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A Breakthrough Concept in the Preparation of Highly-Sustainable Photocatalytic Warm Asphalt Mixtures

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Abstract: The objective of this study is to test the hypothesis that titanium dioxide (TiO_2) can function as a photocatalytic compound when used in the preparation of warm-mix asphalt (WMA). The proposed asphalt mixture would combine the benefits of WMA such as reduced energy consumption and emission during production with the photocatalytic properties of TiO_2 to trap and degrade organic and inorganic particles in the air. Two application methods were evaluated, using TiO_2 as a modifier to asphalt binder in the preparation of WMA and applying TiO_2 to the pavement surface as a water-based solution. Results of the experimental program indicated that the use of TiO_2 as a modifier to asphalt binder was not effective in removing NO_x pollutants from the air stream; however, the application of TiO_2 as part of a water-based spray coating achieved a NO_x reduction efficiency ranging from 39 to 52%.

1. Introduction: The US faces a significant challenge in controlling air pollution resulting from transportation activities. Although attempts are made to lower vehicle emission standards, a method is needed to remove these pollutants once they are emitted to the atmosphere. The potential of titanium dioxide (TiO_2) as an air purifier in urban and metropolitan areas, which suffer from high concentration of air pollutants, has been widely recognized in literature [1, 2]. Evaluation of concrete pavement treated with TiO_2 provided promising results as recent research by the authors and others show that a thin surface coating is able to remove a significant portion of nitrogen oxides (NO_x) and volatile organic compounds (VOC) pollutants from the atmosphere when placed as close as possible to the source of pollution [2 - 4]. However, with 94% of the US road network covered with asphalt, it appears that widespread use of titanium dioxide in air purification applications can only be achieved by the development of a novel asphalt mixture that does not affect the mechanical properties of the mix while incorporating a photocatalytic compound into current highway construction practices [5]. In addition, the use of Warm Mix Asphalt (WMA) will have the added benefits of reduced energy and the associated pollution emissions during production.

The objective of this study is to test the hypothesis that TiO_2 can function as a photocatalytic compound when used in the preparation of WMA. To achieve this objective, a crystallized anatase-based titanium dioxide powder was blended with a WMA asphalt binder classified as PG 64-22 at three percentages by binder weight (3, 5, and 7%). In addition, a second application method was evaluated, especially useful for coating existing pavements, by spraying a water-based solution of TiO_2 to the surface at three coverage levels (0.11, 0.21, and 0.31 kg/m^2). Prepared blends were characterized using fundamental rheological tests (i.e., dynamic shear rheometer, rotational viscosity, and bending beam rheometer), the semi-circular bend (SCB) test for fracture resistance and by measuring the environmental efficiency of the mixture in removing part of the NO_x pollutants in the air stream.

2. Background: The potential of TiO_2 as a photocatalyst was discovered by Fujishima and Honda in 1972 [6]. In the presence of UV light, TiO_2 produces hydroxyl radicals and superoxides, which are respectively responsible for oxidizing and reducing environmental contaminants including VOC and NO_x [7]. A proposed mode of oxidation of NO_x via hydroxyl radical intermediates in the presence of the photocatalyst is described by the following equations:

$$NO + \dot{O}H \xrightarrow{T_iO_2} NO_2 + H^{\cdot}$$
$$NO_2 + \dot{O}H \xrightarrow{T_iO_2} NO_3 + H^{\cdot}$$

Based on this heterogeneous photocatalytic oxidation process, NO_x are oxidized into water-soluble nitrates; these substances can be washed away by rainfall. Titanium dioxide particles crystallize in three forms: anatase, rutile, and brookite. Anatase is a meta-stable phase that transforms into rutile at high temperatures [8]. Research has shown that TiO_2 in the anatase phase is a more powerful photocatalyst than rutile and brookite in environmental purification [9]. Numerous research studies have also reported that the degree of photocatalytic activity depends on the physical properties of TiO_2 including the level of crystallization, surface area, particle size, and surface hydroxyls [10]. In pavement applications, it is desirable to prepare a TiO_2 coating with hydrophobic properties, which provide for a self-cleaning surface. Through this process, particles of contaminants adhere to water droplets in case of rain and are removed from the surface when the droplets roll off of it.

Use of TiO_2 in Pavement Applications: Available TiO_2 technologies have been mostly directed towards concrete pavements in which a fine mixture consisting of cement, sand, TiO_2, and water is applied as a thin surface layer or slurry to the surface. Yet few studies are available for asphalt pavements, TiO_2 has been incorporated into asphalt pavements by integrating it into the binder and as a thin surface layer that is sprayed on existing pavements [11, 12]. The water-based emulsion was applied by two different methods, referred to as hot and cold method; distinguished by the spraying of the emulsion during asphalt paving laying operations when the pavement temperature is over 100°C or on existing pavements at ambient temperatures [11]. The study results showed that the reduction efficiencies were highly dependent on the TiO_2 nanoparticles used in which efficiencies ranged from 20 to 57% of NO_x reductions. Meanwhile, researchers in China mixed TiO_2 with an asphalt binder at a 2.5% content of the binder weight to an emulsified asphalt pavement [12]. Evaluation presented in this study showed that a maximum efficiency in removing nitrogen oxide near 40% was achieved. A more efficient approach may be achieved by concentrating the photocatalytic compound at the pavement surface.

3. Experimental Program: Asphalt cement binder blends were prepared by mixing a conventional WMA binder (WMA additive Evotherm was used at 1% by weight of the binder) classified as PG 64-22 with a commercial crystallized anatase-based TiO_2 powder at three percentages 3, 5, and 7% by weight of the binder. The blends were prepared at a mixing temperature of 163°C. While short-term aging was simulated using the rolling-thin film oven (RTFO), long-term aging was simulated using the pressure aging vessel (PAV). The RTFO test simulated construction hardening and asphalt binder aging by subjecting the material to circulating hot air for 85 min. The PAV test simulated long-term oxidative aging for a period ranging from 5-10 years by subjecting the binder to pressurized air for 20 hrs and a temperature maintained at 100°C.

Prepared blends were characterized using fundamental rheological tests (i.e., dynamic shear rheometry, rotational viscosity, and bending beam rheometer) and by comparing the Superpave Performance Grade (PG) of the modified blend to the unmodified WMA binder. To assess the influence of the photocatalytic compound on the binder aging mechanisms and to ensure that TiO_2 does not oxidize the binder, both the control and modified prepared blends were subjected to UV light for a period of seven days. Binders were characterized using the entire suite of PG grading system as per AASHTO M 320-09 (Standard Specification for Performance-Graded Asphalt Binder). Using the same experimental mix design parameters, two replicas of asphalt concrete samples were prepared for both the fracture and environmental tests. The blends were prepared at a mixing temperature of 163°C and compacted by a gyratory compactor according to AASHTO TP4.

Fracture resistance was assessed using the semi-circular bending (SCB) test developed by Wu *et al.* [13]. This test characterizes the fracture resistance of HMA mixtures based on fracture mechanics principals, the critical strain energy release rate, also called the critical value of J-integral, or Jc. To determine the critical value of J-integral (Jc), three notch depths of 25.4, 31.8, and 38 mm were selected based on an a/r_d ratio (the notch depth to the radius of the specimen) between 0.5 and 0.75. Test temperature was selected to be 25°C. The semi-circular specimen is loaded monotonically till fracture failure under a constant cross-head deformation rate of 0.5 mm/min in a three-point bending load configuration. The load and deformation are continuously recorded and the critical value of J-integral (Jc) is determined using the following equation [13]:

$$J_c = \left(\frac{U_1}{b_1} - \frac{U_2}{b_2}\right)\frac{1}{a_2 - a_1} \qquad (1)$$

where,
b = sample thickness;
a = the notch depth; and
U = the strain energy to failure.

A second application method consisting of applying a thin surface coating was also evaluated at three coverage rates (0.11, 0.21, and 0.31 kg/m^2). The spray coat used was a mixture of TiO_2 anatase nanoparticles suspended in an aqueous liquid at 2% by volume. A thin film was spray coated on each sample in layers using in a cross hatch formation for each of the three defined coverage rates.

Environmental Test Setup: The environmental benefit of the fabricated asphalt blends in trapping and degrading NO_x pollutants from the air stream through a photocatalysis mechanism was investigated. A laboratory test setup that is capable of quantifying the photocatalytic efficiency of asphalt and concrete specimens was used, Figure 1. The test setup was adapted from the Japanese standard JIS TR Z 0018 “Photocatalytic materials – air purification test procedure.” The developed experimental setup consists of a pollutant source, zero air source, calibrator, humidifier, photoreactor, and a chemiluminescent NO_x analyzer as shown in Figure 1. 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 the photoreactor, 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.

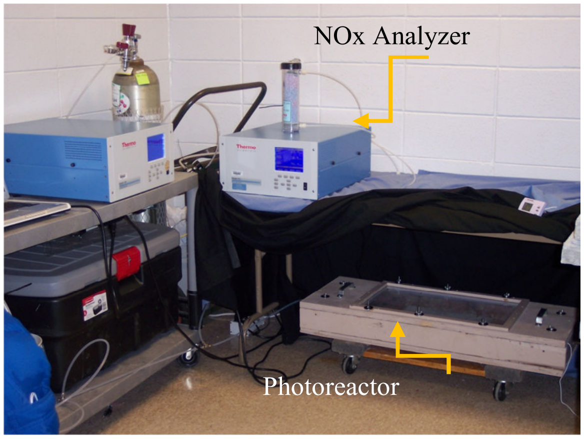

Figure 1: Experimental Laboratory Setup

The photoreactor 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 and after the photoreactor allowed for determination of the absorbed level of pollutants. In this study, NO_x and removal efficiency was measured using the Thermo 42i chemiluminescent NO_x analyzer. Nitrogen oxides were blown over the surface of the asphalt specimens at a concentration of 450 ppb. All tests were conducted at room temperature while the relative humidity was kept constant at 20%.

System Calibration: Before testing, the Thermo 42i was calibrated in accordance to the EPA calibration procedures using the gas phase titration (GPT) alternative. This technique uses the rapid gas phase reactions between the NO and O to produce NO_2 using the following chemical reaction:

$$NO + O_3 \rightarrow NO_2 + O_2$$

The Thermo 146i gas calibrator follows this principle to supply known concentrations of NO and NO_2 used in the NO_x analyzer. The NO_x analyzer was calibrated at five different spans for NO calibration and four different ozone settings for NO_2 calibration to confirm linearity and ozone converter efficiency. The calibration points were chosen between the accuracy ranges that were set from 0 and 500 ppm, typical settings of ambient air monitoring equipment.

4. Results and Analysis: The samples with the TiO_2 in the binder were tested at 1 l/min flow rate and 1 mW/cm^2. The results presented in Table 1 show low NO_x reduction suggesting that the method of incorporation of TiO_2 into the asphalt binder mix may not be environmentally-effective. The low efficiencies could be due that only a small amount of TiO_2 is actually present at the surface. Other possible explanations could be that the asphalt binder inhibits the photocatalytic reaction at the surface. Future research is underway to support the understanding of these results.

Table 1: Average NO_x reduction and NO reduction for TiO_2 incorporated into binder mixes.

Sample	NO_x Reduction %	NO Reduction %
3% TiO_2 64-22	3.9%	5.6%
5% TiO_2 64-22	4.7%	5.8%
7% TiO_2 64-22	3.3%	5.0%

For the second application method consisting of applying a surface spray coating, samples were tested using a flow of 1.5 l/min and a luminosity of 2 mW/cm^2. Figure 2 illustrates the variation of NO_x concentration during the course of the environmental experiment for the asphalt sample treated with a TiO_2 surface spray coat with a coverage rate of 0.21 kg/m^2. The UV light is turned on 2 hours after the start of the experiment in order to ensure equilibrium condition.

The inlet concentration reached equilibrium at 430 ppb before the light was turned on. After the light is turned on, a fast drop of NO concentration in the outlet air stream is exhibited and NO_2 is created from the NO oxidation. During the photocatalytic experiment, the NO_x concentration slightly increased. After 5 hours of testing, the light and gas supply was turned off allowing for any desorption to occur. For the test condition shown in Figure 2, the use of TiO_2 photocatalyst coating had an NO removal efficiency of 83% and the overall NO_x reduction was 69%.

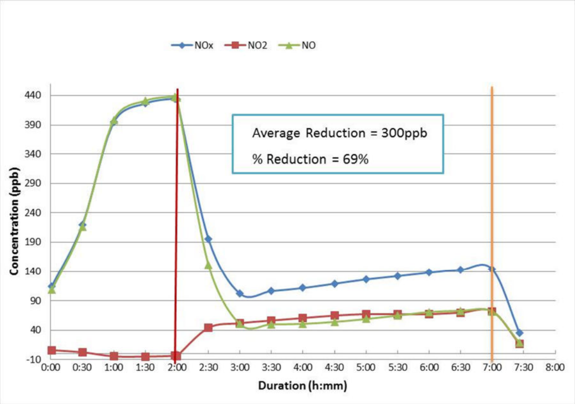

Figure 2: Variation of NO_x Concentration during the Environmental Experiment (TiO_2 applied at a 0.21 kg/m^2 coverage)

The rest of the results for all of the samples are shown in Table 2. Table 2 also presents the measured NO efficiency for the asphalt sample that was not treated with TiO_2. As shown in this figure, the efficiency of the sample without TiO_2 was negligible validating the efficiency of the photocatalytic compound in removing part of the NO pollutants in the air stream when used as a spray coating. By comparing the effect of the TiO_2 coverage rate, it appears that the improvement of NO_x reduction is not linear. In fact, the maximum environmental performance was achieved at the 0.21 kg/m^2 coverage rate. The increase in TiO_2 application rate beyond an optimum coverage rate may block nanoparticles' access to light and contaminants, and therefore, decrease NO_x removal efficiency.

Table 2: Average NOx reduction and NO reduction for TiO_2 incorporated into binder mixes.

Coverage (kg/m2)	NO_x Reduction %	NO Reduction %
Control	2.6%	5.0%
$0.11kg/m^2$	38.9%	51.2%
$0.21kg/m^2$	53.2%	70.3%
$0.32kg/m^2$	40%	52.6%

Effects of TiO_2 on Rheological Properties: Table 3 presents the measured rheological properties of the TiO_2 modified and unmodified WMA binders based on laboratory testing conducted using rotational viscometer, dynamic shear rheometer, and bending beam rheometer.

Table 3: Rheological Test Results of TiO_2-modified Asphalt Binder.

TiO_2 Binder Testing	**Spec**	**Test Temp**	**PG 64 W64CO**	**PG 64 W64CO + UV**	**PG 64 + 7%TiO_2**	**PG 64 + 7%TiO_2 + UV**
Test on Original Binder						
Dynamic Shear, G*/Sin(δ), (kPa), AASHTO T315	1.00^+	64°C	1.15	NA	1.55	NA
	1.00^+	70°C	NT	NA	NT	NA
Rotational Viscosity (Pa·s), AASHTO T316	3.0^-	135°C	0.4	NA	0.5	NA
Tests on RTFO						
Mass Loss, %	1.00^-	----	0.9	NA	0.2	NA
Dynamic Shear, G*/Sin(δ), (kPa), AASHTO T315	2.20^+	64°C	2.69	NA	2.94	NA
	2.20^+	70°C	NT	NA	NT	NA
Tests on (RTFO+ PAV)						
Dynamic Shear, G*Sin(δ), (kPa), AASHTO T315	5000^-	25°C	3459	2580	3798	2812
BBR Creep Stiffness, (MPa), AASHTO T313	300^-	-12°C	167	158	201	145
Bending Beam m-value AASHTO T313	0.300^+	-12°C	0.311	0.342	0.305	0.340
Actual PG Grading			**64-22**	**64-22**	**64-22**	**64-22**

Results are presented for four types of specimen: PG 64-22 conventional WMA binder, PG 64-22 + 7% TiO_2, and PG 64-22 conventional and + 7% TiO_2 subjected to UV light for seven days. Since UV light will only influence the long-term behavior of the binder, rheological testing of specimens subjected to UV light was only performed on the aged samples (RTFO + PAV). Ultra-violet light initiates the photocatalytic process for the sample with TiO_2. Results presented in Table 3 indicate that the addition of TiO_2 only marginally affected the rheological properties of the conventional binder.

Results presented in Table 3 also show that exposing the binder to UV light did not accelerate the aging mechanisms in the material as compared to the sample that was not subjected to UV light. In addition, the use of TiO_2 as an air purification agent did not accelerate the aging mechanisms in the binder. This trend was desirable to ensure that UV light, which is necessary to initiate the photocatalytic process, did not negatively affect the binder rheological properties.

Effects of TiO_2 on the Mix Fracture Resistance: Table 4 presents a comparison of the critical strain energy (Jc) data for the mixtures evaluated in this study. High Jc values are desirable as indicative of fracture-resistant mixtures. As shown by these results, the use of TiO_2 as a binder modifier improved the mix fracture resistance at 3, and 5% while it did not have a noticeable effect when used at a content of 7.0%.

Table 4: SCB test Results for TiO_2 incorporated into binder mixes.

TiO_2 Content	Jc (kJ/m^2)
Control	0.29
3.0 %	0.45
5.0 %	0.46
7.0 %	0.28

5. Summary and Conclusions: This study evaluated the benefits of incorporating titanium dioxide (TiO_2) as an additive to asphalt binder in the preparation of WMA. A commercial crystallized anatase-based titanium dioxide powder was blended with a conventional WMA asphalt binder classified as PG 64-22 at three modification rates (3, 5, and 7%). Prepared blends were characterized using fundamental rheological tests and the SCB test. Two application methods to integrate TiO_2 were evaluated, a water-based titanium dioxide solution applied as a thin coating and using TiO_2 as a modifier to asphalt binder in the preparation of WMA. Based on the results of the experimental program, the following conclusions may be drawn:

- When used as a modifier to asphalt binder in the preparation of WMA, the photocatalytic compound was not effective in degrading NO_x in the air stream. This could be attributed to the fact that only a small amount of TiO_2 is present at the surface.
- When used as part of a surface spray coating, TiO_2 was effective in removing NO_x pollutants from the air stream with an efficiency ranging from 39 to 52%.
- Rheological test results indicated that the addition of TiO_2 did not affect the physical properties of the conventional binder. In addition, exposing the binder to UV light did not appear to accelerate the aging mechanisms in the binder.
- The use of TiO_2 as a binder modifier improved the mix fracture resistance at 3, and 5% while it did not have a noticeable effect when used at a content of 7.0%.

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7. References:

[1]. C.S. Poon, and E. Cheung. NO Removal Efficiency of Photocatalytic Paving Blocks Prepared with Recycled Materials. Construction and Building Materials, Elsevier, Vol. 21, 2007, pp. 1746-1753.

[2]. H. Dylla, M.M. Hassan, L. Mohammad, and T. Rupnow. Evaluation of the Environmental Effectiveness of Titanium Dioxide Photocatalyst Coating for Concrete Pavements. Journal of the Transportation Research Record, Washington, D.C., 2010, In Press.

[3]. Beeldens, A. An Environmentally Friendly Solution for Air Purification and Self Cleaning Effect: the Application of TiO2 as Photocatalyst in Concrete. Proceedings of Transport Research Arena Europe – TRA, Göteborg, Sweden, 2006.

[4]. Hassan, M.M., Dylla, H., Mohammad, L., and Rupnow, T., Evaluation of the Durability of Titanium Dioxide Photocatalyst Coating for

Concrete Pavement. Journal of Construction and Building Materials, Elsevier, 2010, In Press.

[5]. Federal Highway Administration. Our Nation's Highways – Selected Facts and Figures. Office of Highway Information Management, Publication No. FHWA-PL-01-1012, 2000.

[6]. Fujishima, A., and K. Honda. Electrochemical Photolysis of Water at a Semiconductor Electrode. Nature 238, 1972, pp. 37-38.

[7]. Fujishima, A., Rao, T.N., and Tryk, D.A. Titanium Dioxide Photocatalysis. Journal of Photochemistry and Photobiology, C: Photochemistry Reviews, Vol. 1, 2000, pp. 1-21.

[8]. Znaidi, L., Seraphimova, R., Bocquet, J., Colbeau-Justin, C., and Pommier, C. Continuous Process for the Synthesis of Nanosize TiO2 Powders and Their Use as Photocatalysts. Material Research Bulletin, Vol. 36, 2001, pp. 811-825.

[9]. Bilmes, S., Mandelbaum, P., Alvarez, F., and Victoria, N. Surface and Electronic Structure of Titanium Dioxide Photocatalyst. Journal of Physical Chemistry B, Vol. 104, 2000, pp. 9851-9858.

[10]. Ohtani, B., Ogawa, Y., and Nishimoto, S. Photocatalytic Activity of Amorphous-Anatase Mixture of Titanium (IV) Oxide Particles Suspended in Aqueous Solutions. Journal of Physical Chemistry, American Chemical Society, 101, 1997, pp. 3746-3752.

[11]. Venturini, L, and Bacchi, M. Research, Design, and Development of a Photocatalytic Asphalt Pavement. Proceedings of 2nd International Conference on Environmentally Friendly Roads: ENVIROAD 2009, Warsaw, Poland, 2009.

[12]. Li, L., and Qian, C. A Lab Study of Photo-Catalytic Oxidation and Removal of Nitrogen Oxides in Vehicular Emissions and Its Fieldwork on Nanjing No. 3 Bridge of Yangtze River. Technical Note, International Journal of Pavement Research and Technology, Vol. 2, No. 5, 2009, pp. 218-222.

[13]. Wu, Z., Mohammad, L.N., Wang, L.B., Mull, M.A. (2005). "Fracture Resistance Characterization of Superpave Mixtures Using the Semi-Circular Bending Test." Journal of ASTM International, Vol. 2, No. 3