rain and wind;
- the testing machines (analyser and climatic chamber) and the testing protocol should have sufficient sensibility to verify the differences among dissimilar products.

It is important to underline that the experimentation started in January 2006 when Italian regulation references did not provide any specific law for this kind of tests. Therefore, the climatic chamber had been designed in order to verify specimens of big dimensions (50x70 $cm^2$) and a specific testing protocol had been written (Alpha Protocol).

After this approaching phase, which included a series of calibration tests, the UNI 11247 ( Determinazione dell'attività di degradazione di ossidi di azoto in aria da parte di materiali inorganici fotocatalitici) was published in December 2007 with specific reference to photocatalytic inorganic materials. According with the new regulation, both the climatic chamber and the Alpha Protocol have been improved and implemented in a "new little climatic chamber for core" an in the "Beta Protocol".

The "new little climatic chamber for core" allows to determine the NOx reduction for a specimen of dimensions ($\phi$ = 10 cm ).

The final "Beta Protocol" has been compiled considering that:

- the final product should be laid on to asphalt concrete pavements and that the binder is organic;
- the superficial porosity of a asphalt concrete pavement is higher than a concrete or ceramics pavement;
- wind speed should be almost equal to zero;
- the relationship between treated surface and the chamber volume should reflect the roads reality;
- the atmospheric situation should be realistic from a pollution point of view, as for temperatures, humidity and wind;
- the commercial characteristics of polluting gas.

The Beta Protocol resulted more sensitive and useful to satisfy the technical necessities. The sensibility was determined varying both $TiO_2$ contained in the mix and the polluting gas flow; maintaining mix quantity for square meter, irradiance and humidity constant. The tests underlined that minor it is the polluting gas flow, great it is the test sensibility (Fig. 8).

The Beta Protocol Procedure (Fig. 9) follows these steps:

1. pure titanium dioxide is tested in order to verify the photocatalytic ability;
2. primary materials are analysed in order to verify the visual, environmental and health impact;
3. primary materials with titanium dioxide mixture are tested to define the final products;
4. laboratory photocatalytic efficiency of each mixture is evaluated (Fig. 10-11);
5. mix calibration;

6. testing field are realized, both of small dimensions (100cm x 100cm) and large dimensions (entire road branches) for “test fields efficiency” and for the determination of colour, skid an durability (Fig. 12-13).

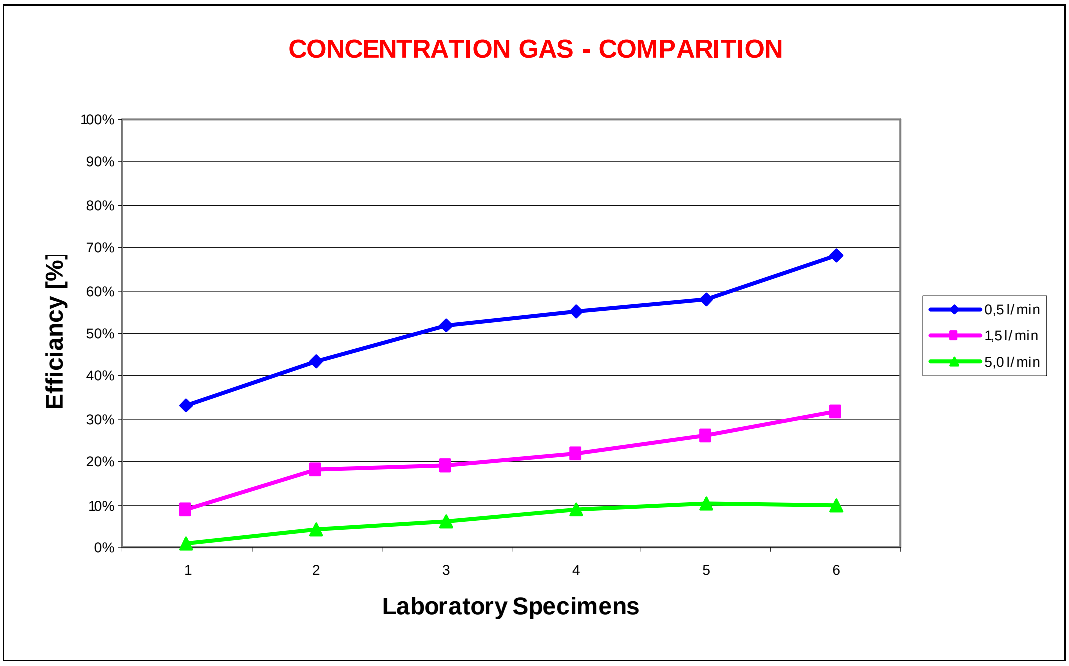


*Figure 8. Test for la determination of sensibility in faction of the polluting gas flow*

During every tests, only two parameters maintained constant:

- UVA laboratory irradiance = UVA solar irradiance = 20±1 W/m$^2$;
- conventional initial humidity = 50%.

Concerning the mix calibration, the procedure adopted is:

- determination of the optimal quantity $TiO_2$/m$^2$ (Fig. 14), maintaining constant quantity Mix/m$^2$ ($Q_c$), humidity (50%), irradiance (20 W/m$^2$) and polluting gas flow (1,5 l/min);
- determination of the optimal quantity Mix/m$^2$ (Fig. 15), maintaining constant quantity TiO2/m$^2$ ($QT_3$), humidity (50%), irradiance (20 W/m$^2$) and polluting gas flow (1,5 l/min).

With this procedure, like in an asphalt concrete, the optimal percentages of $TiO_2$ and mix have been calculated for surface unit.

Until now, the amount of works carried out is represented by:

- pollutant gas used: 1100 l, equivalent to 153 m$^3$;
- analysed specimens: 2200;
- small dimensions testing fields: 80;
- large dimensions testing fields: 9;
- current projects: about 100.000 m$^2$.

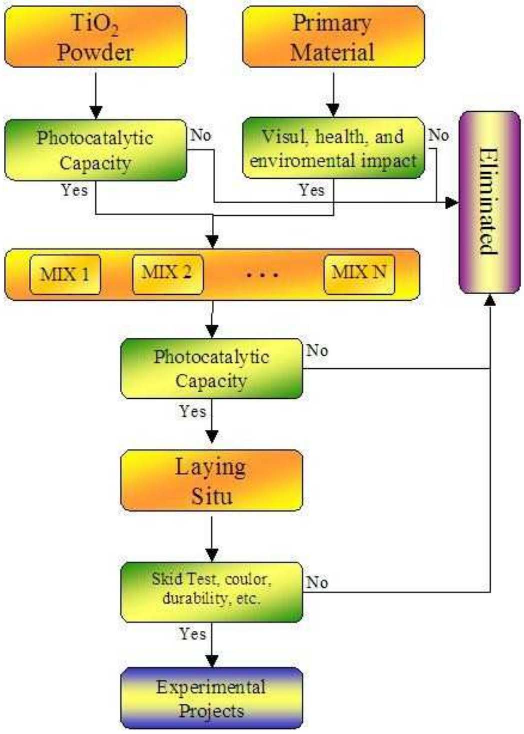


*Figure 9. Flow chart for the tests*

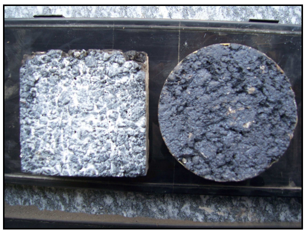

*Figure 10. Laboratory specimens*

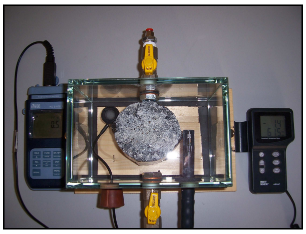

*Figure 11. Climatic chamber*

*Figure 12. Test field and situ specimens*

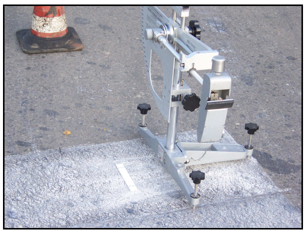

*Figure 13. Skid test in situ*

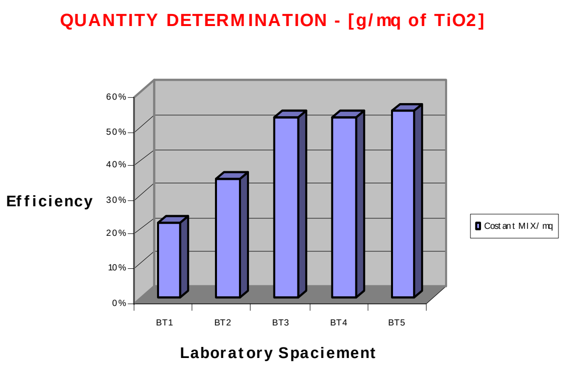


*Figure 14. Determination of TiO2/m²*

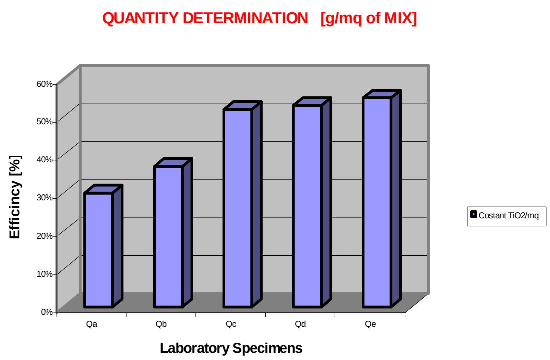


*Figure 15. Determination of Mix/m²*

### 4.2. Research Results

From the data collected it can be reassumed that:

- not every type of titanium dioxide shows a sufficient photocatalytic efficiency, even considering the same crystalline structure;
- photocatalytic products, even if realized with active titanium dioxide, not always show sufficient photocatalytic ability because different primary materials can inhibit the photocatalytic action;
- not every photocatalytic product is suitable for pavements.

In support of this theories:

1. in the figures 19 are plotted three different kinds of titanium dioxide powder, maintaining constant quantity TiO2/m$^2$, initial humidity (50%), irradiance (20 W/m$^2$) and polluting gas flow (1,5 l/min). The results underline that: the first one does not show any photocatalytic efficiency, the second one shows a reduction of the 81,6% of pollutants and the last one shows a $NO_X$ reduction of the 37,7% (furthermore, the analyser can verify not only $NO_x$, but also concentration of NO and $NO_2$ separately in function of time (Fig. 16÷18));
2. in the figure 20 are plotted three different kinds of photocatalytic product, maintaining constant quantity e quality $TiO_2$/m$^2$ (efficiency = 81,6%), quantity Mix/m$^2$, initial humidity (50%), irradiance (20 W/m$^2$), polluting gas flow (1,5 l/min) and varying the primary material. The results highlight that: the first one shows a photocatalytic efficiency of the 20,4%, the second 33,5% and the last one shows a $NO_X$ reduction of the 57,4%;

From the obtained research results it can be assured that, in general, the best catalytic products have an efficiency middle equal to:

- laboratory specimens: 50÷70%;
- cores taken from testing fields: 50÷55%.

The comparison between specimens taken from sites and prepared in laboratory showed different percentages of reduction due to the different preparation methods and it is importance to say that the reference values are those taken from testing fields, while the data collected from laboratory specimens are useful to determine the best titanium dioxide and the best mix.

An important statement investigated during the research was the spray laying temperature that influences the catalytic efficiency and the adherence "pneumatic-pavement treated". In fact the realization of the photocatalytic treatment can be made directly after the asphalt laying-phase (hot-method) or on already existing pavements (cold-method), but the mixes e laying procedures cannot be the same.

Particularly, for hot method the process is:

1. pavement laying and rolling;
2. spraying the micro-emulsion when the heart of the pavement temperature is over 100°C. The application is carried out with a specific instruments applied onto a light vehicle;
3. rolling to smooth the surface;
4. cores extraction to verify the efficiency in laboratory.

From the point of view of the efficiency, the two laying methods don't show different results, but for adherence the results show that (respect no-treated surface):

- hot-method: reduction of 3÷5 BPN
- cold-method: reduction of 6÷8 BPN.

The duration in time of the photocatalytic efficiency was verified through measurement of the adhesion in situ and on specimens taken from cores. These tests had been carried out through a specific calendar to determine the variation in time of the reference parameters. Road safety, especially from the point of view of adhesion, is verified in situ with the British Pendulum (CNR 105/85).

Figure 21 shows the results of a mix lain with the cold method. The testing field is subject to frequent heavy loads, to shearing forces (steering area) and the presence of sand that works as abrasive agent. This situations accelerate the BPN reduction: in fact the diminution from 75 BPN to 58 BPN happened in only 60 days. It has to be noted that a traditional pavement will reached this diminution only after 2 years of vehicular traffic. In the light of this consideration can be assumed that the 600 field test days are comparable with the about 1500 really road days (Fig. 22).

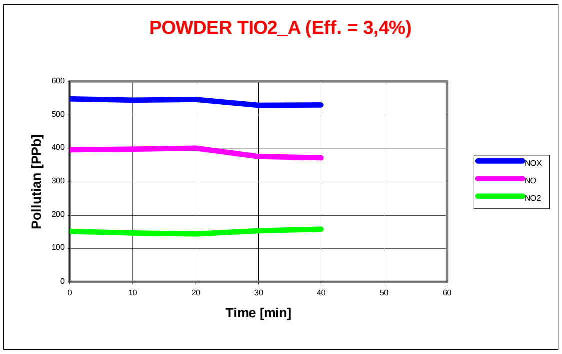


*Figure 16. Efficiency powder $TiO_2$_A*

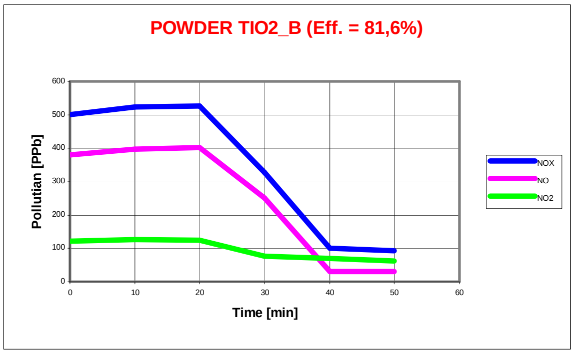


*Figure 17. Efficiency powder $TiO_2$_C*

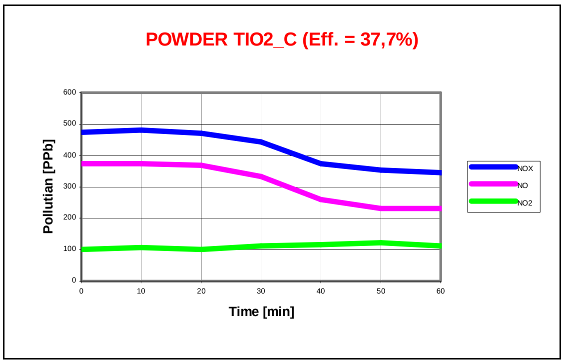


*Figure 18. Efficiency powder $TiO_2$_C*

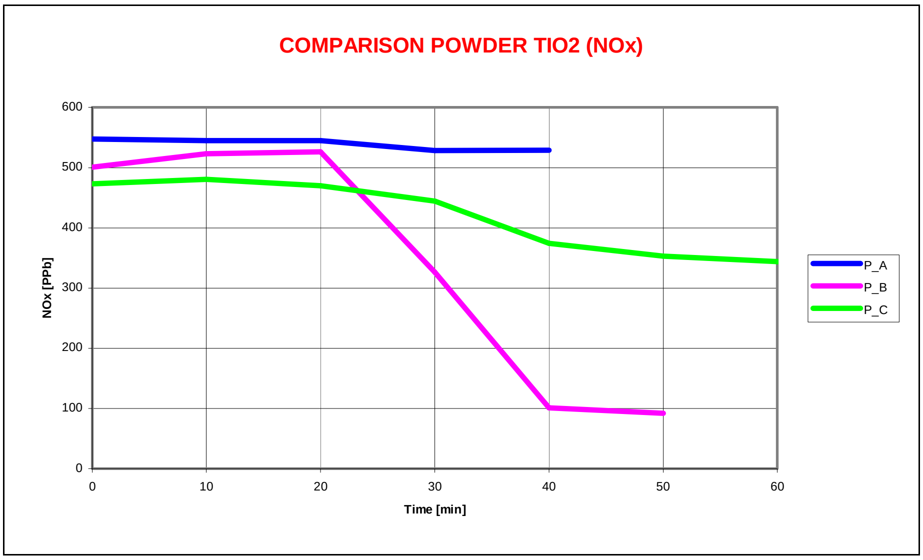


*Figure 19. Comparison efficiency powder TiO2 ($NO_X$)*

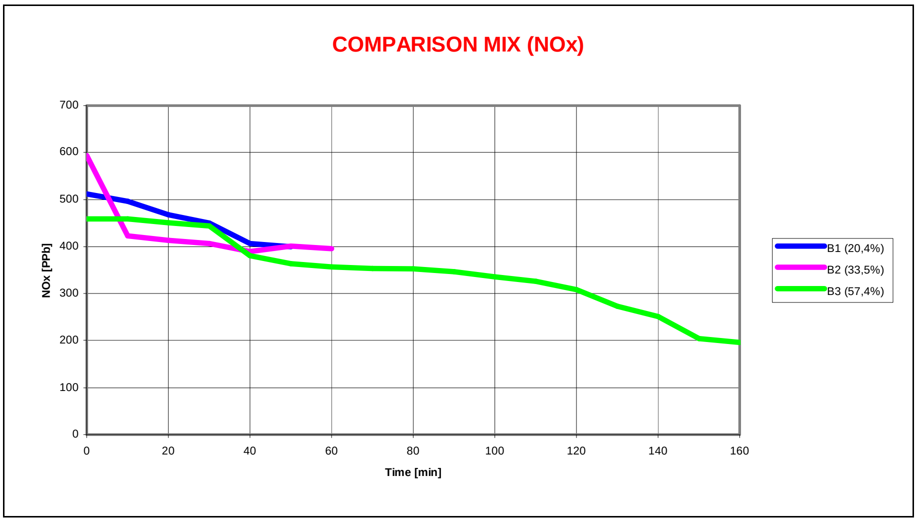


*Figure 20. Comparison efficiency Mix ($NO_X$)*

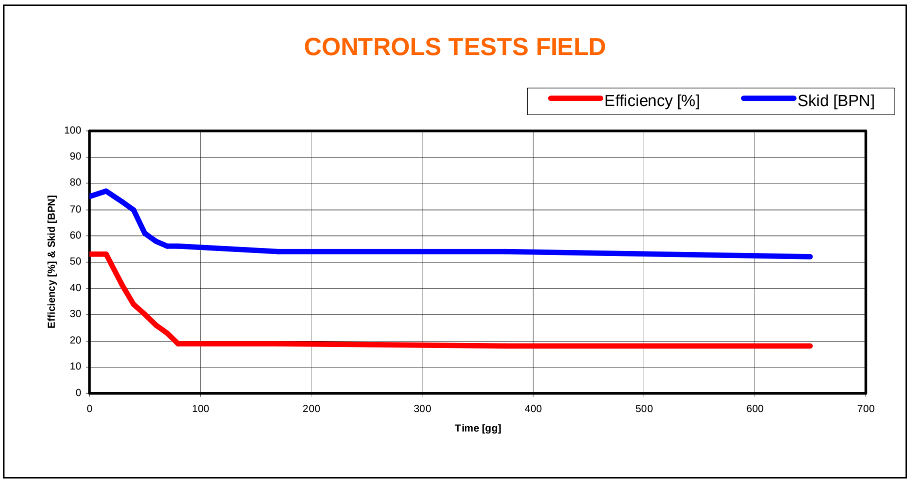


*Figure 21. Efficiency and Skid for the tests field controls*

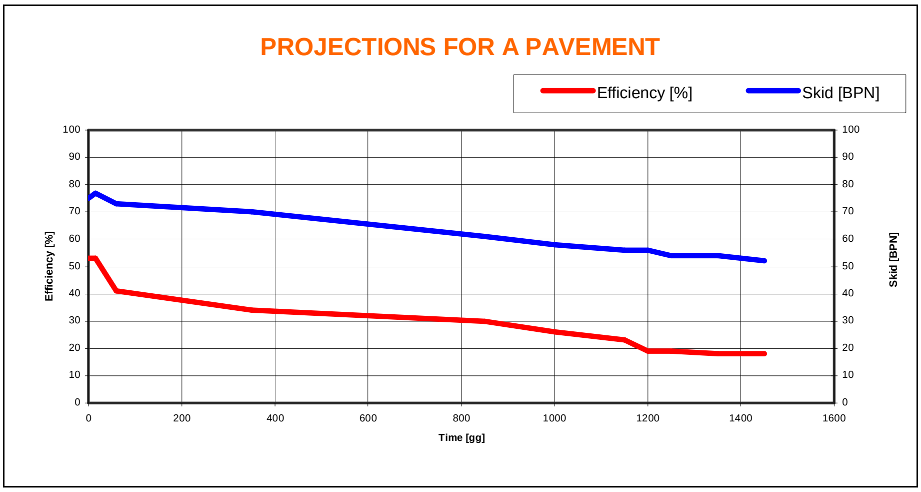


*Figure 22. Results projection for a real pavement*

The other important factors to be considered are the colour visual impact and the horizontal traffic sign visibility, directly correlated to the laying method.

The environmental impact has also been verified. The mix results suitable if it has a “positive impact”, or rather if it is not dangerous for its purposes. Furthermore, the treated asphalt pavements should have equal CER code than a traditional pavement: so to be recycled in the same way.

### 4.3. Same experimental project

a) The ANAS auto-park of Rogoredo, in the hinterland of Milan, is an experimental projects realized with the hot method onto an area of 4000mq (Fig. 23). The results showed a photocatalytic efficiency of the 49% in situ.

b) Another experimental project had been carried out onto the SP70 road in the province of Forlì-Cesena: 2500mq of new traditional pavement that showed an efficiency of the 46%. The research allowed to optimise the cold application on existing asphalt concrete pavements through new instruments able to control the pressure of spraying, guarantee uniformity and control the vehicle speed.

c) Other experimental projects, on existent pavements, had been realized: in Monza (Fig. 24), an efficiency of the 51% had been estimated and in Cantù of the 50%.

d) The oldest experimental project had been realized in the testing-site of Carpiano - Milano. While laying, high efficiency rates were registered; after 4 months, the efficiency was of the 48% and after 18 months of the 22%. The analysed pavement is heavy-loaded due to the frequent presence of heavy vehicles that also steer in the same area. Compared with the near traditional no-treated pavement, a ratio of 1:3 of the life-cycle of the pavement has been registered

***Figure 23. Spray treatment in Rogoredo***

***Figure 24. Treated Pavement in Monza***

## 5. Conclusions

The absence of a specific regulation leads to the necessity to measure the photocatalytic efficiency through a testing protocol that considers the organic nature of the bitumen, the necessity of an additional photocatalytic reduction in case of no wind and the porosity of the support.

Not every kind of titanium dioxide shows the same photocatalytic ability and not every titanium dioxide mix (with the same $TiO_2$) shows the same photocatalytic efficiency.

Naturally, the laboratory efficiency percentages are not the same that in situ, because of the environmental conditions are more varying in the time.

The photocatalytic efficiency is not the only characteristic to be evaluated, but also the safety characteristics and the environmental impact should be evaluated.

The catalytic project mix is a “water based microemulsion” to which titanium dioxide is added. The $TiO_2$ leads to the decreasing of atmospheric pollution, while the mechanical characteristics of the pavements are maintained. The normal life cycle is guaranteed and the environmental impact is positive (the mixture is neither dangerous nor toxic).

## 6. Future development

The future development of this technology should be referred to a better way of laying the product onto already existing pavements (cold method) from the adhesion point of view and the determination of the effective air pollutants reduction in situ.

## 7. References

Amemiya, S., (2004), Titanium-oxide photocatalyst, Three Bond Technical News January 1.

Arezzo, L., Cambiamenti Climatici: cause, effetti, soluzioni, Legambiente.

Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K., Taga, Y., (2001), Visible-light photocatalysis in nitrogen-doped titanium oxides, Science mag, Vol. 293.

Benedix, R., Dehn, F., Quaas, J., Orgass, M., (2000), Application of titanium dioxide photocatalysis to create self-cleaning building materials, Lacer No. 5.

Bessergenev, V.G., Pereira, R.J.F., Mateus, M.C., Khmelinksii, I.V., Vasconcelos, D.A., Nicula, R., Burkel, E., Botelho do Rego, A.M., Saprykin, A.I., (2005), Study of physical and photocatalytic properties of titanium dioxide thin films prepared from complex precursors by chemical vapour deposition, Elsevier: Thin Solid Films.

Chiara, S., (2008), Workshop in cantiere, Le Strade n°5.

Crebelli, R., Carere, A., (2003), Inquinamento atmosferico urbano: impatto sulla salute. Notiziario dell’Istituto Superiore di Sanità, Vol. 16.

Crispino, M., Lambrugo, S., (2007), An experimental characterization of a photocatalyticmortar for road bituminous pavement, RILEM Symposium on Photocatalysis, Firenze, Italia.

D’Elia, I., Contaldi, M., De Lauretis, R., Pignatelli, T., Vialetto, G., (2007), Scenari di emissione di inquinanti atmosferici in Italia, Ingegneria Ambientale n. 06, pp. 308-318.

Da Rios, G., Fiori, F., Lambrugo, S., (2008), Fotocatalisi per l’ambiente urbano, Strade & Autostrade.

Desrosiers, K., Ingraham, W., Van Matre, A., TiO2 photocatalysis for organics. Enve 436.

Diebold, U., (2003), The surface science of titanium dioxide, Elsevier: Surface Science Reports 48, pp. 53-229.

ESA (European Space Agency), (2009), Global air pollution map produced by Envisat’s SCHIAMACHY, News: Observing the Earth.

Frazer, L., (2001), Titanium dioxide : Environmental White Knight ?, Environmental Health Perspectives, Vol. 109, No.4.

Fujishima, A., Rao, T.N., Tryk, D:A., (2000), Titanium dioxide photocatalysis, Elsevier: Journal of Photochemistry and Photobiology C: Photochemistry Reviews 1, pp. 1-21.

Fujishima, A., (2005), Discovery and application of photocatalysis – Creating a comfortable future by making use of light energy - , Japan Nanonet Bulletin.

Giavarini, C., (2004) Il cosiddetto asfalto “mangia-smog”, Rassegna del Bitume, Associazione Italiana Bitume Asfalto Strade, Vol. 46.

Gouvea, C.A.K., Wypych, F., Moraes, S.G., Duran, N., Nagata, N., Peralta-Zamora, P., (2000), Semiconductor-assisted photocatalytic degradation of reactive dyes in aqueous solution, Pergamon: Chemosphere 40, pp. 433-440.

Grzechulska-Damszel, J., Morawski, A.W., Grzmil, B., (2006), Thermally modified titania photocatalysts for phenol removal from water, International Journal of Photoenergy, Vol. 2006.

Guettai, N., Ait Amar, H.; (2005), Photocatalytic oxidation of methyl orange in presence of titanium dioxide in aqueous suspension. Part I: Parametric study. Elsevier: Desalination 185, pp. 427-437.

Gurr, J-R-, Wang, A.S.S., Cheng, C-H-, Jan, K-Y., (2005), Ultrafine titanium dioxide particles in the absence of photoactivation can induce oxidative damage to human bronchial epithelial cells, Elsevier: Toxicology 203, pp. 66-73.

Guerrini, G.L., Peccati, E., (2007), Photocatalytic cementious road for depollution, RILEM Symposium on Photocatalysis, Firenze, Italia.

Hoffmann, M.R., Martin, S.T., Choi, W., Bahnemann, D.W., (1995), Environmental applications of semiconductor photocatalysis, Chem. Rev. 95, pp. 69-96.

Huang, Z., Maness, P-C., Blake, D.M., Wolfrum, E.J., Smolinski, S., (1999), Bactericidal mode of titanium dioxide photocatalysis, J. Photochem. Photobiol. A. Chem.

Ireland, J.C., Klostermann, P., Rice, E.W., Clark, R.M., (1993), Inactivation of Escherichia coli by titanium dioxide photocatalytic oxidation, Applied and Environmental Microbiology, Vol. 59, No. 5, pp.1668-1670.

Jinlong, Z., Bin, H., Anpo, M., (2002), Investigation of nano-titanium oxide photocatalysts for the decomposition of nitrogen oxide in the flow system, Chemistry Mag. Vol. 5, No. 5, p. 36.

Legambiente (2001), Inquinamento Atmosferico.

LumaSense Technology, Photocatalysis: http://www.lumasense.dk/Photocatalysis.pas.0.html

Maness, P-C., Smolinski, S., Blake, D.M., Huang, Z., Wolfrum, E.J., Jacoby, W.A., (1999), Bacterical Activity of Photocatalytic TiO2 Reaction: toward an Understanding of Its Killing Mechanism, Appl. Environ. Microbiol, v.65, pp. 4049-4098.

Masakazu, A., (2000), Utilization of TiO2 photocatalysts in green chemistry, Pure Appl. Chem., Vol. 72, No. 7, pp. 1265-1270, IUPAC.

Mills, A., Le Hunte, S., (1997), An overview of semiconductor photocatalysis, Elsevier: Journal of Photochemistry and Photobiology A: Chemistry 108, pp.1-35.

Mogyorosi, K., Dekany, I., Fendler, J.H., (2003), Preparation and characterization of clay mineral intercalated titanium dioxide nanoparticles, Langmuir, Vol. 19, No. 7, pp. 2938-2946.

Nosaka, Y., Matsushita, M., Nishino, J., Nosaka, A.Y., (2005), Nitrogen-doped titanium dioxide photocatalysts for visibile response prepared by using organic compounds, Elsevier: Science and Technology of Advanced Material 6, pp. 143-148.

Pardon, V., Emeline A.V., Serpone, N., (2002), Glossary of terms in photocatalysis and radiocatalysis, International Jourmal of Photoenergy.

Paspaltis, I., Kotta, K., Lagoudaki, R., Grigoriadis, N., Poulios, I., Sklaviadis, T., (2006), Titanium dioxide photocatalytic inactivation of prions, Journals of General Virology.

Poudyal, K., Clark, D., Brag., A., Titanium Dioxide Photocatalysis of Metals, ENVE 436-01, Hazardous Waste Management.

Sandrolini, F., Giordano, D., (2002) Il biossido di titanio nei materiali da costruzione antinquinamento ed autopulenti.

Sasaki, M., (2001) Development of photocatalytic TiO2 coated curtain, R&D Review of Toyota CRDL, Vol. 36, N.2.

Toraldo, E., Lambrugo, S., (2004), The optimization of photocatalytic mortar for road bituminous pavements, 4th Iconf, Tessaloniki, Greece.

Toma, F-L., Bertrand, G., Klein, D., Meunier, C., Begin, S., (2008), Development of photocatalytic active TiO2 surfaces by thermal spraying of nanopowders, Journal of Nanomaterials, Vol. 2008, Hindawi Publishing Co.

Venturini, L., Martignani, A., (2008), Coverlite: l’evoluzione del trattamento fotocatalitico, La Fiaccola, Lavori Pubblici n. 32.

Zampetti, G., Guadagnini, R., (2006), Mal d’aria di città 2007, Legambiente.

Zhou, J., Takeuchi, M., Zhao, X.S., Ray, A.K., Anpo, M., (2006), Photocatalytic decomposition of formic acid under visible light irradiation over V-ion-implanted TiO2 thin film photocatalysts prepared on quartz substrate by ionised cluster beam (ICB) deposition method, Catalysis Letters, Vol. 106.