Durability of Titanium Dioxide Photocatalytic Layer for Pavement surfaces

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The use of Titanium Dioxide (TiO_2) ultrafine particles as coating for concrete pavement have received considerable attention in recent years as these particles can trap and decompose organic and inorganic air pollutants by a photocatalytic process. In spite of these promising benefits, the durability and resistance to wear of TiO_2 surface coating has not been evaluated. The objective of this study was to determine the abrasion and wear resistance properties of TiO2 coatings and its effect on the coating's environmental performance. To achieve this objective, an experimental program was conducted to measure and compare the environmental performance of titanium dioxide coating before and after laboratory-simulated abrasion and wearing. Microscopic analysis was conducted using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) to determine the distribution of TiO_2 particles on the surface before and after wearing. The measured rut depth using the Loaded-Wheel Tester (LWT) was minimal indicating that the use of the coating did not appear to affect the wear resistance of the surface. Wearing of the specimens with 5% TiO_2 resulted in a small decrease in the coating NO removal efficiency. In contrast, the wearing of the samples with 3% TiO_2 slightly improved the NO removal efficiency.

Keywords: Titanium dioxide, sustainable concrete pavement construction, photocatalyst, nitrogen oxides.

Introduction

For the viability of national, state, and local economies, efficient operation of the US highway network is critical. The US is served by the world's largest highway system, including 6.3 million kilometers of streets, roads, and highways, as well as more than 570,000 bridges. Annually, this transportation system carries—at a level of $775 billion—over four trillion passenger miles of travel and 3.8 trillion ton miles of domestic freight, close to 11% of the Gross Domestic Product (GDP) (Federal Highway Administration, 2000). As no slowdown in freight transportation growth is in sight in the near future, it is imperative that innovative technologies that can improve the energy and environmental efficiencies of highway operations be introduced to ensure continuous growth of the economy.

While the importance of the national transportation network is well established, there is a growing recognition that highway operations have major environmental impacts during construction and service (U.S. Environmental Protection Agency, 1994); (World Bank, 1996). High traffic volumes cause high concentration of nitrogen oxides (NO_x) and volatile organic compounds (VOC) in the air, which have been linked with serious health hazards to the public. These pollutants may also travel long distances to produce secondary pollutants such as acid rain or ozone (Beeldens, 2006). Many organic compounds and air pollutants including nitrogen oxides and sulfur dioxide can be decomposed by ultraviolet (UV) radiation but this process is extremely slow. Photocatalysis compounds such as titanium dioxide (TiO_2) can accelerate this process by trapping and decomposing organic and inorganic particles from the air while removing harmful air pollutants such as NO_x, SO_2, and VOC in the presence of UV light (sunlight) (Hodgson, 2007), (Hassan, 2009). In addition, their hydrophobic properties allow them to self-clean in the presence of rain.

Photocatalysis compounds such as TiO_2 can be utilized to construct air purifying concrete pavements by integrating the nano-particles within the pavement surface. One method of application consists of blending TiO_2 with a

cementitious mortar mixture and applying it as an ultra-thin coating to the concrete pavement surface. Although this technology has the potential to support environmentally friendly road infrastructure, the durability and resistance to wear of TiO_2 surface coating has not been evaluated. This has been identified as one of the major obstacles preventing large-scale application of this technology (Berdahl, 2008). In addition, concerns were raised that the nano-sized particles may be removed by the action of vehicle tires and harsh service conditions (Beeldens, 2006). To this end, the objective of this study was to determine the abrasion and wear resistance properties of TiO_2 coating and its effect on the coating environmental performance. To achieve this objective, effects of tires' action and mechanical loading were characterized using an accelerated loading test and rotary abrasion (RA). The environmental performance of the coating was measured before and after wearing and abrasion. In addition, the resistance to wear and the presence of the nano-particles on the surface was identified using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) analysis. Results of this experimental program allowed us to estimate the abrasion properties of TiO_2 coating and its resistance to delamination and adhesion failure through tires' action.

Background

The potential of titanium dioxide as a photocatalyst was discovered by Fujishima and Honda in 1972 (Fujishima, 1972). This process, which is similar to plant photosynthesis, allows the decomposition of water into oxygen and hydrogen in the presence of light, by means of a TiO_2-anode according to the following reaction (Fujishima, 2000):

$$H_2O + 2hv \rightarrow 1/2O_2 + H_2$$

The oxidation of nitrogen oxide by means of this photocatalyst process is described as follows (Beeldens, 2006):

$$NO + \dot{O}H \xrightarrow{T_iO_2} NO_2 + H^{\cdot}$$

$$NO_2 + \dot{O}H \xrightarrow{T_iO_2} NO_3 + H^{\cdot}$$

Based on this heterogeneous photocatalytic oxidation process, nitrogen oxides are oxidized into water-soluble nitrates while sulfur dioxide is oxidized into water-soluble sulfates; these substances can be washed away by rainfall. Yet many other compounds can be used, titanium dioxide is low-cost and can remove a wide range of organic contaminants (Benedix, 2000). In pavement application, it is desirable to prepare a titanium dioxide coating with hydrophobic properties, which provide for a self-cleaning surface. Through the hydrophobic process, particles of contaminants adhere to water droplets in case of rain. These contaminants are then removed from the surface when the droplets roll of it.

The potential of using TiO_2 as an air purifier in urban and metropolitan areas, which suffer from high concentration of air pollutants, has been recognized in the literature (Benedix, 2000), (Poon, 2007). Being produced in a powder form, a number of research studies have suggested to use it in a thin film form and to apply it as a coating or slurry to various types of substrates including concrete pavement surface (Sopyan, 1996). Titanium dioxide have also been evaluated and patented as environmentally friendly cement (TioCem), architectural concrete (white cement), facade to buildings, and as concrete tiles (Yoshihiko, 2002), (Heidelberg Cement AG, 2008). One study suggested that the use of titanium dioxide in combination with a cementitious material improves SO_2 removal efficiency through action of the alkaline substratum (Crispino, 2007).

Evaluation of concrete pavements treated with titanium dioxide provided promising results as research shows that a thin surface coating is able to remove a significant portion of NO_x, SO_2, and VOC pollutants from the atmosphere when placed as close as possible to the source of pollution (Beeldens, 2006). The efficiency of this technology depends on the size of the surface exposed, the concentration of pollutants, air humidity, and the ambient temperature. Porosity of the surface is also important as the NO_x removal ability is improved as the porosity is increased. The deposition of pollutants on the surface was reported to decrease efficiency of removal but it can be regained through the self-cleaning mechanism (Beeldens, 2008). In spite of these promising benefits, applications of this technology are currently limited to building facades and gateway elements of bridges not subjected to traffic as in the case of the I-35W Bridge over the Mississippi River in downtown Minneapolis. The durability of this technology in pavement application needs to be established before large-scale practical implementation is undertaken.

Experimental Program

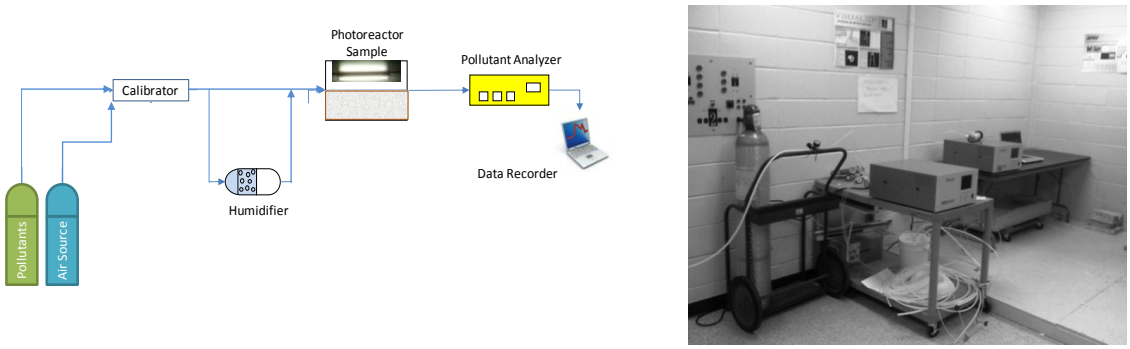
The objective of the experimental program was to measure and compare the environmental performance of titanium dioxide coatings before and after laboratory-simulated abrasion and wearing. For this purpose, laboratory prepared samples were subjected to wearing and abrasion using an accelerated loading test and rotary abrasion. The environmental efficiency of the original and loaded samples to remove nitrogen oxides from the atmosphere was measured using a newly developed laboratory setup. Microscopic analysis was conducted using scanning electron microscopy and energy dispersive spectroscopy to determine the concentration and distribution of titanium dioxide particles on the surface before and after wearing.

Laboratory Samples and Materials Tested

The substrate concrete samples were prepared based on a standard concrete mix design widely used in Louisiana that would achieve a compressive strength of 41MPa. The samples were poured into molds with dimensions of 305mm x 381mm x 25.4mm. The samples were cured by applying a curing compound for a period of seven days before being unmolded. Three replicates were prepared for each testing condition. A surface mixture consisting of ultrafine titanium dioxide, cement, filler (sand with a maximum nominal size of 1.18mm), and water was prepared. The sand aggregate was sieved to remove all fines with a particle size of 300µm or smaller. This is based on past research that showed that a coating with less fine particles result in higher porosity, and therefore improved NO removal efficiency (Poon, 2007). The surface mixture was prepared at a water-cement ratio of 0.6 and was applied to the concrete surface as a 10mm thick coating. A commercially available titanium dioxide nanomaterial (Cristal Millennium PC105) was used at a content of 3% and 5%.

Environmental Test Setup

An experimental setup was built in order to quantify the environmental efficiency of TiO_2 coatings in removing harmful pollutants from the air, Figure 1. The test set up was adapted from the Japanese standard JIS TR Z 0018 which is a test method for air-purification performance of semiconducting photocatalytic materials removal of nitric oxide (JIS, 2004). The setup simulates different environmental conditions by allowing for control of light intensity and air humidity. The pollutants are introduced through an inlet jet stream to a photocatalytic testing device. A zero air generator is used to supply the air stream, which is passed through a humidifier to simulate the desired humidity level.



(a) (b)

Figure 1: Illustration of the Experimental Laboratory Setup

The photocatalytic testing device creates an enclosed controlled environment where the light and the atmosphere can be simulated. Fluorescent lamps, attached to the photocatalytic device, are used to imitate natural sunlight radiation required for photocatalytic activity. The pollutants measured from the recovered air before the photocatalytic device and after allowed for determination of the absorbed level of pollutants. In this study, nitrogen-oxide removal efficiency was measured using the Thermo 42i chemiluminescent NO_x analyzer. The Thermo 146i Gas calibrator was used to supply a defined concentration of gas for the experimental setup at a controlled flow rate. Results

presented in this paper were obtained at room temperature (23°C) and at a relative humidity of 50%. Nitrogen oxide (NO) was blown over the surface at a concentration of 410ppb and at a flow rate 9 l/min. Testing was conducted for a total time of five hours; however, the photocatalytic process was only started after 30 minutes from the beginning of the test to ensure that steady concentration was reached in the environmental chamber.

Laboratory-Simulated Abrasion and Wearing

Wear and abrasion resistance properties of the titanium dioxide surface layer were measured using an accelerated loading test and rotary abrasion. The Hamburg-type Loaded Wheel Tester (LWT), which employs a scaled dynamic wheel passing back and forth over the specimen, was used in this study to simulate loading and wear of the applied coating. The wheel applied a load of 702N at a frequency of 56 passes per minute. Testing was conducted at room temperature under dry conditions, during which progress of surface rutting was monitored. After 20,000 cycles, the test was stopped and samples were obtained to examine the surface using SEM and EDS. A maximum allowable rut depth of 6 mm at 20,000 passes is used in LADOTD Specifications (State of Louisiana, 2000). Rotary abrasion (RA) was conducted using an in-house built device that conforms to ASTM C 944 and that is conducted using a Rockwell freestanding drill press. This test method uses a cutter rotating at 200 rpm under a constant load of 98N for 2 minutes to wear the coating surface. The abrasion resistance is determined by measuring the loss of weight in grams.

Scanning Electron Microscopy and Energy Dispersive Spectroscopy

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) were used in this study to investigate the distribution of TiO_2 in the coating surface before and after wearing. Sample preparation consisted of cutting a 25mm x 25mm specimen from the surface coating before and after durability testing. The samples were coated with a thin layer of carbon conducting film by evaporation. Microscopic analysis was conducted using a JOEL JSM-840A Scanning Electron Microscope at an acceleration voltage of 15kV. Existence and distribution of TiO_2 was determined using NIST/NIH Desktop Spectrum Analyzer (DSTA) software. The SEM images and the corresponding elemental maps were captured using the NIH imaging software to observe the microstructure and TiO_2 distribution in the coating surface.

Results and Analysis

Loaded-Wheel Tester (LWT) and Abrasion Test Results

Figure 2 presents the measured rut depth and its variation with the increase in the number of wheel cycles for the three specimen types (control with no coating, coating with 3% TiO_2, and coating with 5% TiO_2). As shown, the measured rut depth for the three specimens was minimal (less than 1mm) indicating that the use of the coating did not appear to affect the wear resistance of the surface. It is noted that failure in this test is defined at a rut depth of 6mm after 20,000 cycles for asphalt surface. Therefore, the three specimen types provided accepted resistance to wear. The loss of weight for the three specimen types in the LWT was 124.1g, 149.5g, and 114.8g for the control, 3% TiO_2, and 5% TiO_2 respectively. Wearing of the surface and loss of particles may be associated with a loss of mortar, fine, and TiO_2 nanoparticles. These results were investigated using SEM. Results of the rotary abrasion (RA) test followed the same trend with a loss of weight for the three specimen types of 0.01g, 0.2g, and 0.1g for the control, 3% TiO_2, and 5% TiO_2 respectively.

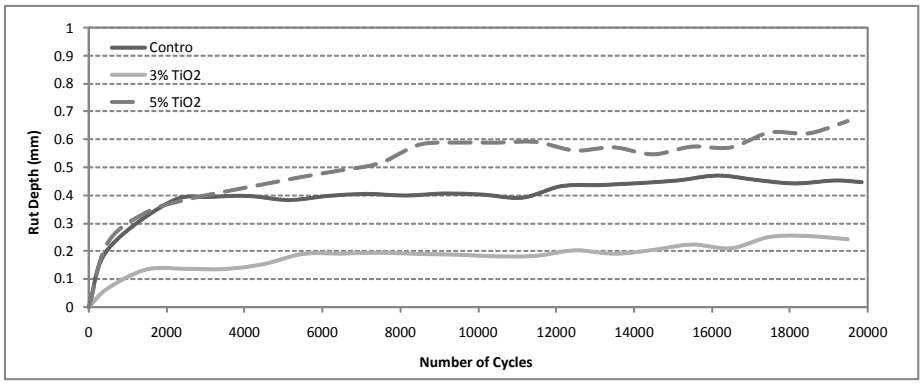


Figure 2: Measured Rut Depth in the Loaded Wheel Tester

Environmental Test Results

Figure 3 illustrates the variation of NO concentration during the course of the experiment for the coating with 5% TiO_2. The inlet concentration is 410 ppb. The UV light is turned on 30 minutes after the start of the experiment. This results in a fast drop of NO concentration in the outlet air stream. After the initial drop, the NO concentration remained mostly constant throughout the experiment. After 5 hours of testing, the light is turned off and the NO concentration is measured. For this test condition, the use of TiO_2 photocatalytic coating had an NO removal efficiency of 26.9%. The removal efficiency depends on many factors including the flow rate, air humidity, and mix design of the coating, the ambient temperature, and the content of TiO_2 in the coating. Table 1 presents the measured NO efficiency for the different samples in the original state. As shown in this table, the coating with 5% TiO_2 was the most efficient in removing nitrogen oxide from the air stream.

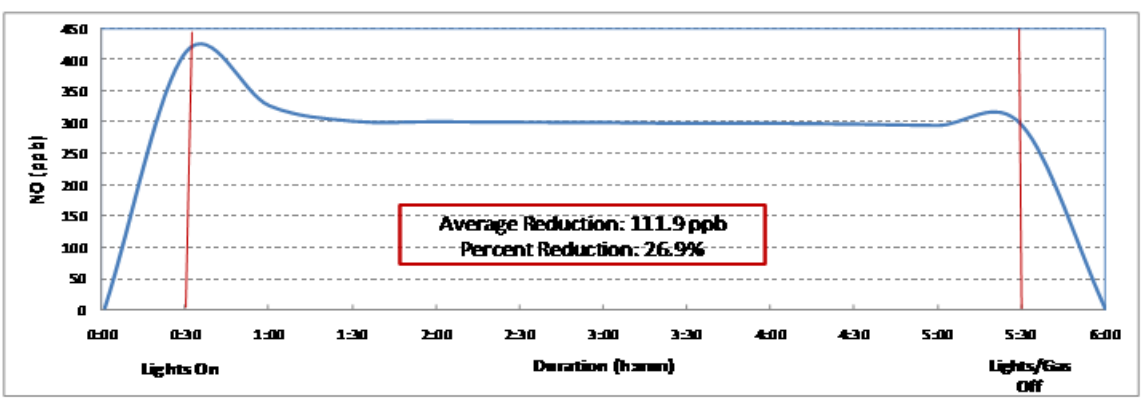


Figure 3: Variation of NO Concentration during the Experiment

Table 1

No Removal Efficiency for Original Samples

Sample	Humidity (%)	Flow Rate (l/min)	NO Removal (%)
Control	50	9.0	2.4
3% TiO2	50	9.0	18.0
5% TiO2	50	9.0	26.9

Effects of Wearing on NO Removal Efficiency

Figure 4 presents the average NO removal efficiencies for the original and worn samples (rotary abrasion and loaded-wheel test samples). As shown in this Figure, the wearing of the samples with 5% TiO_2 resulted in a small decrease in the coating NO removal efficiency (26.9% for the original samples vs. 22.4% for the RA samples and 23.4% for the LWT samples). On the other hand, the wearing of the samples with 3% TiO_2 slightly improved the NO removal efficiency (18.0% for the original samples vs. 21.4% for the RA samples and 24.8% for the LWT samples). This may be due that simulated wearing and abrasion actions exposed part of the embedded titanium dioxide particles in the coating, and therefore, improved its NO removal efficiency.

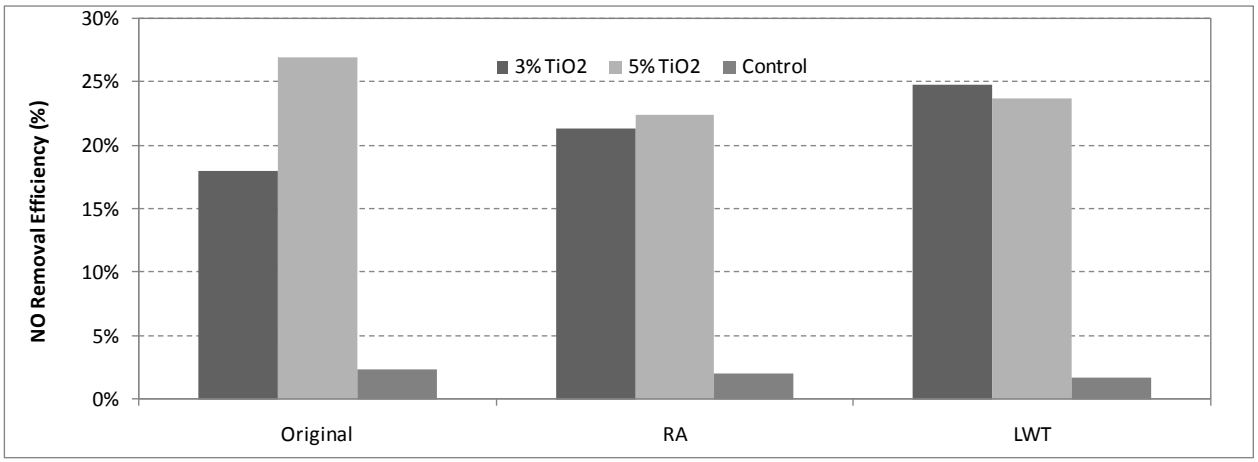


Figure 4: NO Removal Efficiencies for Original and Worn Samples

SEM and EDS Test Results

Figure 5 presents a microscopic image of the coating at 5% TiO_2 content in the original state. Along with the SEM image, results of the EDS analysis are presented. Results of the EDS analysis provide an elemental analysis of the sample, which present the relative concentration of titanium particles on the surface. This is a desirable characteristic to ensure maximum exposure of the nano-particles on the surface, which would provide for maximum NO removal efficiency. Multiple locations in the surface of the specimen were analyzed and revealed comparable concentrations of Ti on the specimen surface.

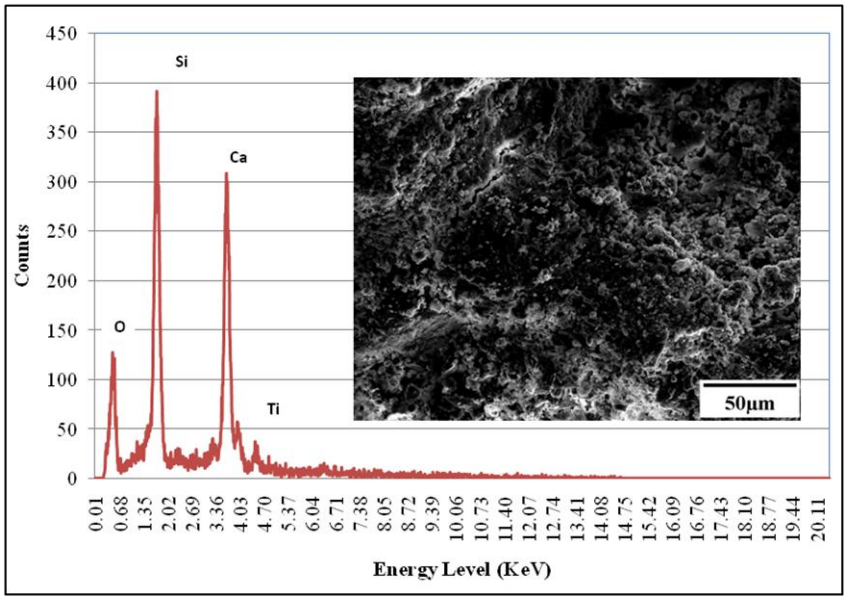
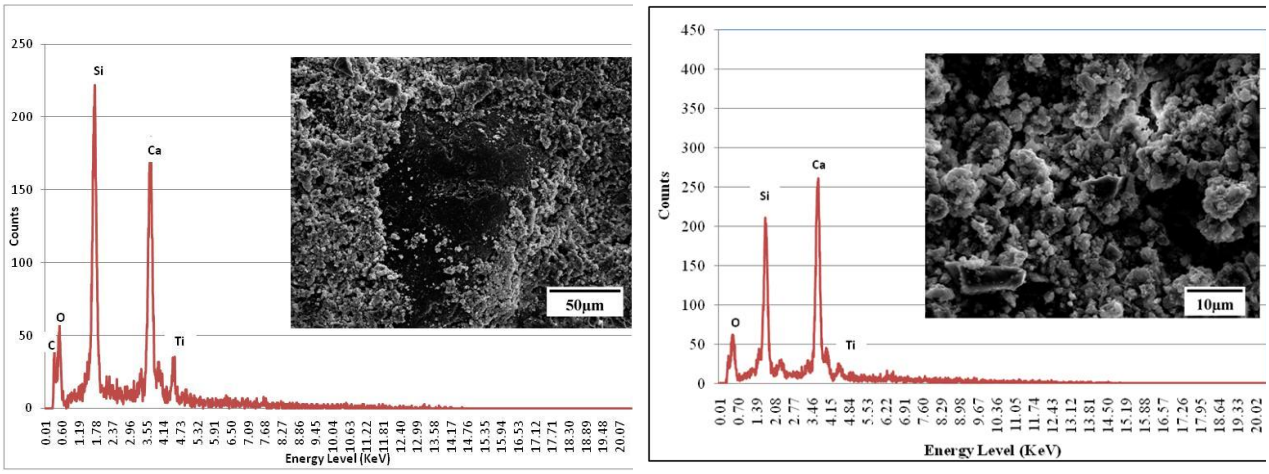


Figure 5: SEM and EDS Test Results for the Original Sample (5% TiO_2)

Similarly, Figs 6 (a and b) present the SEM image and results of the EDS analysis for the worn samples (LWT and RA) for the coating with 5% TiO_2. As shown in this Figure, the concentration of Ti on the specimen surface did not substantially change as compared to the original sample presented in Figure 5. One may also notice from the SEM image shown in Figure 6 (a) that part of the surface did not show any TiO_2 particles possibly due to wearing.



(a) (b)

Figure 6: SEM and EDS Test Results for the Worn Sample (5% TiO_2) for (a) LWT and (b) RA

Conclusions

The use of titanium dioxide coating for pavements has received considerable attention in recent years to improve air quality near large metropolitan areas. In spite of its promising benefits, the durability and resistance to wear of TiO_2 surface coating has not been evaluated. The objective of this study was to determine the abrasion and wear resistance properties of TiO_2 coating and its effect on the coating environmental performance. Based on the analysis conducted, the following conclusions may be drawn:

- The measured rut depth in the LWT for the three specimen types was minimal (less than 1mm) indicating that the use of the coating did not appear to affect the wear resistance of the surface.

- In the original state, the use of TiO2 photocatalyst coating at a 5% content had an NO removal efficiency of 26.9%. The coating with 3% TiO2 had a NO removal efficiency of 18.0%.

- The wearing of the samples with 5% TiO2 resulted in a small decrease in the coating NO removal efficiency. On the other hand, the wearing of the samples with 3% TiO2 slightly improved the NO removal efficiency. Results of EDS analysis confirm that the relative concentration of Ti on the worn specimens did not substantially change as compared to the original samples.

Based on the results presented in this study, further research is recommended to consider factors such as coating application methods and variation of the NO removal efficiency with humidity, coating composition, and flow rate. Research is also needed to validate the efficiency of the technology in the field.

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