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Cincinnati - TiO₂-Bearing Pavement Field Results

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From: Michael Durante, Vice President Finance & Strategic Planning

**Re: Test Results: Photocatalytic Pavements – Pollution Remediation; Heat (Absorption)
Reduction; and Hydrophilic Improvement**

Date: 30 July 2020

Pavement Technology's (PTI) photocatalytic pavement solutions for pollution removal, pavement preservation, Heat Island (UHI) mitigation and other photo-induced properties beneficial to air quality, pavement life-cycle extension and heat sink management now are into scale piloting.

On May 11, 2020, PTI completed a pilot application of **A.R.A.-1 Ti[®]** TiO₂ enhanced Maltene Asphalt Rejuvenator on a newly paved section of Montgomery Road. The test section was three lanes of new

pavement approximating 62,000 sq/yds and 16,000 linear feet. The application rate was 0.05 gallons per square yard with 3.5% photocatalytic grade TiO_2 ¹ by volume concentrate.

A.R.A.-1 Ti[®] Trial
Montgomery Road, Cincinnati, Ohio
May 11, 2020



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A.R.A.-1 Ti[®] is a specialized version of a **Maltene Replacement Technology (MRT)** product enhanced to impart both the **regenerative properties** of a maltene rejuvenator and the beneficial sustainability and environmental properties of imbedded photocatalytic grade **Titanium Dioxide (TiO₂)**.

As a photocatalyst material (semiconductor), TiO_2 is a multifaceted photo-responsive material² rapidly gaining increased scientific and commercial interest for near-roadway microenvironments as it advances a host of preservation and environmental benefits, including:

- **Depolluting** near-pavement air (or water) cleaning applications, where TiO_2 reacted surfaces are able to oxidize a variety of pollutants and contaminants such as those emitted by vehicles, especially NO_x and VOCs, and even worn tire residue (microplastic) reducing ozone pollution and mitigating acid rain formation
- **“Cool Pavement”** applications where TiO_2 treated surfaces provide a solar-reflective top boundary, which lessens pavement related radiative forcing (RF) by reducing the convective re-release or

¹ n-type semiconductor containing >99.5% TiO_2 content comprised of no less than 80% anatase crystallite by weight (plus or minus 5%) in a particle size averaging 21nm (plus or minus 5nm) with a small portion of rutile crystalline content.

² *Polymers, Light and the Science of TiO₂*, DuPont[™] Ti-Pure[®] Titanium Dioxide, DowDuPont, www.dow-dupont.com.

emissivity of solar radiation that leads to the undesired UHI effects and enhances the life-cycle assessment of pavements by slowing-down oxidation³

- **Super-Hydrophilic** surfaces, which provide a rapid **water-desorbing pavement**, which is self-cleaning to remove contaminants (e.g., mold) and staining; protects against water intrusion; and is indicated for inclement weather-related safety (rain displacing; ice inhibiting) improvements for roadways⁴

As a radiant heat mitigator, photocatalytic grade TiO₂ simultaneously absorbs solar radiation away from the pavement substrate and efficiently redirects the energy back into the atmosphere, thereby protecting the pavement from oxidative deterioration and eliminating excess pavement emissivity (especially in asphalts), creating a so-called – “**cool pavement**” which greatly slows-down oxidative damage while improving air quality.⁵

TiO₂-bearing pavements also exhibit a **Photoinduced Superhydrophilicity State** when exposed to sunlight (UV radiation), which enables water to more efficiently disperse and desorb across a TiO₂-treated surface.⁶
⁷ This not only protects the substrate from damaging water intrusion, it holds significant highway safety improvement implications including reduced hydroplaning, less windshield visibility impairment, and possibly ice formation mitigation. A PSH is why TiO₂ treated surfaces are mechanically “self-cleaning” and both anti-mold and antimicrobial.⁸

Cincinnati Test Results:

Core samples (2 = 1 treated and 1 untreated) from the Montgomery Road test site were sent to the Texas A&M Transportation Institute to complete laboratory testing of these field samples for photocatalytic oxidation for pollution removal (NO_x Reduction %); solar reflectance index for heat absorption or Urban Heat Island effect mitigation; water contact angle for hydrophilic analysis; and X-ray Fluorescence for TiO₂ load and dispersion efficiency under:

³ Gopalakrishnan K, et al.

⁴ Arainpour F and Farzaneh M, On Hydrophobic and Icephobic Properties of TiO₂-Doped Silicon Rubber Coatings, Department of Applied Sciences, Universite du Quebec, *International Journal of Theoretical and Applied Nanotechnology*, 2012.

⁵ EPA, *Reducing Urban Heat Islands: Compendium of Strategies, Urban Heat Island Basics*, www.epa.org.

⁶ Mechanism of Photoinduced Superhydrophilicity on the Photocatalyst Surface, *The Journal of Physical Chemistry*, American Chemistry Society, 2005, Masato T, et al.

⁷ Vassilia Z, *Hydrophilic TiO₂ Surface Without Photocatalytic Activation*, Lawrence Berkeley National Laboratory, University of California at Berkeley.

⁸ Kubacka A, Suarez Diez M, et al., Understanding the Antimicrobial Mechanism of TiO₂- based Nanocomposite Films in a Pathogenic Bacterium, *Nature Journal*, 2014.

JIS TR Z 0018 *Photocatalytic Materials – Air Purification Test Procedure;*

ASTM E1980 - 11 *Standard Practice for Calculating Solar Reflectance Index of Horizontal and Low-Sloped Opaque Surfaces;*

ASTM C1549-16 *Standard Test Method for Determination of Solar Reflectance Near Ambient Temperature Using a Portable Solar Reflectometer.*

ASTM D7334 - 08(2013) *Standard Practice for Surface Wettability of Coatings, Substrates and Pigments by Advancing Contact Angle Measurement*

Cincinnati Cores Results – Photocatalytic Properties

Date	Sample ID #	Treatment	NO Reduction (%)	Titanium Concentration (ppm)	SRI Values	Water Contact Angle (WCA)	Specification
6/9/20	1	A.R.A.-1Ti	30.21	3205	0.1442	56.34	6325 Montgomery Rd. (Center Lane) South of untreated test
	2	A.R.A.-1Ti	31.55	3104	0.1345	66.17	6325 Montgomery Rd. (Center Lane) South-west of untreated test
	Control	Untreated	9.18	-	0.0821	76.86	6325 Montgomery Rd. (Center Lane)

Source: Texas A&M Transportation Institute (TTI)

The Montgomery Road **A.R.A.-1 Ti[®]** trial results were successful; exceeded PTI performance specifications; and were consistent with PTI’s expected results. All photocatalytic properties tested were validated. Based on the field test results, PTI recommends the City of Cincinnati expand **A.R.A.-1 Ti[®]** to full use.

X-ray Fluorescence (TiO₂ Delivery)

The Montgomery Road TiO₂ concentrations were observed at efficient photo-reactivity levels (e.g., >2000 parts per million and a dielectric constant reading ≥ 5) through wearing-course depth, producing the expected PCO activity. The Montgomery Road TiO₂ loads averaged **150% of PTI’s performance specifications**, which call for:

TiO₂ Penetration Test: A non-destructive analytical procedure shall be used to determine the percent of Titanium Dioxide nanoparticles present in each two-millimeter (2mm) layer of the field core sample matrix for a total depth of six millimeters (6mm) from the top of the treated sample core. The method of measurement shall be by fluorescent X-ray emitted from the surface when excited by a principal X-ray source that is exceptional for the given element. A hand-held XRF analyzer is acceptable for this testing.

The minimum required concentration of Titanium Dioxide nanoparticles per each two-millimeter (2mm) section shall be 2000 parts per million (ppm).

Photocatalytic Oxidation (PCO) of NO_x

The PCO rate reflected the initial test protocol TiO₂ delivery and impregnation consistent with the XRF results. **NO (nitric oxide) reduction effectiveness was 30%-32%** which correlated to the photocatalyst material concentration and **A.R.A.-1 Ti[®]** application rate. The pollution reduction rate was **125% of PTI's performance specifications**, which call for:

NO_x Reduction Effectiveness: Verification of the effectiveness of the air pollution remediation of the Titanium Dioxide nano-particle portion of the TiO₂ Enhanced Asphalt Rejuvenating Agent shall be by laboratory analysis of core samples extracted from the treated pavement as directed and required by the Engineer. The cores shall be a minimum of four inches (4") in diameter and in pairs at each location directed by the Engineer. The cores shall be tested by an accredited laboratory or university with the equipment and capability to perform the following test procedures.

NO_x Reduction Test: A photo reactor test chamber shall be employed that allow for the evaluation of the efficient photocatalytic reduction of introduced NO_x gas of a known and controlled concentration within the chambers volume. The chamber light source shall be a UV lamp having a wavelength of 375 nanometers. The interior chamber environment shall be at 77°F with a constant humidity of 55% ±5%. The test total duration shall be five hours. The analysis test system shall be based on a Japanese Industrial Standard (JIS) TR Z0018 "Photocatalytic Materials-Air purification test procedure". NO removal efficiency shall be measured using a Model 42i Chemiluminescence NO-NO₂-NO_x Analyzer (Thermo Fisher Scientific Inc.).

The minimum NO reduction following the heretofore outlined test procedure evaluating field core samples shall average 25% for all cores tested.

Solar Reflectance

The SRI value also reflected the impact of the TiO₂ penetration and dispersion consistent with the XRF results. The **solar reflectance index readings were 0.13-0.14** which were a 70% improvement to the untreated test section and correlated to the photocatalyst material concentration and material application rate of 0.05 gallons per sq/yd. The Montgomery Road pilot area met the US Green Building Council (USGBC) minimum threshold of 50% x 0.29 for LEED credits as well as American Public Works Association (APWA) ISI Envision credits.

PTI's performance specifications call for:

Solar Reflectance Effectiveness: Verification of the effectiveness of the solar reflectivity the Titanium Dioxide nano-particle portion of the TiO₂ Enhanced Asphalt Rejuvenating Agent shall be by laboratory analysis of core samples extracted from the treated pavement as directed and required by the Engineer. The cores shall be a minimum of four inches (4") in diameter and in pairs at each location directed by the Engineer. The cores shall be tested by an accredited laboratory or university with the equipment and capability to perform the following test procedures.

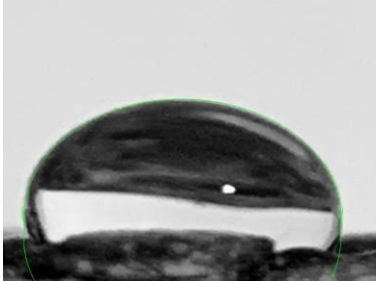
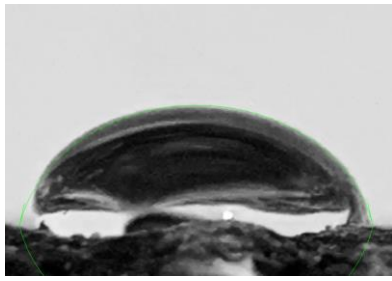
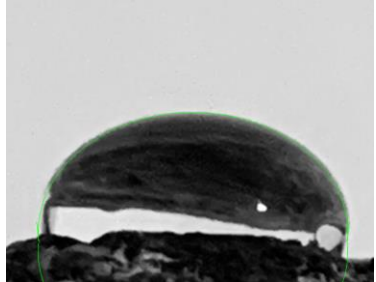
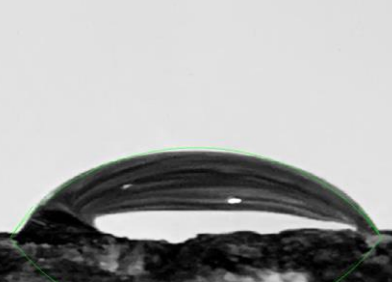
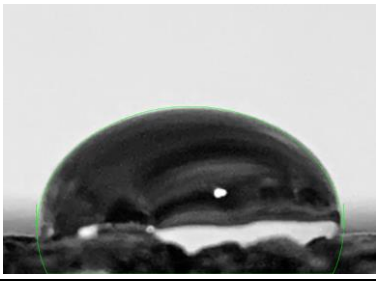
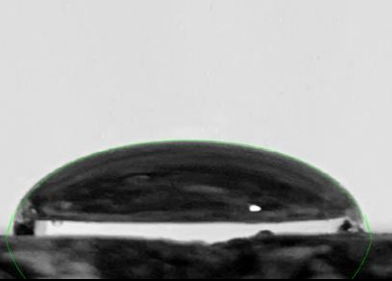
Solar Reflectance Test(s): Solar reflectivity shall be determined by measuring the treated core samples for a Solar Reflectance Index (SRI) value. SRI is a measure of the constructed surface's ability to reflect solar heat, as shown by a small temperature rise. It is defined so that a standard black surface (reflectance 0.05, emittance 0.90) is 0 and a standard white surface (reflectance 0.80, emittance 0.90) is 100.

The minimum SRI value following the heretofore outlined test procedure(s) evaluating field core samples shall average 0.29 for all cores tested, which meet the minimum standard ($\geq 50\%$ 0.29 SRI) for the U.S. Green Building Council (USGBC) hardscape threshold for Leadership in Energy and Environmental Design (LEED) credit or the minimum standard for the American Public Works Association (APWA) / Institute for Sustainable Infrastructure (ISI) Envision Superior ($\geq 60\%$ 0.29 SRI) level of achievement credit.

Hydrophilic Improvement

The WCA observed on the **A.R.A.-1 Ti[®]** pilot section cores reflected the impact of the TiO₂ penetration and dispersion consistent with the XRF results as well. The **water contact angle improved to 56°-66°** which correlated to the photocatalyst material concentration and 0.05 gallons per sq/yd application rate. The untreated (control) section of asphalt recorded a 77° WCA or 30%-40% higher than the TiO₂ treated section. At a higher TiO₂ content of 4.0% to 4.5% by volume concentrate (at an 0.05 rate), the Montgomery Road test area would see as much as 50% or more improvement in WCA, approaching technical superhydrophilicity ($\leq 25^\circ$).

Water Contact Angle of Core Samples

#	Contact Angle under Visible Light	Contact Angle under UV Irradiation
C		
	$\theta=86.65^\circ$	$\theta=76.86^\circ$
#1		
	$\theta=87.31^\circ$	$\theta=59.34^\circ$
#2		
	$\theta=89.22^\circ$	$\theta=66.17^\circ$

Source: Texas A&M Transportation Institute (TTI)

PTI's performance specifications call for:

Hydrophilic Improvement: Verification of the improvement in hydrophilic property of the Titanium Dioxide nano-particle portion of the TiO₂ Enhanced Asphalt Rejuvenating Agent shall be by laboratory analysis of core samples extracted from the treated pavement as directed and required by the Engineer. The cores shall be a minimum of four inches (4") in diameter and in pairs at each location directed by the Engineer. The cores shall be tested by an accredited laboratory or university with the equipment and capability to perform the following test procedures.

Wettability Test: Hydrophilic improvement shall be determined by measuring the treated core samples for Water Contact Angle (WCA). WCA is a common measurement of a constructed surface's ability to improve wettability or the ability of water to develop a stronger boundary (less resistance) with the surface as shown by a decline in water contact angle. A WCA of > 90° is considered hydrophobic or high resistance while a WCA <90° is considered hydrophilic or low resistance.

The minimum WCA reduction following the heretofore outlined test procedure evaluating field core samples shall average 20% for all cores tested.

Rheological Improvement

Rheology tests on the A.R.A.-1 Ti[®] pilot section on Montgomery Road was completed by APART. Those reports are available separately ([table provided is an abstract](#)).

Summary of Testing:

The top 3/8-inch of each core was removed for testing. The asphalt from each core was extracted and recovered as prescribed by California Test Method 365. Viscosities, phase angles, and moduli were determined on the recovered asphalt binder of each sample using a DSR as prescribed by AASHTO T315. Test data are as follows:

Sample	Viscosity 60°C, P	Phase Angle, °	MODULUS, 60°C, Pa		
			Complex	Elastic	Viscous
6325 Montgomery Road					
Untreated	19983	68.2	20226	7420	18555
Treated	10592	70.8	10677	4919	9651

Source: APART

A.R.A.-1 Ti[®] binder rejuvenation efficacy was validated. The test section showed a 47% reduction in viscosity; an improvement in phase angle; and improvement in modulus, all meeting or exceeding specification.

Conclusion and Recommendation

Based on the validation of the Montgomery Road **A.R.A.-1 Ti**[®] photocatalytic property field tests for the City of Cincinnati, PTI recommends the city consider **A.R.A.-1 Ti**[®] for scale deployment citywide for the indicated beneficial regenerative, preservation and environmental impacts of photocatalytic pavement retrofits.

Included as an addendum is the full **A.R.A.-1 Ti**[®] performance specification for additional reference.

Pollution-Remediating Polymerized Maltene Asphalt Rejuvenator

Description: TiO₂ Enhanced Asphalt Rejuvenating Agent

The work specified in this section shall consist of furnishing all labor, material, and equipment necessary to perform all operations for the application of a penetrating polymerized asphalt rejuvenating agent to asphaltic concrete surface courses. The asphalt binder rejuvenation shall be affected through the petroleum Maltene Replacement Technology method. In addition, and with the same penetrating carrier liquid, apply photocatalytic-grade titanium dioxide (TiO₂) to create a pollution reducing pavement microenvironment. The rejuvenation of surface courses shall be by spray application of a polymerized maltene based cationic rejuvenating agent composed of petroleum oils and resins emulsified with water and containing photocatalytic titanium dioxide in a minimum parts per million at a minimum depth as hereafter specified.

All work shall be in accordance with the specifications, the applicable drawings, and subject to the terms and conditions of this contract.

Figure 2.1 A.R.A.-1 Ti[®] Application



Source: Pavement Technology, Inc.; Cary, NC 2019

1 Materials and Performance: TiO₂ Enhanced Asphalt Rejuvenating Agent

The TiO₂ Enhanced Asphalt Rejuvenating Agent shall be a cationic emulsion composed of a petroleum resin oil base uniformly emulsified with water. Each bidder must submit a bid with a certified statement from the TiO₂ enhanced asphalt rejuvenating agent manufacturer showing that the asphalt rejuvenating emulsion conforms to the required physical and chemical requirements.

Table 1 Test of Emulsion and on Residue

	Test Methods		Requirements	
	ASTM	AASHTO	Min	Max
Tests on Emulsion				
Viscosity @ 25°C, SFS	D-244	T-59	15	40
Residue, %W ¹	D-244(Mod.)	T-59(Mod)	60	65
Miscibility Test ²	D-244(Mod.)	T-59(Mod)	No Coagulation	
Sieve Test, %W ³	D-244(Mod.)	T-59(Mod)		0.1
Particle Charge Test	D-244	T-59	Positive	
Percent Light Transmittance ⁴				80
Tests on Residue from Distillation:				
Flash Point, COC, °C	D-92	T-48	196	
Viscosity @ 60°C, cSt	D-445	-	100	200
Asphaltenes, %w	D-2006-70	-		1.00
Maltene Dist. Ratio ⁵	D-2006-70	-	0.3	0.6
PC/S Ratio ⁵	D-2006-70	-	0.5	
Saturated Hydrocarbons, S ⁵	D-2006-70	-	21	28

¹ ASTM D-244 Modified Evaporation Test for percent of residue is made by heating 50-gram sample to 149°C (300°F) until foaming ceases, then cool immediately and calculate results.

² Test procedure identical with ASTM D-244-60 except that .02 Normal Calcium Chloride solution shall be used in place of distilled water.

³ Test procedure identical with ASTM D-244 except that distilled water shall be used in place of two percent sodium oleate solution.

⁴ Procedure for Determining Percent Light Transmittance on Asphalt Rejuvenating Agent:

a. Scope: This procedure covers the determination of percent light transmittance of the asphalt rejuvenating agent.

b. Apparatus:

1. Container may be glass, plastic or metal having a capacity of 6,000 ml.
2. Graduated cylinder, 1,000 ml, or greater
3. Light transmittance measuring apparatus, such as Bausch and Lomb or Lumberton spectrophotometer
4. Graduated pipette having 1 ml capacity to 0.01 ml accuracy
5. Suction bulb for use with pipette
6. Test tubes compatible with spectrophotometer, 3/4" X 6, Bausch and Lomb, Catalog No. 33-17- 81, (B&L)

c. Calibration of spectrophotometer:

1. Calibrate spectrophotometer as follows:

- a. Set wavelength at 580 mu,
- b. Allow spectrophotometer to warm-up thirty minutes,
- c. Zero percent light transmittance (%LT) scale,
- d. Rinse test tube three times with tap water and fill to top of circle marking on B&L test tube or approximately 2/3 full,
- e. Place tube in spectrophotometer and set %LT scale at 100, and,

f. Repeat steps (c) (e) two times or until no further adjustments necessary.

d. Procedure:

1. Shake, stir or otherwise thoroughly mix emulsion to be tested. Place sample of emulsion in beaker and allow to stand one minute.
2. Place 2,000 ml tap water in container.
3. Suck 1.00 ml emulsion into pipette using suction bulb. Wipe off outside of pipette.
4. Using suction bulb, blow emulsion into container.
5. Rinse pipette by sucking in diluted emulsion solution and blowing out.
6. Clean pipette with soap or solvent and water. Rinse with acetone.
7. Stir diluted emulsion thoroughly.

8. Rinse out tube to be used with the diluted emulsion three times and fill to top of circle.
9. Calibrate spectrophotometer.
10. Place diluted emulsion sample tube in spectrophotometer, cover and read %LT to nearest tenth.
11. Repeat steps 9 and 10 until three identical consecutive readings are achieved.
12. The elapsed time between addition of emulsion to dilution of water and final %LT reading should not exceed 5 minutes.

⁵ Chemical Composition by ASTM Method D-2006-70 -- (Free) Maltene Distribution Ratio (MDR) can be defined as:

$$\frac{PC + A_1}{S + A_2}$$

Where:

PC = Polar Compounds A₁ = First Acidaffins

A₂ = Second Acidaffins S = Saturated Hydrocarbons

2 Maltene Replacement (“Rejuvenation”) Test

The TiO₂ Enhanced Asphalt Rejuvenating Agent shall have the capability to penetrate the asphalt pavement surface and shall be absorbed and incorporated into the asphalt binder. Verification that said incorporation of the TiO₂ Enhanced Asphalt Rejuvenating Agent into the asphalt binder has been effected shall be by the petroleum maltene fraction replacement method and analysis of the chemical properties of said asphalt binder therein i.e., viscosity shall be reduced by said method.

For pavements less than two-years old and receiving the original application of TiO₂ Enhanced Asphalt Rejuvenating Agent, the viscosity shall be reduced by a minimum of twenty (20%) percent as determined by the dynamic shear rheometer (DSR) method for asphalt testing in accord with AASHTO T315-05. For treatments of pavements older than two-years and/or after an initial treatment with a petroleum maltene asphalt rejuvenator, the viscosity shall be reduced by petroleum maltene replacement method a minimum of thirty percent (30%) in accord with same. This analysis shall apply to extracted asphalt binder, taken from cores extracted fifteen to thirty days following application, in the upper 3/8” of pavement. The treated areas shall be densified or resistant in depth to the intrusion of air and water.

The TiO₂ Enhanced Asphalt Rejuvenating Agent shall have a record of at least two years of satisfactory service as a TiO₂ enhanced petroleum maltene based emulsion asphalt rejuvenating agent and in-depth densifier. Satisfactory service shall be based on the capability of the material to decrease the viscosity of the asphalt binder by the petroleum maltene replacement method and provide an in-depth seal. **A.R.A.-1 Ti[®]**, a Pavement Technology, Inc. product manufactured by D&D Emulsions, Inc., Mansfield, Ohio, is a product of know quality and accepted performance.

The bidder must submit with his bid the manufacturer's certification that the material proposed for use is in compliance with the specification requirements. The bidder must submit with his bid previous use documentation and test data conclusively demonstrating that; the TiO₂ Enhanced Asphalt Rejuvenating Agent has been used successfully for a period of two years by government agencies such as state, county and municipal governments or "SCMs", etc.; and that the enhanced rejuvenating agent has been proven to perform, as heretofore required, through field testing by government agencies as to the required change in asphalt binder rheology and photocatalytic properties as hereinafter detailed. Testing data shall be submitted indicating such product performance on a sufficient number of projects to insure product consistency. In addition, field testing data shall be submitted to indicate said product performance over a minimum testing period of two years to insure reasonable sustainability.

The Engineer may require that untreated and treated core samples, a minimum of four inches in diameter, be removed by the Contractor at locations indicated by the Engineer. The treated core sample shall be taken in the same lane in close proximity to each untreated sample. A minimum of one untreated and treated core sample shall be taken for each pavement group or one per 50,000 square yards of treated pavement in each pavement group.

3 Photocatalytic Properties Testing

3.1 TiO₂ Penetration Test: The TiO₂ Enhanced Asphalt Rejuvenating Agent shall have a non-destructive analytical procedure applied to determine the percent of Titanium Dioxide nanoparticles present in each two-millimeter (2mm) layer of the field core sample matrix for a minimum depth of six millimeters (6mm) from the top of the treated sample core. The method of measurement shall be by fluorescent X-ray emitted from the surface when excited by a principal X-ray source that is exceptional for the given element. A hand-held XRF analyzer is acceptable for this testing.

The minimum required concentration of Titanium Dioxide nanoparticles per each two-millimeter (2mm) section up to the minimum depth of 6mm shall average 2000 parts per million (ppm).

3.2 NO₂ Reduction Effectiveness: The TiO₂ Enhanced Asphalt Rejuvenating Agent shall be verified for the effectiveness of the air pollution remediation of the Titanium Dioxide nanoparticle portion by laboratory analysis of core samples extracted from the treated pavement as directed and required by the Engineer. The cores shall be a minimum of four inches (4") in diameter and in pairs at each location directed by the Engineer. The cores shall be tested by an accredited laboratory or university with the equipment and capability to perform the following test procedures.

3.3 NO₂ Reduction Test: A photo reactor test chamber shall be employed that allow for the evaluation of the efficient photocatalytic reduction of introduced NO_x gas of a known and controlled concentration within the

chambers volume. The chamber light source shall be a UV lamp having a wavelength of 375 nanometers. The interior chamber environment shall be at 77°F with a constant humidity of 55% ±5%. The test total duration shall be five hours. The analysis test system shall be based on a Japanese Industrial Standard (JIS) TR Z0018 “Photocatalytic Materials-Air purification test procedure”. NO removal efficiency shall be measured using a Model 42i Chemiluminescence NO-NO₂-NO_x Analyzer (Thermo Fisher Scientific Inc.).

The minimum NO reduction following the heretofore outlined test procedure evaluating field core samples shall average 25% for all cores tested.

3.4 Solar Reflectance Effectiveness: Verification of the effectiveness of the solar reflectivity the Titanium Dioxide nano-particle portion of the TiO₂ Enhanced Asphalt Rejuvenating Agent shall be by laboratory analysis of core samples extracted from the treated pavement as directed and required by the Engineer. The cores shall be a minimum of four inches (4”) in diameter and in pairs at each location directed by the Engineer. The cores shall be tested by an accredited laboratory or university with the equipment and capability to perform the following test procedures.

3.5 Solar Reflectance Test(s): Solar reflectivity shall be determined by measuring the treated core samples for a Solar Reflectance Index (SRI) value. SRI is a measure of the constructed surface’s ability to reflect solar heat, as shown by a small temperature rise. It is defined so that a standard black surface (reflectance 0.05, emittance 0.90) is 0 and a standard white surface (reflectance 0.80, emittance 0.90) is 100. The relevant standards for measuring solar reflectance are:

Table 2 Test of Solar Reflectance

Value	Test Method
Solar Reflectance	ASTM C1549 – Standard Test Method for Determination of Solar Reflectance
Solar Reflectance Index	ASTM E 1980 – Standard Practice for Calculating Solar Reflectance Index of Horizontal and Low-Sloped Opaque Surfaces

Based on these standards, the SRI is a measure of the relative steady-state temperature of a surface with respect to a standard white surface (SRI=100) and a standard black surface (SRI=0) under standard solar and ambient conditions.

Under normal ambient conditions, the steady-state temperature for the black and white reference surfaces is 355.61 kelvin (K) or 180°F and 317.76 K (110°F), respectively.

A Solar Reflectance Index (SRI) can be defined as:

$$SRI = \frac{T_b - T_s}{T_b - T_w}$$

Where:

- Steady-state Surface Temperature (Ts)—the temperature of the surface, in K, under the standard solar conditions. The surface temperature Ts (°C)=Ts (K)-273

- Reference Black Surface Temperature (T_b)—the steady-state temperature of a black surface with a solar reflectance of 0.05 and infrared emittance of 0.9, under the standard solar and ambient conditions
- Reference White Surface Temperature (T_w)—the steady-state temperature of a white surface with a solar reflectance of 0.80 and infrared emittance of 0.9, under the standard solar and ambient conditions
- Sky Temperature (T_{sky})—the temperature of a black body that would radiate the same power in the thermal infrared spectrum (5 to 40 nm) toward the earth as does the sky

The minimum SRI value following the heretofore outlined test procedure(s) evaluating field core samples shall average 29 (or 0.29) for all cores tested, which meet the minimum standard ($\geq 50\%$ 29 SRI) for the U.S. Green Building Council (USGBC) hardscape threshold for Leadership in Energy and Environmental Design (LEED) credit or the minimum standard for the American Public Works Association (APWA) / Institute for Sustainable Infrastructure (ISI) Envision Superior ($\geq 60\%$ 29 SRI) level of achievement credit.

3.6 Hydrophilic Improvement: Verification of the improvement in hydrophilic property of the Titanium Dioxide nano-particle portion of the TiO₂ Enhanced Asphalt Rejuvenating Agent shall be by laboratory analysis of core samples extracted from the treated pavement as directed and required by the Engineer. The cores shall be a minimum of four inches (4") in diameter and in pairs at each location directed by the Engineer. The cores shall be tested by an accredited laboratory or university with the equipment and capability to perform the following test procedures.

3.7 Wettability Test: Hydrophilic improvement shall be determined by measuring the treated core samples for Water Contact Angle (WCA). WCA is a common measurement of a constructed surface's ability to improve wettability or the ability of water to develop a stronger boundary (less resistance) with the surface as shown by a decline in water contact angle. A WCA of $> 90^{\circ}$ is considered hydrophobic or high resistance while a WCA $< 90^{\circ}$ is considered hydrophilic or low resistance. The relevant standard for measuring WCA is:

Table 3 Test of Water Contact Angle

Value	Test Method
Water Contact Angle	ASTM D7334 - 08(2013) Standard Practice for Surface Wettability of Coatings, Substrates and Pigments by Advancing Contact Angle Measurement

The minimum WCA reduction following the heretofore outlined test procedure evaluating field core samples shall average 20% for all cores tested.

2 Equipment

2.1 Distributor: The distributor for spreading the emulsion shall be self-propelled and shall have pneumatic tires. The distributor shall be designed and equipped to distribute the asphalt rejuvenating agent uniformly on variable widths of surface at readily determined and controlled rates from 0.04 to 0.10 gallons per square yard of surface, and with an allowable variation from any specified rate not to exceed 5% of the specified rate.

Distributor equipment shall include full circulation spray bars, pump tachometer, volume measuring device and a hand hose attachment suitable for application of the emulsion manually to cover areas inaccessible to the distributor. The distributor shall be equipped to circulate and agitate the emulsion within the tank.

The rate of application shall be controlled by an onboard computer control system designed to control the selected application rate uniformly and consistently in gallons per square yard regardless of the forward speed of the distributor truck.

A check of distributor equipment as well as application rate accuracy and uniformity of distribution shall be made when directed by the Engineer.

2.2 Aggregate Cover Truck: The truck used for cover aggregate application shall be equipped with a spreader that allows the aggregate to be uniformly distributed onto the pavement. The spreader shall be able to apply 1/2 pound to 3 pounds of cover aggregate per square yard in a single pass. The spreader shall be adjustable so as not to broadcast cover aggregate onto driveways or to lawns.

The cover aggregate to be used shall be free flowing, without any leaves, dirt, stones, etc. Any wet aggregate shall be rejected from the job site.

Any equipment that is not maintained in full working order, or is proven inadequate to obtain the results prescribed, shall be repaired, or replaced at the direction of the Engineer.

2.3 Calibration: Distributor- prior to construction, calibrate the distributor in accordance with ASTM D2995-99 in the presence of the Engineer. The distributor shall be moving forward at the proper application speed at the time the spray bar is opened. If at any time a nozzle becomes clogged or not spraying a proper pattern, the operation shall be immediately halted until repairs are made.

3 Construction

3.1 Layout: The Contractor will be responsible for the lay out of the roadway and project planning and sequencing to meet traffic control requirements prior to paving.

3.2 Weather and Seasonal Limitations: The TiO₂ Enhanced Asphalt Rejuvenating Agent shall not be applied to a wet surface or when rain is occurring, or the threat of rain is present immediately before placement. The surface treatment shall not be applied when the temperature is less than 40° in the shade. When applying emulsions, the temperature of the surface shall be a minimum of 45°F, and no more than 150°F.

If unexpected rain occurs prior to material penetration and cover aggregate application, the agent shall be reapplied at no cost to the agency. Further, the contractor's traffic control and project monitoring shall continue until the application has penetrated, area has been sanded and the resultant surface is acceptable to the Engineer for vehicular travel.

3.3 Preparation of Surface: The contractor will be responsible for blowing or sweeping the road immediately ahead of the application operation to make sure the road is free of standing water, dirt, loose aggregate, and other debris. The surface shall be clean and dry prior to the application.

3.4 Application of TiO₂ Enhanced Asphalt Rejuvenating Agent: The TiO₂ Enhanced Asphalt Rejuvenating Agent shall be applied by a distributor truck at the temperature recommended by the manufacturer and at the pressure

required for the proper distribution. The emulsion shall be so applied that uniform distribution is obtained at all points of the areas to be treated. Distribution shall be commenced with a running start to ensure full rate of spread over the entire area to be treated. Areas inadvertently missed shall receive additional treatment as may be required by hand sprayer application.

3.5 Material Placement of TiO₂ Enhanced Asphalt Rejuvenating Agent: Application of TiO₂ Enhanced Asphalt Rejuvenating Agent shall be on one-half width of the pavement at a time. When the second half of the surface is treated, the distributor nozzle nearest the center of the road shall overlap the previous application by at least one-half the width of the nozzle spray. In any event the centerline construction joint of the pavement shall be treated in both application passes of the distributor truck.

Before spreading, the TiO₂ Enhanced Asphalt Rejuvenating Agent shall be blended with water at the rate of two parts rejuvenating agent to one-part water, by volume or as specified by the manufacturer. The combined mixture of asphalt rejuvenating agent and water shall be spread at the rate of 0.04 to 0.10 gallons per square yard, or as approved by the Engineer following field testing.

Where more than one application is to be made, succeeding applications shall be made as soon as penetration of the preceding application has been completed and the Engineer grants approval for additional applications. Grades or super elevations of surfaces that may cause excessive runoff, in the opinion of the Engineer, shall have the required amounts applied in two or more applications as directed.

The Contractor shall furnish a quality inspection report showing the source, manufacturer, and the date shipped, for each load of TiO₂ Enhanced Asphalt Rejuvenating Agent. When directed by the Engineer, the Contractor shall take representative samples of material for testing.

3.6 Test Strip for Application Rate: Prior to start of the project, the contractor shall perform test strip applications as directed by the engineer. Test strips shall be performed for each pavement group of similar age and type within the project area.

The test strips shall be applied at a minimum width of 6 feet and for a length of 50 feet. A total of three test strips shall be applied at application rates of 0.04, 0.08 and 0.10 gallons per square yard, respectively. The time, in minutes, for essentially complete absorption of the asphalt rejuvenating emulsion shall be recorded for each test strip. The optimal rate to be used in a given area shall be that rate essentially absorbed within 20 minutes.

In the event that all three of the standard test rates are absorbed completely within the 20-minute timeframe, then the Contractor and the Engineer shall agree on a fourth test strip application rate.

Upon completion of the test strips for each pavement group, the Engineer will determine the final application rate to be applied to each pavement group.

3.7 Cover Aggregate Application: After the TiO₂ Enhanced Asphalt Rejuvenating Agent emulsion has penetrated, and when recommended by the Contractor and approved by the Engineer, a coating of dry cover aggregate shall be applied to the surface in sufficient amount to protect the traveling public as required.

All cover aggregate used during the treatment must be removed no later than 24 hours after treatment of a roadway. This shall be accomplished by a combination of hand and mechanical sweeping. All turnouts, cul-de-sacs, etc. must be cleaned of any material to the satisfaction of the Engineer. Street sweeping will be included in the price bid per square yard for asphalt rejuvenating emulsion.

If, after the cover aggregate is swept and in the opinion of the Engineer a hazardous condition exists on the roadway, the contractor must apply additional cover aggregate and sweep same no later than 24 hours following reapplication. No additional compensation will be allowed for reapplication and removal of materials.

3.8 Handling of TiO₂ Enhanced Asphalt Rejuvenating Agent: Contents in tank cars or storage tanks shall be circulated at least 45 minutes before withdrawing any material for application. The distributor truck will be cleaned of all of its asphalt materials and washed out to the extent that no discoloration of the emulsion may be perceptible. Cleanliness of the spreading equipment shall be subject to the approval of the Engineer.

3.9 Street Sweeping: The Contractor shall be responsible for sweeping and cleaning the streets after treatment. All cover aggregate used during the treatment must be removed no later than 24 hours after treatment of the street. This shall be accomplished by a combination of hand and mechanical sweeping. All turnouts, cul-de-sacs, etc. must be cleaned of any material to the satisfaction of the Engineer.

If, after cover aggregate is swept and in the opinion of the Engineer a hazardous condition exists on the roadway, the contractor must apply additional cover aggregate and sweep same no later than 24 hours following reapplication. No additional compensation will be allowed for reapplication and removal of cover aggregate.

3.10 Resident Notification: The contractor shall distribute by hand, a typed notice to all residences and businesses on the street to be treated. The notice will be delivered no more than 24 hours prior to the treatment of the road. The notice will have a local phone number that residents may call to ask questions. The notice shall be of the door hanger type, which secures to the door handle of each dwelling. Unsecured notices will not be allowed. The contractor shall also place the notice on the windshield of any parked cars on the street. Hand distribution of this notice will be considered incidental to the contract.

3.11 Traffic Control: The Contractor shall furnish all necessary traffic control, barricades, signs, and flagmen, to ensure the safety of the traveling public and to all working personnel. Traffic shall not travel on fresh TiO₂ Enhanced Asphalt Rejuvenating Agent until penetration, in the opinion of the Engineer, has become complete and the area is suitable for traffic. The Contractor shall submit an M.O.T plan indicating all facets of traffic control for the project area. The M.O.T. plan must be approved in writing by the Engineer prior to commencing any work. All traffic control shall be in accordance with the DOT Roadway Design Standards (most current edition). Traffic control devices shall be checked daily and periodically throughout the project for compliance; and where adjustments or corrections are needed, prompt revisions shall be made.

3.12 Method of Measurement: The TiO₂ Enhanced Asphalt Rejuvenating Agent emulsion shall be paid at the Contract bid unit prices for the actual square yards of pavement treated as field measured. Said payment is compensation in full for all costs of furnishing and applying the material as specified, including cleaning the existing pavement, purchase of cover aggregate, delivery of cover aggregate, all labor, equipment, and materials necessary for the placement of the TiO₂ Enhanced Asphalt Rejuvenating Agent emulsion, sweeping of any loose material after construction and other requirements as specified. Traffic control for maintaining traffic for constructing TiO₂ Enhanced Asphalt Rejuvenating Agent emulsion shall be considered incidental.

Payment for removal of untreated and treated cores shall be paid for as each at the unit price bid for Test Core Removal.

3.13 Basis of Payment:

<u>Pay Item</u>	<u>Unit</u>
• TiO ₂ Enhanced Asphalt Rejuvenating Agent	Per Sq/Yd
• Field Core Removal*	Each
• Field Core Laboratory Analysis – Viscosity*	Each
• Field Core Laboratory Analysis -Titanium Dioxide Penetration*	Each
• Field Core Laboratory Analysis - Titanium Dioxide NO ₂ Reduction*	Each
• Field Core Laboratory Analysis - Titanium Dioxide Solar Reflectance Index (SRI)*	Each
• Field Core Laboratory Analysis - Titanium Dioxide Water Contact Angle (WCA)*	Each
• Mobilization	Per Project

*When required by the Engineer