INNOVATIVE CONCEPT FOR CREATING AN AIR PURIFICATION PAVEMENT SURFACE COATING BY ATMOSPHERIC PRESSURE COLD PLASMA

By

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of JOSEPH WESTERGREEN find it satisfactory and recommend that it be accepted.

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Abstract

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Air pollution from automobiles, in the form of nitrogen oxides (NO_x) and volatile organic compounds (VOCs) are increasing continuously due to the rapid development of transportation activities, which can cause a number of environmental and social issues and impact public health. Nano titanium dioxide (TiO_2) has been found to have photocatalytic properties, which, under UV light can oxidize and remove VOCs and NO_x from the atmosphere. Although TiO_2 treated paving materials have great potential to improve air quality, current techniques to adhere TiO_2 to substrate materials are either not durable or reduce direct contact of TiO_2 with UV light, reducing the photocatalytic effect. To solve this technical difficulty, this study innovatively introduces atmospheric pressure cold plasma (APCP) techniques to transportation engineering to coat TiO_2 to pavement. The objective of this study is to test the concept of using APCP techniques to create a durable TiO_2 coating on the surface of paving materials to reduce NO_x and VOCs at the street level. An APCP generator was developed to produce activated radicals from precursor molecules using high voltage streamers as the plasma source, and to immobilize nano

TiO_2 powder to substrate pavement materials. Preliminary results are promising, showing that TiO_2 can be incorporated successfully into an APCP environment. Evidence of TiO_2 has been identified based on field emission scanning electron microscope (FE SEM) images. The TiO_2 coated material with APCP shows some ability to reduce nitrogen oxides when exposed to UV light in an environmental chamber. However, such effect is limited which is hypothesized due to either limited deposition rate of the plasma polymerized film or the plasma polymerized film blocking the direct contact of TiO_2 with the UV light. Further research is therefore recommended to optimize the APCP generator for improved efficiency. Also a more in depth study should be conducted on the plasma polymerized film and its interaction with the TiO_2.

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Dedication

This thesis is dedicated to my family for their continued support throughout my life and educational career.

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

Throughout the United States, population density in urban cities is continuing to grow. With these high population densities arise many concerns. One significant problem is controlling air pollution from the large density of vehicles. The main pollutants emitted by vehicles are carbon monoxide (CO), nitrogen oxides (NO_x), volatile organic compounds (VOCs) and particulates. According to the EPA motor vehicles are estimated to account for 29% of the VOCs, 35% of the NO_x, and 58% of the CO emitted in the United States (Kuhns et al. 2004). These concentrations are often higher in urban areas where large structures create canyons and prevent dispersion of pollutants (Bekowicz et al. 2006; Thoma et al 2008). A number of regions in the United States and throughout the world have air pollution levels exceeding national air quality standards. For example London is facing a $500 million fine for exceeding annual pollution limits (Morales 2011).

There have been many health hazards associated with NO_x and VOCs, especially in urban areas near roadways (Bekowicz et al. 2006; Thoma et al 2008). Studies have linked increases in respiratory infections and asthmatic/allergic symptoms to traffic-related pollutants (Brauer et al. 2002; Brunekreef et al. 1997). Also NO_x and VOCs can react with sunlight and lead to the formation of ozone and acid rain causing environmental problems far away from the pollutant source (Bleedens 2006).

Automobile manufacturers have made progress in reducing pollutants emitted from new vehicles, but it will take many years for the majority of vehicle users to adopt these technologies

(Berkowicz et al. 2006). New catalytic converters are able to dramatically reduce CO and VOCs from gasoline vehicles, but NO_x emissions are still a problem. Diesel engines still emit high levels of NO_x and VOCs. So, being able to reduce these concentrations at the street level once pollutants are emitted into the atmosphere would be useful in managing air quality. One potential solution is to utilize heterogeneous photocatalysis, which accelerates the natural pollution decomposition process that takes place in nature (Fox and Duley 1993).

It has been shown that titanium dioxide (TiO_2) has photocatalytic properties, and that it can effectively be used to reduce VOCs and NO_x (Beeldens 2006; Chen and Poon 2009; Hassan et al. 2009). In this photocatalyst process TiO_2 traps and absorbs pollutant molecules from the air and converts them to harmless inorganic anions in the presence of UV sunlight (Fujishima and Zhang 2006). TiO_2 is relatively cheap, has fast reaction rates, and can convert a wide range of organic compounds. In addition TiO_2 has hydrophilic properties allowing self-cleaning in the presence of rain, and it is a catalyst so theoretically it can be used indefinitely (Fujishima et al. 2000). These properties make TiO_2 the ideal photocatalyst to incorporate onto existing infrastructure for improved air quality.

There is a lot of emerging technology utilizing the self-cleaning and air purifying properties of TiO_2. For pavement applications most of the research has been focused on applying photocatalytic TiO_2 to concrete or paving bricks, and these products have shown great potential for self-cleaning and air purifying applications (Cassar et al. 2003; Chen and Poon 2009; Frazer 2001). The problem is most of the methods have focused on concrete, but asphalt covers more than 94% of the paved roads in the United States according to the National Asphalt Pavement Association. So finding a durable TiO_2 surface treatment that can attach to asphalt would be

beneficial. There have been some recent attempts to put TiO_2 on the surface of asphalt by using TiO_2 emulsion applications, but the durability of these surface treatments could be improved (Crispino et al. 2010; Hassan et al. 2011; Mureta et al. 2002). Identifying new, potentially more durable methods to attach TiO_2 to asphalt and other engineering materials is desired.

Atmospheric pressure cold plasma (APCP) surface treatment is known to be a powerful process to modify surface characteristics of both metallic and polymeric materials. The process can be used to improve adhesion of additives to engineering materials. Plasma is generated by exciting gas molecules with a source of electrical energy (Jama and Delobel 2007). APCP results when this excitation causes electron avalanches and streamers to appear in intense electric fields. This results in chemical bond scission and conversion of precursor molecules to activated radical species. These activated radical species can combine with each other and other substances to create a strong interlocking layer (Lieberman and Lichtenberg 2005). With APCP the entire process is done at atmospheric pressure making it efficient, non-polluting, and economical (Vons et al. 2006), making it a practically promising technology for vast pavement engineering applications. This exploratory study introduces APCP techniques to pavement engineering to enhance the interface bonding of materials.

1.2 PROBLEM STATEMENT

There are two main issues that make this research a necessity. The first problem is VOCs and NO_x concentrations from vehicles are too high, especially in urban areas. The automobile industry has been working to reduce car emissions, but a pollution reducing method at the street level is a viable complementary solution. Automobile pollution levels within 100 meters of

roadways are particularly a large concern because tall structures prevent dispersion of pollutants. In these areas an air purifying pavement would be especially successful because of the long residence time of pollutants with the road surface.

The second problem is currently there are not effective processes to adhere TiO_2 to the surface of asphalt. Most of the pavement applications involving photocatalytic TiO_2 focus on mixing TiO_2 into concrete slurries, paints, and other materials. These are not the most effective methods for utilizing the photocatalytic properties of TiO_2 because direct sunlight is required to initiate the photocatalyst reaction. So finding a more durable and efficient way to adhere TiO_2 to construction materials is desired.

1.3 RESEARCH OBJECTIVES

The overall objective is to test the concept of using APCP techniques to create a durable TiO_2 coating on the surface of paving materials to reduce NO_x and VOCs at the street level. To complete this objective the specific goals are to:

1. Develop an APCP generator, and use radicals produced by the generator to securely bond TiO_2 to an asphalt substrate.

2. Evaluate the performance of the TiO_2 coating with respect to the effectiveness of the TiO_2 in removing NO_x, and the durability of the coating.

1.4 ORGANIZATION OF THESIS

This dissertation describes the process of using atmospheric pressure cold plasma to adhere titanium dioxide to pavement with the goal of creating an air purifying pavement. Chapter 1 provides the background, problem statement, and research objectives. Chapter 2 contains the

literature review and a summary of the existing research findings. Chapter 3 describes the experimental setup and procedure. Chapter 4 describes experiments with the initial APCP generator design. Chapter 5 describes experiments after APCP generator modifications. Chapter 6 provides preliminary findings of the study and recommendations for future work based on the preliminary research findings.

CHAPTER 2: LITERATURE REVIEW

This chapter reviews past, current, and ongoing research that focuses on using titanium dioxide (TiO_2) as a photocatalyst. Specifically applying TiO_2 to roadway infrastructure with the intent to make self cleaning pavement is identified. The second half of the literature review focuses on plasma processing applications. Then atmospheric pressure cold plasma (APCP) is specifically identified as a promising and innovative technology to improve bonding of materials. This chapter reviews research using these two separate and innovative technologies with the intent to combine them to make an efficient and durable air purifying pavement coating.

2.1 TITANIUM DIOXIDE AND PHOTOCATALYTIC APPLICATIONS

Titanium is the world's fourth most abundant metal, ninth most abundant element, and was first discovered in England by Reverend William Gregor in 1791 (Carp et al. 2004). TiO_2 is a naturally occurring oxide in titanium metal and can have three different crystal structures: anatase, rutile and brookite. The crystal structures can be identified by their octahedral chain configurations. Based on octahedral design and thermodynamic calculations rutile is found to be the most stable phase at all temperatures followed by anatase (Carp et al. 2004). Figure 2.1 shows these three crystal structures of TiO_2.

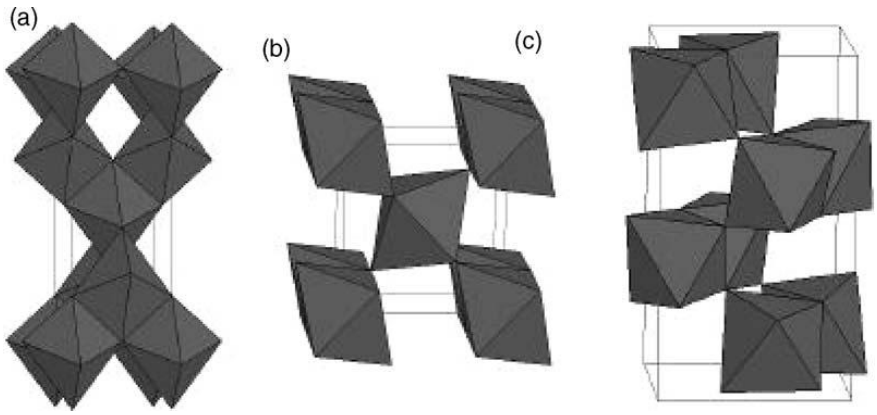


Figure 2.1 TiO_2 crystal structures: anatase (a), rutile (b), and brookite (c), (Carp et al. 2004)

TiO_2 has been used as a white pigment since ancient times because of its white color and availability (Hashimoto et al. 2005). It first became a common industrial product in the 20th century replacing toxic lead oxides as pigments for white paint. Now the world's production of TiO_2 exceeds 4 million tons per year, and approximately 98% is used to make white pigments (Carp et al. 2004). It is used as a white pigment in paints, plastics, paper, toothpaste, sunscreen, and many other products (Beeldens 2006). The primary reason it is used in products like sunscreen is because TiO_2 can absorb UV light without being consumed in the reaction (Beeldens 2006). Also, because of the high refractive index of TiO_2 it is being used as anti-reflection coatings in silicon solar cells, roofing materials, and many other commercial products. TiO_2 in these applications has proven to increase light reflectance, reduce heat buildup, and help mitigate the urban heat island effect (Kalessi et al. 2009; Levinson et al. 2009; Macleod 1986). Since the 1980's there has been a lot of interest in the photocatalytic properties of TiO_2 (Hashimoto et al. 2005).

2.1.1 Photocatalyst Effect of Titanium Dioxide

The photocatalyst effect of TiO_2 was discovered by Fujishima in the late 1960s when he used TiO_2 to decompose water into oxygen and hydrogen in the presence of sunlight (Fujishima and Honda 1972). Sunlight will decompose organic materials over time, but a photocatalyst can be used to speed up the process (Chusid 2009). A photocatalyst is defined as a material that uses solar energy to accelerate chemical reactions without being consumed or depleted in the process (Chusid 2009). Anatase and rutile are the most common crystal structures of TiO_2, both have photocatalytic properties, but anatase has shown to be more photocatalytic for most applications (Banerjee et al. 2006; Beeldens 2006). This is because anatase has a higher fermi level, lower capacity to absorb oxygen, and higher degree of hydroxylation (Carp et al. 2004).

TiO_2 is a stable compound in darkness, but in the presence of UV light it becomes active inducing chemical reactions (Hashimoto et al. 2005). To initiate the oxidation process UV-light with wave lengths lower than 387 nm is required (Beeldens 2006). The photocatalytic reaction occurs by the formation of electron-hole pairs initiated by sunlight or other UV sources, resulting in the formation of hydroxyl radicals ($OH^{\cdot}$) (Fujishima et al. 2000; Fujishima and Honda 1972). These hydroxyl radicals are strong oxidizing and reducing agents and can decompose organic and inorganic compounds (Hassan et al. 2010; Fujishima and Zhang 2006). For example nitrogen oxide can be decomposed into nitrate and sulfur dioxide into sulfate (Beeldens 2006; Hassan et al. 2010; Katzman 2006). In this process the pollutant is absorbed on to the surface, oxidized to a less harmful pollutant by UV-light, and then washed off the surface (Beeldens 2006). Figure 2.2 illustrates the oxidation of nitrogen oxide into nitrate. (Beeldens 2006; Dalton et al. 2002).

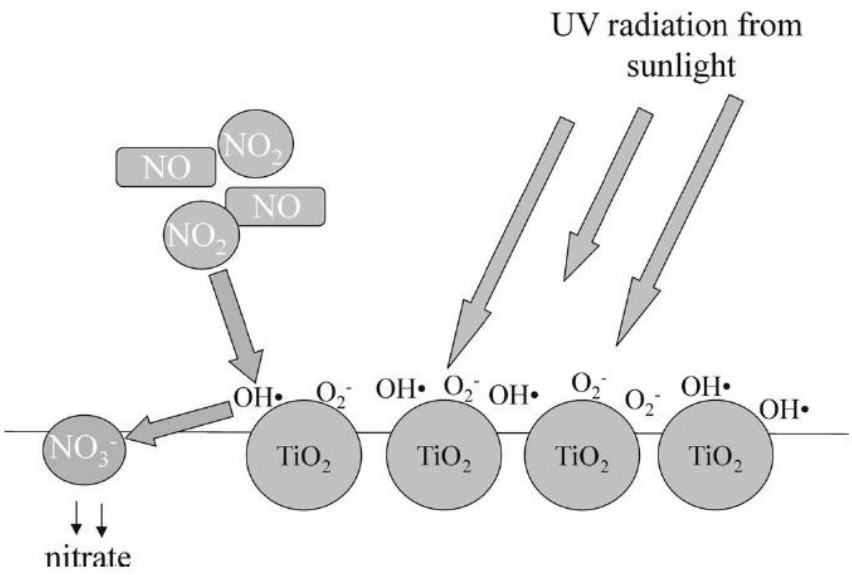


Figure 2.2 Schematic illustrating NO_x removal process (Dalton et al. 2002)

TiO_2 is an ideal photocatalyst and can be used for a lot of different applications because it is relatively inexpensive, chemically stable, and the photo-generated holes are highly oxidizing (Carp et al. 2004; Fujishima et al. 2000). Photocatalytic TiO_2 can degenerate and convert organics, bacteria, viruses, and fungi into CO_2, H_2O, and harmless inorganic anions (Banerjee et al. 2006). Most current photocatalytic TiO_2 applications fall into four main categories: self cleaning, air purification, water purification, and anti-bacteria sterilization (Fujishima et al 2000).

2.1.2 Self-cleaning Applications for Photocatalytic Materials

When TiO_2 is activated by UV light it has hydrophilic properties allowing self-cleaning in the presence of water or rain (Fujishima, and Zhang 2006; Beeldens 2006). Self-cleaning glass and concrete are becoming common products all over the world (Puzenat 2009). A thin TiO_2 film

is applied to the substrate that has two photo-induced properties. First it has the ability to oxidize organic stains and pollutants that come into contact with the TiO_2 film. Secondly the film creates a hydrophilic surface by increasing the wettability allowing for organic and inorganic pollutants to be washed off the surface (Puzenat 2009). Being hydrophilic the water layer is attracted to the surface and gets between the dirt and the surface. The best self-cleaning results are reported on smooth surfaces like glass and ceramic tiles (Beeldens 2006). The hydrophilic properties of TiO_2 also provide an anti-fogging function that is being incorporated into mirrors and glass (Hashimoto et al. 2005; Puzenat 2009). Photocatalytic TiO_2 was first incorporated into cement materials to self-clean and help retain the white color for aesthetic appeal (Cassar et al. 2003). An example of using TiO_2 for long lasting asthetic appeal is the Jubilee Church in Rome that was constructed in 2003 (Chusid 2009).

Figure 2.3 Jubilee Church in Rome (Courtesy of Chusid 2009)

Also self cleaning silk and wool fabrics are being manufactured, which have the ability to decompose dirt, stains, odors, and some harmful microorganisms without changing the texture and feel of the material. The self-cleaning keratin fibers are often produced by applying an anatase TiO_2 coating to the fabric fibers by dip coating (Daoud et al. 2008). Fabric samples were stained with red wine and placed in sunlight for 20 hours. After 20 hours the fabric with the TiO_2 coating showed little signs of the red stain, as shown in Figure 2.4.

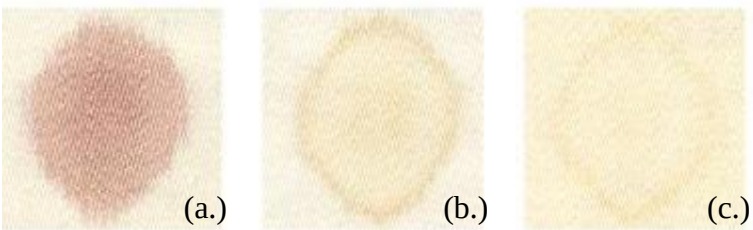


Figure 2.4 (a) Red wine stain initially; (b) after 8 hours, and (c) after 20 hours of exposure to UV light (Daoud et al. 2008)

Additionally, in Japan photocatalyst wool has showed an ability to decompose bad odors from acetaldehyde, ammonia, and hydrogen sulfide with exposure to UV light (Photo-catalytic Materials Inc.).

Other commercially available products utilizing photocatalytic TiO_2 include air purifying products that can remove harmful microorganisms. These include spray products that are made of TiO_2 and water, and air purifying filters that use sterilizing UV lamps and a photocatalyst ceramic honeycomb to chemically decompose air impurities (Photo-catalytic Materials 2011). One large advantage is these air purifying products destroy the microorganisms compared to just trapping them in a filter (Photo-catalytic Materials 2011). This technique was first used in

nursing homes to eliminate bacteria and smells from body waste (Photo-catalytic Materials 2011).

2.1.3 Air Purification Applications for Photocatalytic Materials

Now a lot of research is focusing on utilizing the air purification capabilities of TiO_2 to reduce urban air concentrations of nitrogen oxides (NO_x) and volatile organic compounds (VOCs) from automobile exhaust emissions (Beeldens 2006; Chen and Poon 2009; Hassan et al. 2010). In the last 10 years there have been many patented designs that apply TiO_2 to the surface layer of concrete blocks or tiles during the manufacturing process (Husken et al. 2007; Mureta et al. 2002; Puzenant 2009). These patented paving blocks have shown the ability to decompose pollutants in a laboratory setting (Husken et al. 2007; Mureta et al. 2002). Also, a lot of research is focusing on applying photocatalyst coatings to roadways, tunnels, and sound barriers by mixing nano TiO_2 powder into paints, concrete slurries, and other products (Carp et al. 2004; Beeldens 2008).

For roadway applications the goal is to put as much TiO_2 on the surface as possible without losing TiO_2 to abrasion or weathering, and to obtain uniform distribution of TiO_2 to ensure maximum exposure of the nano-particles at the surface (Beeldens 2006; Hassan et al. 2010). Generally, the higher the catalyst loading rate the higher the pollution decomposition rate (Carp et al. 2004). Although, too much TiO_2 has shown to increase the opacity of the surface reducing the light penetration and the pollution decomposition rate (Carp et al. 2004).

For the photocatalytic concrete blocks or tiles generally the TiO_2 is mixed into the top wearing layer of the blocks, allowing new TiO_2 to be exposed to the surface as the tile wears

from traffic (Husken et al. 2007; Mureta et al. 2002; Puzenant 2009). The European market has a variety of these air purifying stones available for commercial use. Husken et al. (2007) did a comparative study of the NO_x removal efficiency of five different photocatalytic paving products following ISO Standard TC 206/SCN for degradation of NO_x in an environmental chamber. The products showed an average 40% NO reduction, but there was large variation depending on the product ranging from 4.0% NO reduction to 44.6% NO reduction (Husken et al. 2007). Four of the products were paving stones from different producers and one was a cementitious suspension of TiO_2 in cement that is designed to be applied to asphalt pavements to fill in the porosity of the pavement and create an air purifying surface (Husken et al. 2007).

Photocatalytic pavement overlays are becoming a popular concept because they are cheaper than photocatalytic paving stones and more durable than mixing TiO_2 with paints or other materials (Beeldens 2006; Hassan et al. 2010; Mureta et al. 2002). Mureta et al. (2002) has patented a NO_x cleaning paving structure that defines a three layer structure consisting of a concrete base layer, a paving layer, and a surface layer. The surface layer is composed of cement, TiO_2, and aggregates. This patented air cleaning design is recommended for use as an overlay on existing concrete or asphalt, and specifies layer thicknesses and materials based on the existing pavement conditions (Mureta et al. 2002).

Many of the current pavement applications involve mixing nano TiO_2 powder in concrete slurries, applying TiO_2 on top of wet pavement, or apply liquid coatings to cured concrete (Hassan et al 2009). Louisiana State University (LSU) compared these three application methods based on durability and NO_x removal efficiency. Concrete coatings were applied to cured concrete as 10 mm thick coatings containing 3% and 5% TiO_2 by slurry weight. The

coating consisted of TiO_2, cement, water, and sand with a maximum nominal size of 1.18mm. For method two a commercial liquid TiO_2 product (PURETI) was applied to cured concrete, and method three consisted of sprinkling nano TiO_2 powder on fresh concrete before curing. Then pollution removal efficiency and visual inspection of the surface treatments were made before and after abrasion. Before abrasion the 5% TiO_2 coating and PURETI treatment showed the highest NO reduction. Based on scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) surface analysis, after abrasion the PURETI surface treatment appeared significantly damaged and the pollution removal efficiency slightly decreased. For the sprinkling method the NO reduction increased after abrasion because more of the TiO_2 became exposed at the surface (Hassan et al. 2010).

To improve the photocatalytic properties of TiO_2 paving blocks researchers are creating paving blocks that include non-traditional materials (Cheung 2005; Chen and Poon 2009). In Hong Kong photocatalytic TiO_2 paving blocks were made from local construction waste materials. With two objectives in mind: (1.) to help clean the air, and (2.) reduce the amount of construction waste materials. Waste materials including recycled aggregate, furnace bottom ash and recycled glass were mixed into paving blocks with TiO_2 (Cheung 2005). The blocks were prepared in two layers with TiO_2 being added to the top layer only. It was found that the higher the porosity of the block the higher the NO removal (Cheung 2005). Also, when recycled glass was used as an aggregate the NO removal increased significantly because more light was transmitted into the sample. This showed it might be possible for the light to reflect off the glass and activate TiO_2 below the surface as well on the surface, especially in more porous structures (Cheung 2005). In 2009, Chen and Poon farther tested this theory and found that replacing sand

in concrete mixtures with recycled glass cullets dramatically improved the photocatalytic effects. The NO removal efficiency increased from 1 mg h^{-1} m^{-2} to 3 mg h^{-1} m^{-2} when glass replaced 100 percent of the fine aggregates (Chen and Poon 2009).

In a recent study at Washington State University photocatalytic TiO_2 was applied to pervious concrete. Permeable pavements are becoming more popular because they can significantly reduce storm water runoff and recharge the groundwater (Montes and Hasselbach 2006). So, applying photocatalytic TiO_2 surface treatment to pervious concrete to reduce air pollution will make this product even more sustainable. An advantage of the pervious concrete compared to traditional concrete is the high porosity and surface roughness allow more TiO_2 particles to have contact with UV light increasing the pollution removal efficiency (Shen et al. 2011). Different TiO_2 application methods were used to adhere TiO_2 to the pervious concrete surface. High pollution reduction rates were seen for TiO_2 mixed with driveway protector, the commercial PURETI coating, TiO_2 in water, a commercial TiO_2 sol product, and cement-water slurry with low cement concentration. Each treatment method showed good NO reduction; but the VOCs (trimethylbenzene and toluene) had more variability in pollutant removal rates (Shen et al. 2011).

2.1.4 Field Investigations

Photocatalytic pavements have been proven to show high NO reduction in laboratories. Now the next step is to test the materials in the field. There are a lot of challenges with evaluating the photocatalyst products in the field. Many factors such as wind, climate, and traffic rates make it very challenging (Berdahl and Akbari 2008; Beeldens 2008; Cheung 2005). Also

there are no standards so it is difficult to compare results from experiment to experiment. Field investigations are critical to answer questions such as what is the minimum surface needed related to traffic density, and how often should maintenance be done on photocatalytic pavement (Beeldens 2008). Also field investigations are important to identify the durability of the material and efficiency of the photocatalyst over time (Beeldens 2008).

Concrete paving blocks containing recycled glass, sand, metakaolin, carbon and cement in the surface layer and recycled aggregate and cement in the base layer were prepared in a factory then laid in the field. NO reductions of 12% were reported at the ground level and 8% at the breathing level. After four months the blocks were removed and then tested in a laboratory again to see if the NO reduction efficiency had decreased, and it had decreased by 23% (Cheung 2005). A 4-year project was conducted in Antwerp Belgium and results were obtained in the laboratory and on-site. On-site 10,000 m^2 of photocatalytic paving blocks were inserted on the parking lanes as illustrated in Figure 2.5.

Figure 2.5 Photocatalytic paving blocks in Antwerp Belgium (Courtesy of Cheung 2005)

After one year in service a reduction of 20% of air purification efficiency was measured. The results were determined by removing some of the paving blocks after different periods of time and measuring the NO_x efficiency in the laboratory. The results are promising, but the translation from the laboratory to the site is still in question (Beeldens 2008).

At Eindhoven University of Technology (EUT) in the Netherlands researchers repaved 1000 square meters of roadway with a new chemical mixture of TiO_2 and concrete. The University had proven that the product reduced NO_x in a laboratory setting, but this was the first outdoor trial. In the test NO_x reductions between 25% and 45% were measured at the roadway compared to traditional concrete (Loveday 2010). The cost of the new mix including TiO_2 was approximately 50% more than regular cement, but the overall cost of the road building process was only increased by 10%. The problem is implementation of this technology involves repaving existing roads which is costly and time consuming (Loveday 2010).

The Essroc Italcementi Group is producing a new cement product called TX Active that uses TiO_2 to reduce pollutants and provide self-cleaning properties. The technology is being used to keep structures more aesthetically pleasing, to reduce exterior maintenance and cleaning, and to help improve air quality (Cassar 2003; Essroc Italcementi 2009). Tests on a road near Milan showed TX Active reduced the NO_x level by as much as 65% (United Press International 2006). The product is now marketed worldwide as a product to reduce air pollution.

In California a quantitative analysis of photocatalyst pavements was used to estimate that each square meter of high-quality photocatalytic TiO_2 coating could remove NO_x from 200 m^3 of air per day when exposed to sunlight (Berdahl and Akbari 2008). This depends on many factors including, size of treated surface, pollution concentration, humidity, and ambient temperature

(Berdahl and Akbari 2008, Dylla et al. 2010). Field investigations of roadway applications are showing promising results that the high pollution reductions reported in laboratories can be transferred to real world applications, but a lot of work still needs to be done (Beeldens 2008). It is also difficult to compare different photocatalytic pavement coatings because there are no standards to measure NO_x reduction from pavement in the field (Beeldens 2008; Berdahl and Akbari 2008). Another way to understand the potential long term benefits and durability of photocatalytic pavements is by creating numerical models (Meggos et al. 2007).

Meggos et al. (2007) developed a numerical modeling simulation tool that can account for climatologically data and the street canyon effect. In this experiment three artificial street canyons were developed at a 1:5 scale and continuous NO_x measurements were taken inside the canyons at the street level. It was found that the street canyons with TiO_2 coated panels had NO_x levels 36.7% to 82.0% lower than the reference canyon with no TiO_2 present (Meggos et al. 2007).

2.1.5 Photocatalytic Asphalt Pavement

There has not been as much research done to find successful (durable and efficient) ways to incorporate photocatalytic TiO_2 onto asphalt pavements, and this is an important problem to investigate because asphalt covers 94% of the roads in the United States according to the National Asphalt Pavement Association. So far most of the attempts to apply photocatalytic TiO_2 to asphalt fall into two categories: applying cementitious slurries on top of asphalt pavement, or applying a TiO_2 emulsion to the surface of asphalt (Crispino et al. 2010; Hassan et al. 2011; Mureta et al. 2002).

Applying photocatalytic cement mortar over open-grade asphalt has shown to be successful way to bond TiO_2 onto an existing pavement as illustrated in Figure 2.6 (Crispino et al. 2010).

Figure 2.6 Photocatalytic mortar on asphalt (Courtesy of Crispino et al. 2010)

The pores in the open-graded asphalt allow for a better overlay and better durability of the photocatalytic layer to the asphalt (Crispino et al. 2010). The problem is these coatings can be expensive and cover the asphalt surface changing it to a concrete surface (Mureta et al. 2002; Crispino et al. 2010).

In Politecinico Milano TiO_2 emulsion sprays have been applied to cold and hot asphalt surfaces. The aqueous suspension or emulsion is sprayed directly on the surface using spray bars attached to a vehicle. The coating has shown good photocatalytic activity with up to 40% NO_x reduction. The photocatalytic emulsion was then subjected to the Wheel Loading Test to simulate wearing that takes place throughout the pavement life. After wearing the NO_x efficiency

decreased by 50% (Crispino et al. 2010). Also, Chen and Liu (2010) applied a TiO_2 spray onto the surface of an asphalt road and measured NO_x decomposition rates between 6% and 12%.

At LSU TiO_2 was also incorporated into the preparation of warm mix asphalt (WMA). Two application methods were tested. First TiO_2 was mixed with WMA binder at 3, 5 and 7% by weight of binder. The second method consisted of applying the PURETI surface coating at coverage rates of 0.11, 0.21 and 0.31 kg/m^2. When TiO_2 was used as a modifier and mixed into the WMA, low NO_x reductions were measured (3.3 to 5.8% reduction). For the surface coating NO_x reduction levels were between 38 and 53% (Hassan et al 2011). Also at LSU researchers are applying the PURETI coating to two sections of road. One section is asphalt and one is concrete, but there are no results yet for this outdoor experiment (Wold 2010).

2.1.6 Impact Factors on Photocatalytic Effect

The main environmental factors affecting the oxidation conversion rate are temperature and relative humidity. The higher the temperature and lower the humidity the better the oxidation results (Beeldens 2006; Dylla et al. 2010). It has been reported that the best photocatalytic results are obtained at high temperatures, low relative humidity, high light intensities and long contact time (Beeldens 2006; Dylla et al. 2010; Katzman 2006). This correlates to hot sunny days with no wind, which is when the risk of smog formation due to high pollution levels is the largest (Beeldens 2006; Beeldens 2008; Dylla et al 2010). Also for outdoor applications the speed of traffic affects the residence time (Beeldens 2008).

Human intrusion can also reduce the pollution removal efficiency of the photocatalytic coating. In Hong Kong TiO_2 paving blocks were exposed to environmental conditions for 4

months and 12 months at 5 different roads (Chai-Mei Yu 2003). The photocatalytic activity of the paving blocks decreased in areas of heavy pedestrian traffic, where more contaminants accumulated on the surface (Chai-Mei Yu 2003). Surface area was lost from accumulation of dust, dirt, oil, grease, and other products such as chewing gum (Chai-Mei Yu 2003). In the non-pedestrian areas the NO_x removal efficiency did not significantly decrease. In this trial washing the blocks with water did not effectively recover the photocatalytic activity (Chai-Mei Yu 2003).

2.1.7 Health Concerns of Nano-Particles

There is a growing concern about the health risks of nano TiO_2 particles because these nano particles are being created for new applications at a rapid rate, and their effects on living tissue are just beginning to be understood. Tokyo University of Science injected pregnant mice with nano TiO_2 particles and found effects on genes in the central nervous system of the developing mice (Science Centric 2009). This study adds to the current concern that nanomaterial may be harmful to human health. The study notes that the gene expression data cannot be directly related to human health, and that particles were injected at high doses so the relevance to real life exposure is limited, but this is something that is continuing to be studied more as nano TiO_2 particles are used for self-cleaning and pollution removal applications (Science Centric 2009). According to the PC105 safety data sheet the nano TiO_2 powder is not expected to present a signification acute health hazard with short term exposure. Although, nano TiO_2 powder is still listed as a possible carcinogenic for humans. This is based on inadequate evidence of carcinogenicity in humans and sufficient evidence in experimental animals (Cristal Global 2007). So, there is a concern that breathing high concentrations of nano TiO_2 can lead to

respiratory problems. When working with nano TiO_2 powder on a regular bases people should take precautions such as wearing dust masks when mixing the powder.

2.2 PLASMA APPLICATIONS

2.2.1 Types of Plasma

A plasma consists of a mixture of electrons, ions, and neutral species that are electrically neutral on average (Boulos 1991). Plasmas can have very high or low temperatures depending on how they are activated. To create plasma gas is ionized by heat, radiation, or electric discharge (Kamenetskii 1972; Lieberman and Lichtenberg 2005). The ionization creates positive ions and negative electrons among the gaseous atoms and molecules (Lieberman and Lichtenberg 2005).

When all of the particles are at the same temperature it is called equilibrium plasma, otherwise it is non-equilibrium plasma. The temperature required to form thermal equilibrium plasmas from pure substances is between 4,000 K and 20,000 K (Lieberman and Lichtenberg 2005). A lot of the visible universe is composed of thermal plasma in equilibrium, including stars and most of the matter that exists between the star systems (Lieberman and Lichtenberg 2005). On the earth naturally occurring plasmas are not as common because of the lower temperatures and higher pressures. The most known natural plasma on earth is lightning, but a lot of man-made plasma processing takes place on earth (Gurnett and Bhattacharjee 2005).

Man-made plasmas are important for many different applications. In a laboratory and industrial setting the most common method of forming plasma is by electrical discharge. Common electrical sources used to create plasma include direct current (DC), alternating current (AC), radio frequency (RF) or microwave sources (MW) (Jama and Delobel 2007). Thermal or

equilibrium plasmas are characterized by high energy densities and equal temperatures of the heavy particles and electrons (Boulos 1991). Cold or non-equilibrium plasmas have lower energy densities, and the electron temperatures are a lot higher than the heavy particles (Boulos 1991).

In cold plasmas the particles (charged and neutral molecules) are at low temperatures and the electrons are at relatively high temperatures. Also cold plasmas often have low degrees of ionization (Jama and Delobel 2007). Cold plasma is usually created by exciting/ionizing the gaseous products under vacuum conditions using electrical discharges. These plasma discharges are started and sustained by electron collisions created from the vacuum and low power (Jama and Delobel 2007). Low pressure cold plasmas are often used for plasma etching and deposition processes (Boulos 1991). When cold plasma is created without the use of vacuum and at atmospheric pressure it is referred to as atmospheric pressure cold plasma (APCP).

APCP is usually classified as a weakly ionized plasma discharge. Weakly ionized plasmas are generally electrically driven, have charged particle collisions with neutral gas molecules, have boundaries where surface losses are important, and the ionization of the neutral species sustains the plasma in a steady state (Leiberman and Lichtenberg 2005). Also the electrons are not in thermal equilibrium with the ions, and there is a sheath region where the plasma and substrate meet (Leiberman and Lichtenberg 2005).

The inorganic gases that are generally chosen from to generate low temperature plasmas are helium, neon, argon, nitrogen, oxygen, air, nitrous oxide, nitrogen dioxide, carbon monoxide and dioxide, sulphur dioxide, hydrogen sulphide, hydrogen, chlorine, fluorine and hydrogen chloride. According to Vedore (1989) out of these gases argon and carbon monoxide are usually the preferred choices. Also cross linking agents are often used to accelerate the surface cross

linking process produced by the cold plasma treatment. Often these cross linking agents contain allyl groups and acrylic and methacrylic esters (Vedore 1989).

2.2.2 Advantages of APCP

Compared to traditional thermal plasma APCP is a cheaper process and easier to operate (Vons et al. 2006). Also the cold plasma process has low environmental impacts and since the plasma gas is at room temperature it is possible to modify any organic materials with it (Jama and Delobel 2007). Compared to traditional plasma less energy is needed because only the electrons are heated making the process more economical and efficient (Vons et al. 2006). Another advantage is because particles are equally charged it is possible to maintain high particle concentrations without coagulation (Vons et al. 2006).

There are also many advantages of cold plasma compared to conventional wet chemistry to improve material properties. Advantages are that creating plasma is a dry process, it can be developed in a wide pressure range, and it is more energy efficient. Another important advantage is that it alters only the very top layer of the substrate surface leaving the properties of most of the substrate unchanged (Jama and Delobel 2007). A drawback to using atmospheric pressure plasma is that it requires high gas consumption compared to low pressure plasmas and it is more difficult to control the deposition chemistry (Lommatzsch Ihde 2009).

2.2.3 Plasma Processing

Plasma processing technology is very important to some of the largest manufacturing industries in the world including electronics, aerospace, automotive, steel, biomedical, and toxic waste management (Lieberman and Lichtenberg 2005). Plasmas can be used to fabricate

materials and surface structures that no other commercial methods can (Lieberman and Lichtenberg 2005). Some general types of plasma processes include: etching, chemical vapor deposition, sputtering/physical vapor deposition, implantation, sprays, chemical production/destruction, and medical sterilization (Goeckner 2011). With the wide range of plasma temperatures the possible applications are infinite. Plasma can be used to deposit or grow a film, to dope or modify a surface, or to etch or remove (Lieberman and Lichtenberg 2005).

2.2.3.1 Thermal Plasma Applications

Thermal plasmas have the ability to heat, melt, and sometimes vaporize the material being treated (Boulos 1991). Thermal plasma devices include torches, plasma sprays and electric arc welders. These devices are often used to destroy harmful-toxic substances, or produce thick film coatings (Jama and Delobel 2007; Gurnett and Bhattacharjee 2005). Plasma spray torches produce a plasma jet usually by a DC arc between a cathode and a nozzle shaped anode (Pfender 1998). Some common applications of plasma spray torches include producing wear-resistant coatings, producing coatings for corrosion protection of large structures, and restoring worn metallic parts (Pfender 1998). Also powders are being injected into the plasma jet to improve deposition, efficiency, and quality of material coatings (Pfender 1998). Plasma spraying has also been used to produce thin deposits of TiO_2 from nanopowder and liquid suspensions (Toma et al. 2005). Presently there is increased interest in using thermal plasma to synthesis high-purity substances to create new materials (Boulos 1991).

2.2.3.2 Cold Plasma Applications

With the low temperatures present in cold plasma it can be used to improve functionalism of most organic and inorganic polymeric surfaces. Plasma-assisted deposition, implementation and surface modification are important materials processes that cold plasma can be used for. Another important application is the production of plasma polymerized films on substrate surfaces to modifying surface characteristics (Lieberman and Lichtenberg 2005). The electron temperature is higher than the ion temperature and the active plasma particles break the chemical bonds of the precursor material creating free radicals that can be used to create thin plasma polymerized films (Kang et al 2006). The production of a plasma polymerized film starts as nodules that grow in size until they merge into what appears to be a continuous film. This creates different properties between the surface and the rest of the substrate (Jama and Delobel 2007; Kang et al. 2006).

Cold plasma can also be used to improve properties such as hardness, resistance to chemicals and abrasion, good biocompatibility, and low gas permeability. Also new applications have been using cold plasma to create fire-retardant coatings. These processes are valuable because they allow for preserving mechanical and physical properties of the polymer and concentrating fire-retardant properties at its surface (Jama and Delobel 2007). Also corrosion protection of aluminum and other low-adhesion surfaces has been improved by using atmospheric pressure plasma jets. Plasma surface technology has also been extended to the development of paint technology for automobile parts. Cold plasma allows for parts to be painted without primer because the plasma improves the wettability and adhesion qualities of the polymer surface (Jama and Delobel 2007).

Plasma can be used to increase or decrease the wetting of a surface (Jama and Delobel 2007). For example the Smart and Innovative Textile Materials Group at Indian Institute of Technology used APCP to create a hydrophobic finishing for textile substrates. On the non-treated textile samples water absorbed in less than one second. For the plasma treated samples the water droplet did not absorb after 60 minutes. After washing the plasma treated textile samples the droplet on the top surface absorbed after 250 seconds, and after 180 seconds on the bottom side (Samanta et al. 2008). These results show that it is possible to significantly alter the surface characteristics by using APCP (Samanta et al. 2008).

Plasma processing is also used to improve adhesion between different substrates by adding a plasma polymerized crosslinking layer between the substrates. Airoudj et al (2011) demonstrated increased adhesion between an aluminum substrate and EPDM (ethylene-propylene diene terpolymer) by creating a plasma polymer layer containing double bonds on the aluminum substrate before cross linking. Also Vedore (1989) identified methacrylic esters as an efficient precursor agent for hydrocarbon materials such as asphalt. Plasma was used to make a composite sheet for impervious coating of construction components by using cold plasma to make a crosslinking layer to adhere a vinyl material with a hydrocarbon material (Vedore 1989). In this process the cross linking agent was incorporated into the composition of the treated layer (Vedore 1989). To help improve adhesion a “duty cycle” has been recommended for some applications. A “duty cycle” allows the radicals to arrive at the growing film followed by the power being turned off and the original unmodified monomer being applied (Airoudj et al. 2011).

Atmospheric pressure plasmas have been used to deposit plasma polymerized acetylene on various substrates (Pedrow et al. 1990; Kang et al. 2006). Acetylene is a common gas to use in plasma processing because it has shown to produce strong plasma polymerized films at high deposition rates in a variety of different plasma processing applications. Plasma polymerized acetylene films have been deposited to rubber compounds to improve adhesion (Kang et al. 2006). Also, recently acetylene plasma was used to immobilize proteins on silicon (Yin et al 2009). The plasma polymerized surface was shown to provide covalent bonding sites to immobilize a solution containing proteins (Yin et al. 2009). Also under radio frequency plasma carbon/hydrogen films have been created from acetylene and para-xylene for increased adhesion strength and increased hardness (Louh and Hon 2005). In similar research, microwave plasma was used to deposit diamond like carbon films from acetylene and methane (Lai et al 2001).

Benedikt et al. 2006 developed an atmospheric pressure micro jet to deposit thin acetylene films. Argon was the carrier gas, and it was used to separate the atmosphere gases from the growth region of the acetylene film. Soft polymer-like carbon films were deposited at rates of a few nm per second (Benedikt et al. 2006). Deposition occurred when the substrate was placed in the plasma jet (Benedikt et al. 2006). Also, Herbert et al. (2009) created a soft plasma polymerization of gas state precursors from an atmospheric pressure corona discharge.

At Washington State University (WSU) the Cold Plasma Group (CPG) is conducting ongoing research to use high voltage streamers to process materials. Past work of WSU CPG members included testing the concept of using APCP to treat fresh fruits for improved preservation (Fernandez-Gutierrez 2010). Currently work is being done to use APCP polymerization to make improved wood composite materials. In this experiment so far plasma

polymerized film has been obtained on mica, glass, and wood veneers, and the characteristics of these films have been investigated using atomic force microscopy (AFM) and Fourier Transform Infrared Spectroscopy (FTIR). Recently, another researcher in the WSU CPG modified the surface of surgical-grade 316L stainless steel with APCP processing to help mitigate bacterial adhesion on the surface of biomedical implants.

To help identity plasma-induced chemical changes on substrate surfaces tools such as FTIR and contact angle measurements can be used (Morent et al. 2008). FTIR can be used to obtain an infrared spectrum of absorption, emission, and photoconductivity of a solid, liquid, or gas. FTIR is often used to verify cross linking of plasma polymerized films (Benedikt et al. 2006; Lommatzsch and Ihde 2009; Pedrow et al. 1990; Kang et al. 2006). FTIR can identify chemical changes and identify the film characteristics including information about what molecules are present on the surface. Also contact angle measurements often are helpful to understand characteristics of plasma polymerized films (Morent et al. 2008).

Various adhesion tests are often used to show improved adhesion from plasma polymerized films (Airouji et al. 2011; Kang et al. 2006; Lommantzsch and Ihde 2009). The peel test is commonly used to measure adhesion strength, especially for adhesion to metal substrates (Airoudji et al. 2011). These tests apply adhesive tape to the substrate, and then the tape is removed and inspected for how much of the film, if any, it removed (Lommatzsch and Ihde 2009). Also, often specific industries have standard pull-out force adhesion tests that are used to confirm improved adhesion by the addition of plasma polymerized deposition (Kang et al 2006).

Cold plasma can also be used to aid in the chemical process to directly reduce air polluted flows. In an article by Hammer (2002) cold plasma was used to reduce NO_x emissions in diesel

exhaust gas directly. Cold plasma was used to initiate chemical reactions to oxidize NO into NO_2, and to reduce other harmful emissions in the diesel exhaust as illustrated in Figure 2.7.

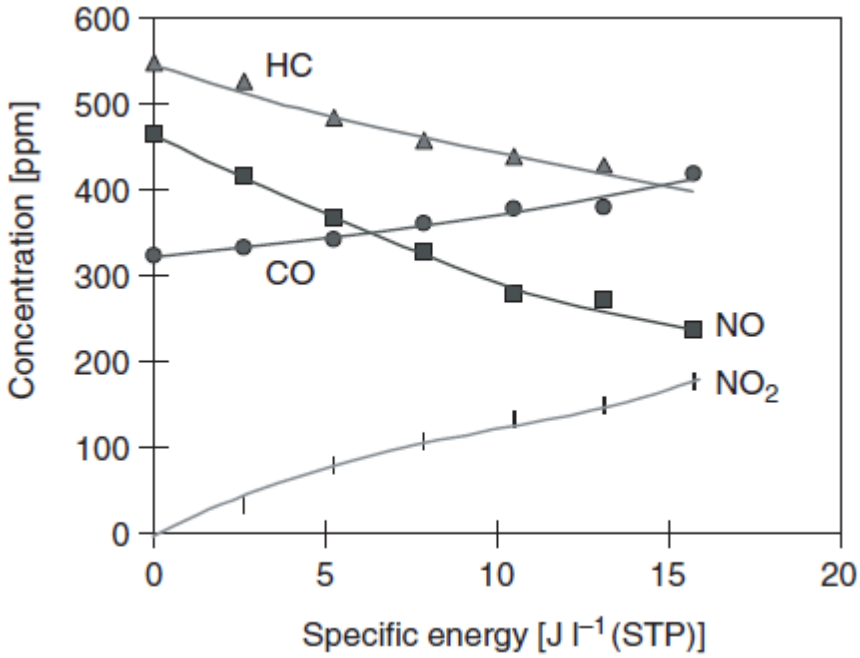


Figure 2.7 Conversion of NO into NO_2 as specific energy increases (Hammer 2002)

In an article by Kim (2004) cold plasma along with a wet chemical process were used to convert pollutants to non-harmful by-products. Also Pasquiers (2004) investigated the use cold plasma and catalysis to improve removal efficiencies and cut down on the amount of undesired by-products being produced during the removal of NO_x and VOCs. These studies involve a different, but effective technique of reducing pollutants by using plasma to initiate and aid in the oxidation process.

2.3 SUMMARY

In this literature review it has been shown that TiO_2 is effectively being used as a photocatalyst to reduce NO_x and VOC levels. This review also identified that it is necessary to create a more durable and efficient way to adhere TiO_2 to pavement surfaces by showing results from past experiments. The APCP process is also evaluated in this chapter showing that it is a viable way to enhance surface characteristics of organic and inorganic materials. APCP technology has proven to be useful in the paint, textile, and medical industries and we want to apply it to the asphalt pavement industry. This literature review also identifies precursor and carrier gases that work well. Based the literature review we have decided to use Argon as our carrier gas because of its inert properties. From the literature review we believe APCP is the most viable tool to strongly adhere TiO_2 to asphalt pavement in an efficient manner.

CHAPTER 3: EXPERIMENTAL METHODOLOGY

This research developed an atmospheric pressure cold plasma (APCP) generator to produce weakly-ionized plasma, and test the concept of using APCP to activate and bond nano TiO_2 powder to substrate materials. The APCP generator system consists of four main parts: the power source, the plasma generator tube, the TiO_2 powder supply, and the gas dispersion components. A schematic of the APCP generator system is shown in Figure 3.1. These parts are necessary to produce APCP and the TiO_2 surface coating. Each component will be described in detail in this chapter. Also, the methodology that was used to create APCP, and the TiO_2 coating in APCP will be described in this chapter.

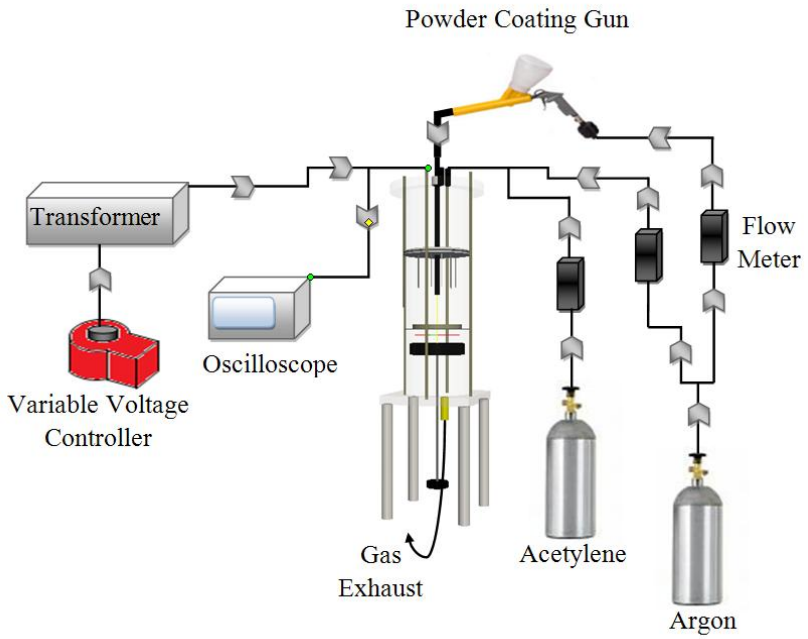


Figure 3.1 Schematic of the Plasma Generator System

3.1 POWER SOURCE

The power source used in this experiment is a high voltage (HV) transformer that was designed for use as an oil furnace starter. It consists of a 10 kV transformer enclosed in a steel-box with an on/off switch. Originally a 5 kV transformer was used, but this was upgraded to produce more APCP deposition. The HV transformer plugs into a Variable Voltage Regulator (VARIAC). The VARIAC controls the amount of power provided to the APCP generator, by controlling the percentage of the maximum power output. The HV transformer and VARIAC apply alternating current (AC) at 60 Hz frequency to the APCP generator by a HV wire that connects the transformer to a screw on the top of the APCP generator. To display the voltage and current applied to the APCP generator an oscilloscope is used. A voltage divider and Rogowski coil plug into the oscilloscope to measure voltage and current respectively. The Rogowski coil rings upon excitation and is useful for observing the mean time between current pulses, and the voltage divider measures the voltage entering the APCP generator. The Rogowski coil and voltage divider are also helpful to identify when acetylene is present in the APCP generator, because different current and voltage patterns are observed when acetylene is present compared to when only argon is flowing.

3.2 APCP GENERATOR

The largest design task was the development of the APCP generator tube. The tube consists of three different regions: a gas mixing section, the plasma or ionization region, and the processing region. AutoCAD was used to create preliminary APCP generator designs. Then

ParaView, an open-source software for multi-platform data analysis and visualization applications, was used to create a 3-D drawing of the APCP generator as illustrated in Figure 3.2a. The final APCP generator is shown in Figure 3.2b. As a unique feature of this design, the APCP generator can generate plasma at atmospheric pressure without the need of using vacuum equipment which is more economical, simpler and safer.

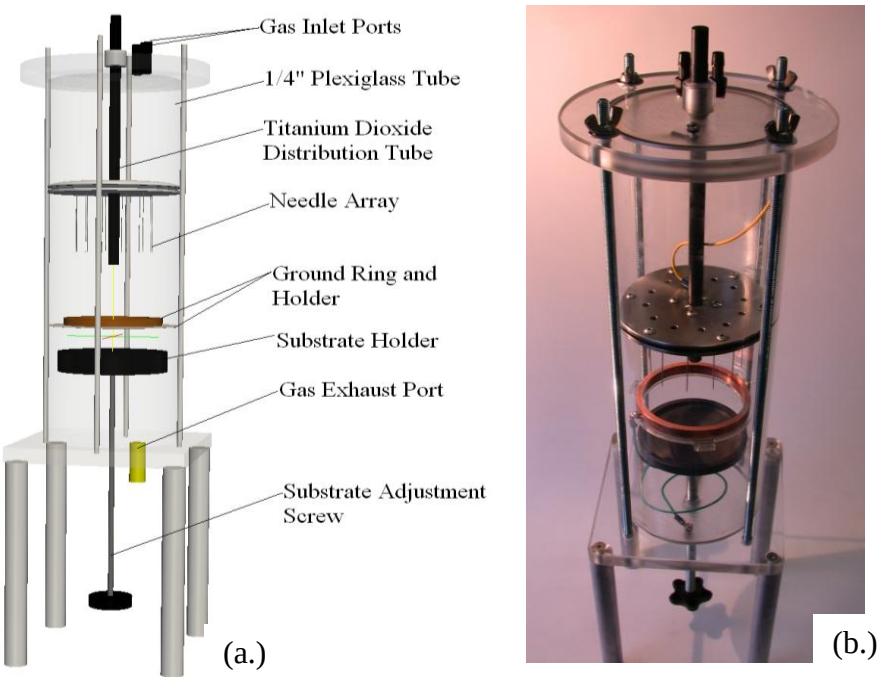


Figure 3.2 APCP Generator: (a.) ParaView design, (b.) Final product

The APCP generator is composed of an 18 inch tall ¼ inch Plexiglass tube with an inside diameter of 5.5 inches and outside diameter of 6 inches. On the Plexiglass lid are three inlets for introducing the carrier gas, precursor gas, and the TiO_2 particles. The TiO_2 enters through the center of the chamber in ½ inch diameter Teflon tubing that extends past the electrode plates to

disperse the powder in the plasma region. Later APCP generator modifications included a TiO_2 inlet on the side of the Plexiglass tube which will be described in Chapter 5.

Also on the lid of the reactor is the HV connection, which allows the power source and voltage divider to be attached to the outside of the APCP generator, and is connected by an HV wire to the bottom of the screw inside the APCP generator to power the system. Below the top Plexiglass lid is a large mixing section created by the lid and the electrode plates to allow the carrier gas and precursor to become completely mixed before ionization of the gases begins in the plasma region. A HV wire runs through the mixing section that provides power from the HV power source to the electrode plates. The size of the mixing chamber can be adjusted by moving the electrode plates up or down inside the Plexiglass tube. During this research project the electrode plates were approximately 6 inches below the lid creating a mixing section with a volume of approximately 95 cubic inches.

The electrode system consists of two stainless steel plates holding an array of 12 stainless steel needles. The top electrode plate is 1/8 inch thick and has eight uniform ¼ inch holes to allow mixed argon and acetylene to enter the needle ends evenly. Also there are 12 evenly distributed notches in a circular pattern in the top electrode plate that hold the needles in place. The bottom electrode plate is ¼ inch thick and contains five small holes with the same diameter as the needles at each of the 12 needle locations. One hole for the needle to go through and four small holes around each needle to force the gases towards the needle tips. The two electrode plates are clamped together with screws in between a rubber o-ring to ensure a tight seal. The 12 needles are evenly spaced in a circular configuration with has an approximate diameter of 3.5 inches centered around the TiO_2 tube.

The needles are 3 inch long sewing needles from Jo Ann fabrics and the tips have radius of curvatures between 50 and 55 µm. The corona plasma streamers emanate from the needle tips with excitation from the power source in the form of electron avalanches. This creates the APCP region between the needle tips and the ground ring. A modified design of the electrode plates that can hold 40 needles are also experimented in this study, which will be described in Chapter 5.

Below the needle tips is the ground ring and ground ring holder. The ground ring holder is made of Plexiglass with three spring arms. The ground ring holder can be adjusted to different heights, and his held in place by wedging the Plexiglass spring arms against the 5.5 inch diameter Plexiglass tube. This allows the ground ring to be adjusted to different distances from the needle tips. The purpose of the ground ring is to complete the circuit and neutralize the free electrons. The ground ring was originally made from copper and was a ¼ inch thick with a 4 inch inner diameter and ½ inch height. Later the ground ring was replaced with a stainless steel ring and mesh screen that will be described in Chapter 5.

Below the ground ring is the substrate holder. It is made from hard plastic and designed to hold a 4 inch diameter asphalt sample, or any smaller samples. The substrate holder is a flat 4 inch diameter platform with a ¼ inch high ledge to securely hold the samples in place. The substrate holder is mounted on a 12 inch long ¼ thick screw with a handle to easily change the distance from the needle tips and ground ring to the substrate.

Below the substrate holder is the wire connecting the ground ring to the grounding screw on the bottom of the reactor. The grounding screw is used to ground the whole system, and is screwed into the plexiglass frame that holds the APCP generator tube. The power source, voltage

divider, and grounding stick are all grounded by attaching to this screw. The grounding stick is a 1.5 foot piece of Plexiglass with a wire attached to it, and it is used to touch the high voltage screw after the APCP generator has been turned off to check that the system is not energized. Also on the bottom of the reactor is an outlet with ½ inch tubing to allow gases to exit the APCP generator, and the whole system is operated in a fume-hood to ensure safety. Figure 3.3 shows the APCP generator tube below the mixing section illustrating the placement of the two stainless steel electrode plates, the needle array, the ground ring, the substrate holder, and the APCP generator tube on top of the platform base.

Figure 3.3 Lower portion of APCP generator

3.3 GASEOUS MATERIALS

The selection of appropriate carrier gas and precursor gas is another critical component of the plasma generator design to ensure the immobilization of the TiO_2 particles to the substrate. The purpose of the precursor agent is to provide suitable cross linking between the TiO_2 and the substrate materials (asphalt primarily). Acetylene was chosen as the precursor material in this study because of its ability to produce thick polymerized films. Acetylene is a hydrocarbon with the chemical formula C_2H_2. It is a colorless gas that is widely used in fuel and as a chemical building bock. Approximately 20 percent of acetylene is consumed for oxyacetylene gas welding and cutting. Acetylene with oxygen produces a flame of over 3300 °C (Butterfield 2010; Poling et al. 2001). In this design, no oxygen is allowed in the generator to avoid producing high temperature plasma flames.

Argon was used as the carrier gas due to its inert properties even at high temperatures, and it is relatively cheap. Also Argon has low thermal conductivity, ionizes easily, and provides an excellent current path making it ideal for cold plasma applications (Poling et al. 2001). Argon gas was used to assist and adjust the concentration of the acetylene precursor and to control the rate of the TiO_2 powder entering the APCP generator.

At first vinyl tubing and hose clamps were used to connect the gas tanks to the APCP generator. Later these were upgraded to Teflon tubing and compression fittings to avoid leaks, and the Teflon tubing is more robust so the tubing will be less likely to kink. To control the flow rate of the argon and acetylene two flow meters from Cole-Parmer were used. The flow meter for argon has a flow range from 30.0 ml/min to 687 ml/min. The flow meter for acetylene has a flow

range from 8.50 ml/min to 125 ml/min and a high resolution valve to accurately control the amount of precursor.

3.4 POWDER COATING GUN

Particle dispersion is a large challenge with small particles such as the TiO_2 nano powder used in this research project. Research has shown the smaller the particle size the stronger the inter-particle Van Der Waal's forces are which creates large agglomerates. Large agglomerates are hard to transport evenly and reduce the surface area. Because high surface area to volume ratio contributes to the effectiveness of TiO_2 photocatalysis, it is important to disperse the TiO_2 particles appropriately (Tang et al. 2007).

To input TiO_2 into the plasma generator at a controlled rate a powder coating gun was purchased from Chicago Electric Power tools considering its capability of distributing particles evenly and the relatively low cost. The gun is designed for powder coat painting and we modified it to disperse TiO_2. The major modification was to use argon instead of compressed air to transport the powder. This was critical because acetylene and oxygen mixtures have the potential to produce high temperature flames. Instead of using the electrically charged dispenser that comes with the original design, our study only used the pressure from the argon tank and a flow meter to disperse the TiO_2 so that the discharge rate can be controlled easily.

A schematic of the powder coating gun is show in Figure 3.4. The argon stream enters through the bottom of the gun handle, and then enters the powder cup through a small input pipe.

The input pipe has a small diameter to build up pressure and help disperse the powder. Then the powder goes through the larger outlet pipe and down the gun barrel to exit in a mist of powder.

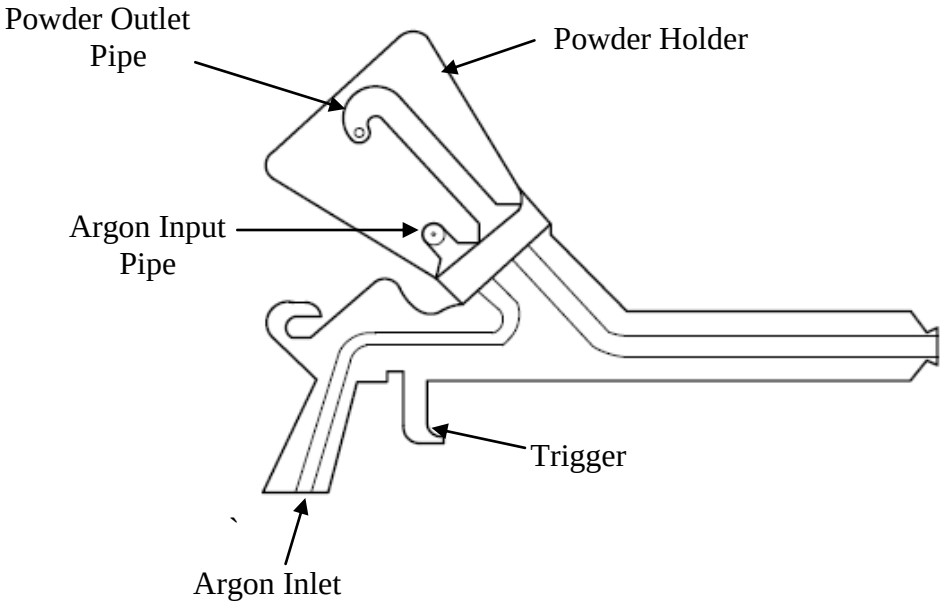


Figure 3.4 Powder coating gun (Harbor Freight Tools 2006)

A series of tubing and plumbing connections were used to decrease from the 1.25 inch gun diameter down to the ½ inch tubing going into the APCP plasma generator. Also a valve was installed to be able to purge the gun to make sure only argon was in the line before the tubing enters the APCP generator. Then the ½ inch Teflon tube inside the APCP generator was adjusted to disperse the TiO_2 at different heights within the plasma region. Figure 3.5 shows the setup to transport the TiO_2 from the powder coating gun into the APCP generator.

Figure 3.5 TiO_2 system from powder coating gun to APCP generator

The photocatalytic TiO_2 used in this research project was PC 105 from Cristal global. It is a fine white powder with average crystallites between 15 and 25 nanometers, an agglomerate size of 1.2 µm, and approximate surface area of 90 m^2/g. The TiO_2 is in the anatase form and recommended for use in photocatalytic applications.

3.5 CREATE APCP

Once the experimental setup was complete the APCP generator was energized for the first time. At first only argon gas was used and the first test involved figuring out what parameters are needed to see streamer/current pulses on the oscilloscope, and what parameters were needed to visually see the needle tips glow. The voltage, flow rate, and distance between the needles and ground ring were adjusted until the needles sustained a consistent glow. There was plasma glow at gap distances of 3 cm and less when the voltage was greater than 3 kV RMS.

We were not able to see luminous streamers tubes with argon, and it was concluded that a precursor gas needs to be present to see luminous streamer tubes. Once it was assured that the generator worked properly then acetylene was added to the plasma system as the precursor agent. Through experimental tests it was found that a 10:1 ratio of argon to acetylene produced bright luminous streamer tubes as seen in Figure 3.6.

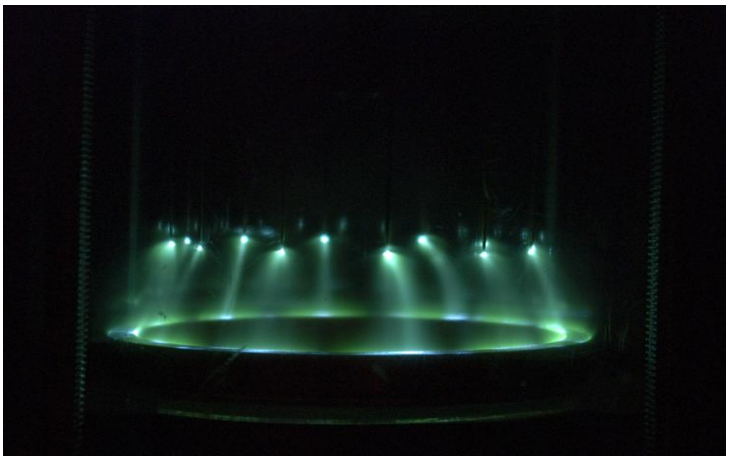


Figure 3.6 APCP streamers produced in argon and acetylene gas

3.6 IDENTIFICATION OF PLASMA DEPOSITION

After the APCP generator was running properly and luminous streamer tubes were visible the next important step was to produce plasma polymerized acetylene deposition. Identifying plasma deposition was necessary to make progress towards using the deposition to adhere TiO_2 to asphalt. It was also important to identify where the plasma deposition is forming to help optimize the APCP generator with respect to flow rates and sample placement to target the highest deposition rates. It was difficult to identify because acetylene polymerized deposition is usually clear or has a light yellow tint making it difficult to see.

Glass cover slips and transparency paper were used as test strips to try to observe plasma polymerized deposition in the APCP generator. The glass cover slips used were Fisher Brand microscope cover glass that are 22mm wide, 22 mm long, and 1 mm thick. These test strips were placed at different distances and locations from the needles to try to understand where plasma deposition was occurring. Transparency paper was used in addition to glass because it could be cut into strips and taped to the APCP generator walls to provide more information. After running the APCP generator the test strips were looked at under a Hitachi S-570 Scanning Electron Microscope (SEM) to identify plasma deposition.

Figure 3.7 Hitachi SEM equipment (Courtesy of Franceschi Microscopy and Imaging Center)

The transparency paper scratched easily and did not appear uniform under the SEM making it difficult to identifying plasma deposition, and was discarded as a test strip material. Glass cover slips appeared uniform under the SEM and were used in the later study. Figure 3.8

shows a typical image of the glass coverslip under the SEM that has not been inside the APCP Generator. The noticible item on the image is a small scratch. This image is representative of the other glass control samples that were viewed under the SEM.

Figure 3.8 Control glass cover slip under SEM

Trials were run with the APCP generator varying APCP generator properties including flow rates, applied voltage, APCP generator running time, and distances. The distance from the test strips to the needles, and distance from the needles to the ground ring are both important factors that were constantly being investigated. Glass cover slips were run in the APCP generator at these different parameters. Then the cover slips were scratched with the edge of another glass cover slip, and the samples were gold coated and viewed in the SEM. The samples did not show noticeable deposition.

Then the transformer was upgraded from a 5 kV transformer to a 10 kV transformer. After the power source was upgraded the same procedure of using glass cover slips as test strips

to identify plasma deposition was conducted. After optimizing the test parameters plasma deposition was seen on the glass cover slips as illustrated in Figure 3.9 by scratching through the deposition layer and identifying it under the SEM.

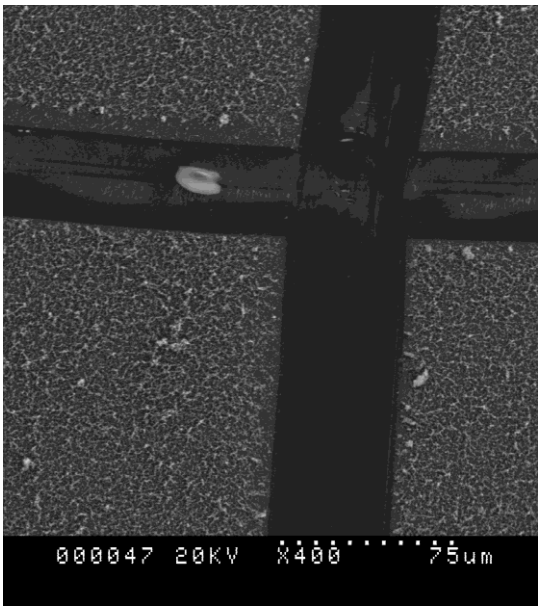


Figure 3.9 APCP deposition on glass under SEM

A Veeco Multimode Picoforce atomic force microscope (AFM) was also used to identify plasma deposition on glass samples and give more information about the potential plasma films.

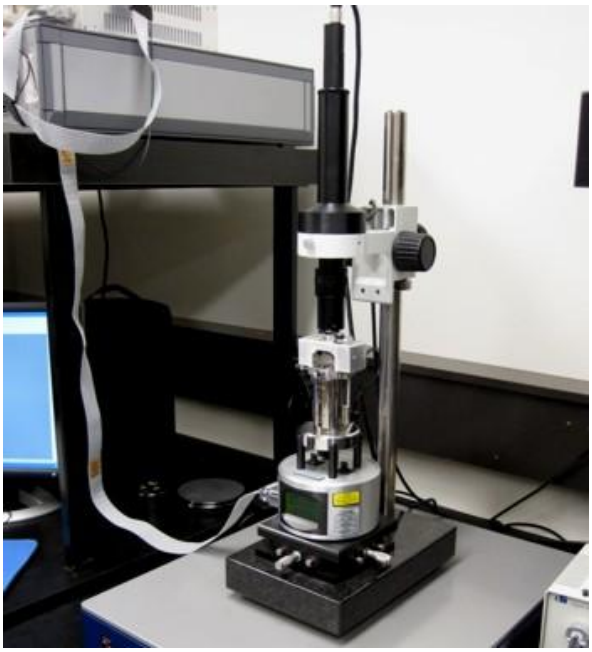


Figure 3.10 Veeco Multimode Picoforce AFM (Courtesy of University of Guelph)

The AFM was used in tapping mode to measure height, amplitude and phase of a sample. To use the AFM first the sample is placed on the metal plate underneath the cantilever tip. Then manually the tip is brought close to the sample, and the tip is engaged using the Nanoscope V6 software. Then the tip scans the sample and the amplitude set point, integral gain, and proportional gain are adjusted until the trace and retrace lines of the scanning tip match up. It is suggested to scan the same spot twice to make sure an accurate scan is getting documented. Once an area is scanned the image can be captured, and adjusted to remove noise and a 3-D plot of the surface can be displayed. With the AFM plasma deposition was looked at on metal, firmica, and glass. Glass was chosen to be used for future tests because it was the most uniform and therefore

easiest to identify plasma deposition on. Figure 3.11a shows plasma deposition on glass after 20 minutes of APCP processing with a 4 cm gap between the needle tips and the substrate, and 7.3 kV RMS. It is compared to a control glass sample (Figure 3.11b).

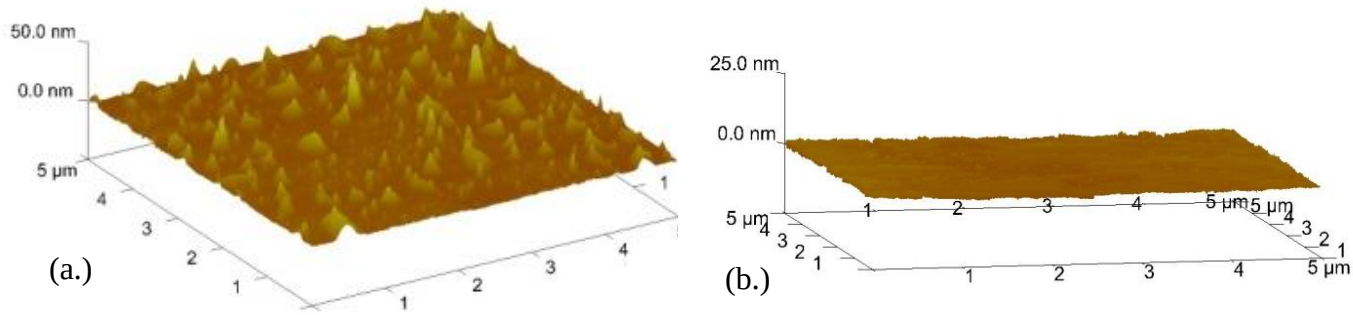


Figure 3.11 AFM images: (a.) Plasma deposition on glass (b.) Glass control sample

3.7 ADDITION OF TITANIUM DIOXIDE

Once plasma deposition was identified the next step was to add TiO_2 into the plasma generator. At first TiO_2 was added manually through a funnel placed on top of the generator. Then the APCP generator was turned on with only argon flowing through it. It was observed that TiO_2 built up on the needles and ground ring. TiO_2 was also placed in a sealed beaker and we tried to blow it into the reactor with argon flows, but the flow rates were not high enough and the particles created large agglomerates. Then TiO_2 was put into the powder coating gun to evenly disperse the powder flow.

There was a concern about the interaction of TiO_2 and acetylene within an APCP environment. So, at first TiO_2 was added with argon only, and then acetylene was slowly added

to the TiO_2 and plasma. All materials mixed well within the APCP generator. It was noted if too much TiO_2 is added at once there is a tendency for sparks within the reactor. To help control the amount of TiO_2 entering the APCP generator a flow meter was added to control the argon rate going into the powder coating gun.

3.8 PROCEDURE TO CREATE APCP TIO_2 COATING

The first step is to clean the APCP generator to remove unwanted contaminants such as dust that can lead to sparks. The reactor is cleaned with soap and water, and rinsed before use. Also the stainless steel needles and the copper ground ring are cleaned with a scruffy pad to get off any residue. After the reactor is cleaned and dried a sample is put on the substrate holder and the reactor is sealed with 4 wing nuts on the top plate. Then the sample and ground ring are adjusted to the desired height and argon and acetylene flows are started. For most tests argon was put into the APCP generator at a rate of 500 sccm and acetylene at a rate of 50 sccm. It was calculated that the gases need to be flowing into the reactor for at least 15 minutes at these flow rates to ensure that all oxygen is flushed out of the APCP generator. Based on these calculations we allow gases to flow for at least 20 minutes before any voltage is applied to ensure proper mixing and flushing of the reactor. Then the power is applied by turning on the HV transformer and VARIAC, and the percentage on the VARIAC is increased until plasma streamers are seen. Most tests were run at 85% power on the VARIAC, but the amount of power that can be applied without creating a spark depends on the parameters for that test. Once consistent luminous streamers are present TiO_2 is added by pulling the trigger on the powder coating gun. Then the

trigger is pulled at the desired frequency for the desired length of the test. The parameters that can be altered during each run to try to create the optimum coating include:

1. Distance from the sample to the needle tips
2. Distance from the needle tips to the ground ring
3. Distance from TiO_2 to needle tips
4. Argon flow rate
5. Acetylene flow rate
6. TiO_2 flow rate in Argon
7. TiO_2 application rate (Frequency of pulling the gun trigger)
8. Applied voltage
9. Coating time

3.9 PROCEDURE TO EVALUATE COATING LAYER

To evaluate the pollution removal efficiency of the APCP and TiO_2 treated samples an environmental chamber was used. The chamber is a $0.12m^3$ Teflon chamber with plexiglass sides and supported by a metal frame. The chamber is illuminated with six 25W black lights mounted to the top of the chamber and six 15W black lights mounted to the side of the chamber. These lights are used to simulate UV sunlight.

Inside the chamber, the sample surface sat about 18 inches below the chamber lights. The irradiance of the lights were measured and compared to the solar irradiance on the roof in October and November in Pullman, WA. The 25W and 15W lights were within the wavelength

region (below 387 nm) where TiO_2 is photoactive. Most of the 25W and 15W lights output energy was between 300-400 nm. When both sets of lights were turned on the irradiance of the lights was approximately 12.60 W/m^2, comparable to a clear fall day in Pullman, WA. When only the top set of lights was used the irradiance was approximately 6.11 W/m^2, comparable to a cloudy fall day in Pullman, WA. Figure 3.12 compares irradiance values on fall days in Pullman, WA to the irradiance of the chamber lights.

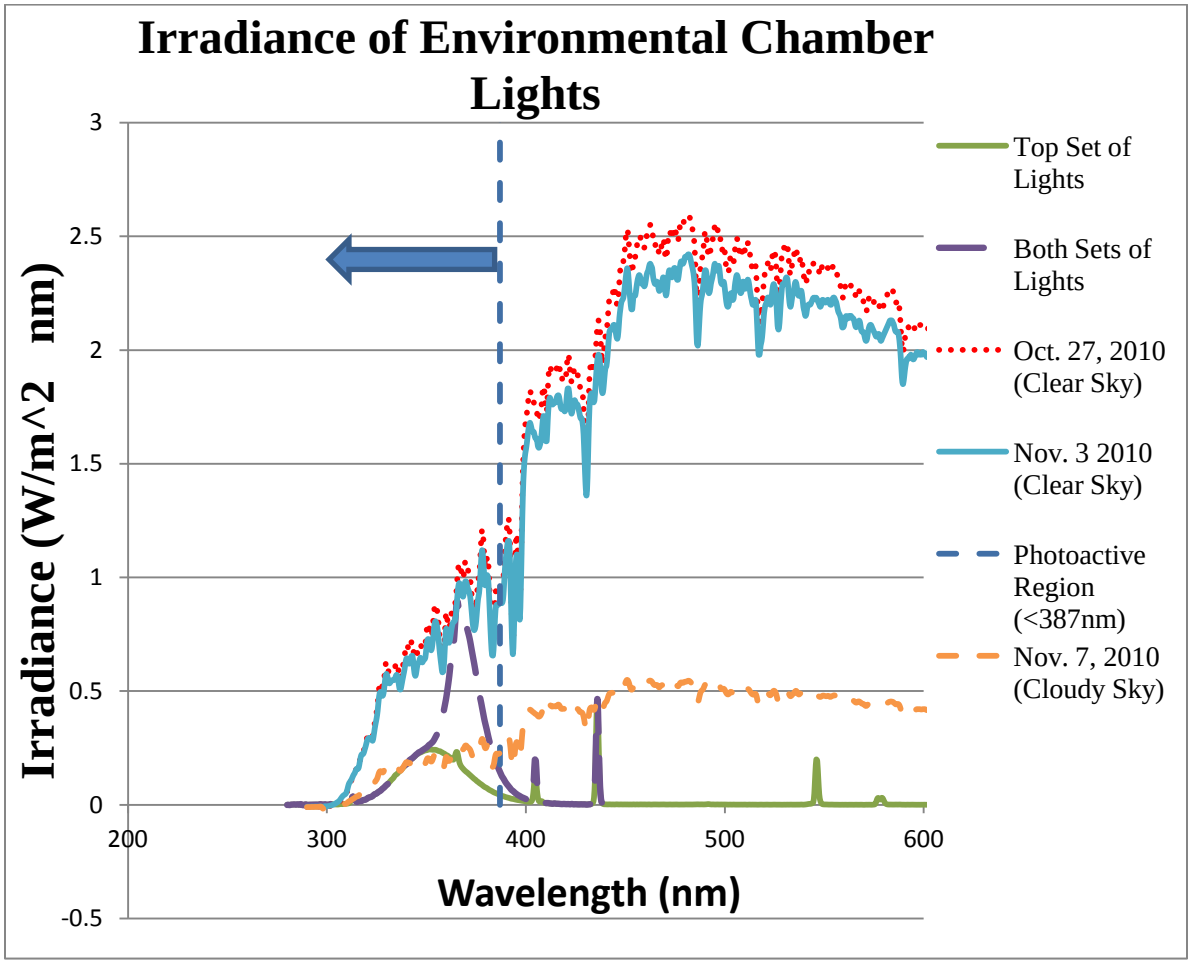


Figure 3.12 Comparison between Chamber lights and Pullman fall solar irradiances

A compressed gas cylinder (Scott Marrin Inc.) of nitric oxide (NO) in nitrogen was used as the pollutant. The gas cylinder has a concentration of 500 ppmv of NO and the rest is oxygen-free nitrogen. The NO cylinder and dilute air from a Balston zero air generator flow into the chamber through mass flow controllers and a series of Teflon tubing and T-fittings. There is a 20 slpm mass flow controller connected to the zero air generator and a 50 sccm mass flow controller connected to the NO tank. Then the two flows combine and flow through a mixing coil. After the gases are mixed the line goes into a T-fitting and one end goes into the environmental chamber and the other goes to a 3-way solenoid. On the other side of the chamber is an outlet line that also goes to the solenoid. Then there is a line going from the solenoid to a two channel chemiluminescent NO analyzer. The chemiluminescent analyzer measures NO and NO_2 with detection limits of 0.40 ppbv for 1 minute average times. The 3-way solenoid valve is used to alternate the flows that go to the chemiluminescent analyzer. It alternates between the chamber air and the inlet air into the chamber. This is used to see when a steady state concentration is reached within the chamber and to confirm the chamber concentration is equal to the inlet concentration. The chemiluminescent analyzer is connected to a computer and a program called DAQ Factory that is used to acquire and display the NO and NO_x concentration data. The chemiluminescent analyzer updates every ten seconds so DAQ Factory is set up to report NO and NO_x concentration every 10 seconds. This allows real time NO_x concentrations to be observed, and the data is automatically saved for later analysis. Figure 3.13 shows a schematic of the environmental chamber system.

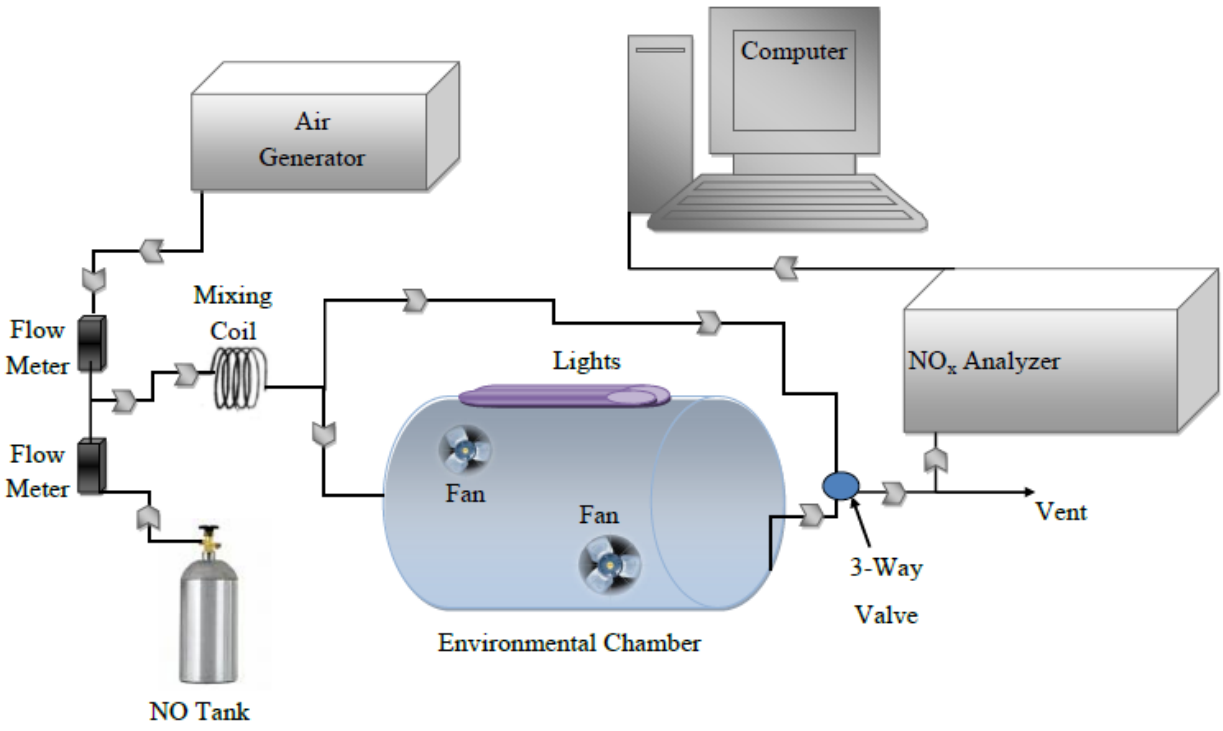


Figure 3.13 Environmental Chamber Schematic

After coating with TiO_2 and plasma, the samples were put into the environmental chamber for analysis of pollution removal efficiency, as shown in Figure 3.14. Typically six samples are tested at the same time because of the large volume of the environmental chamber. The chamber was run in dynamic mode, having continuous flow of air and NO through the chamber during testing. The samples were tested at room temperature (75 °F) and 25% humidity. NO and zero air generator flow rates were adjusted to reach an inlet concentration of 430 ppbv of NO. Then the chamber air was measured until a steady concentration was reached. Then the lights were turned and the NO concentration decreased in the chamber even though the same inlet concentration was entering the chamber. The test is allowed to run until this decreasing

concentration levels flattens out and starts increasing again. The relationship between NO concentration change and time was generated for comparison.

Then the samples were washed and lightly scrubbed with a toothbrush to remove any nano TiO_2 powder that was not strongly immobilized, and tested again in the environmental chamber.

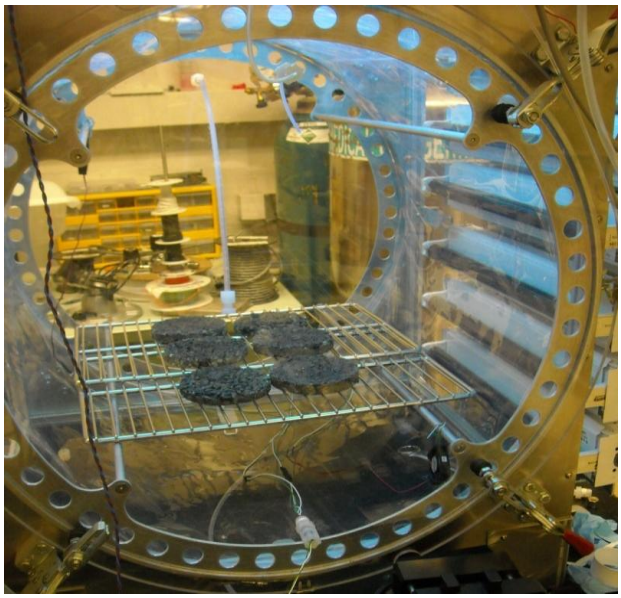


Figure 3.14 TiO_2 and APCP coated asphalt samples in Environmental Chamber

CHAPTER 4: EXPERIMENTS WITH 12-NEEDLE APCP GENERATOR DESIGN

After APCP and TiO_2 were successfully introduced into the APCP generator system as described in chapter 3, asphalt samples were coated with TiO_2 and APCP to create a potential air purifying coating. The parameters described in section 3.8 were altered to identify high NO_x reduction levels in the environmental chamber. Four types of samples were evaluated in the environmental chamber; control asphalt samples with no TiO_2 coating, asphalt samples coated with TiO_2 using APCP without washing, asphalt samples coated with TiO_2 using APCP after washing and scrubbing, and asphalt samples coated with commercial TiO_2 products. Two commercial TiO_2 products were coated onto asphalt to compare with the APCP TiO_2 method: a liquid TiO_2 sol and a patented electrostatic spray technology.

The environmental chamber experiments conducted in this chapter used both sets of lights yielding a light irradiance of approximately 12.60 W/m^2. At first only the top set of lights was used yielding an irradiance of 6.11 W/m^2, but low NO reductions were observed for all sample types. So, the higher light irradiance was used to show more NO reduction, and better distinguish which APCP generator parameters show the most promising results for pollution removal efficiency and durable immobilization of TiO_2 after washing. For all of these experiments 6 asphalt samples were coated using the same technique then ran in the environmental chamber at the same time yielding a surface treatment area of 75.4 in^2.

4.1 GROUP A EXPERIMENTS

These experiments involved applying a high concentration of TiO_2 on the surface and then identifying if coating over the samples with more APCP will help the TiO_2 remain immobilized after washing. Another goal of the group A experiments is to identify if covering TiO_2 with APCP may reduce the photocatalyst effect of TiO_2. The experiments consisted of three testing steps:

Test A1: Six plain asphalt samples were ran in the environmental chamber and showed a NO reduction of 1.63%.

Test A2: These six asphalt samples were coated with TiO_2 and APCP. After coating in the APCP generator these samples were immediately ran in the environmental chamber and showed a NO reduction of 34.80%. This test had a high TiO_2 application rate (1.7 lpm in a stream of argon) and a short plasma processing time (5 minutes) in the APCP generator. Figure 4.1 shows the sample in the APCP generator immediately after coating. The sample has a white layer of TiO_2 on it. Also the TiO_2 is on the ground ring and needle tips. TiO_2 is a semi conductor and it was observed that the powder is attracted to the charged needle tips and ground ring during testing.

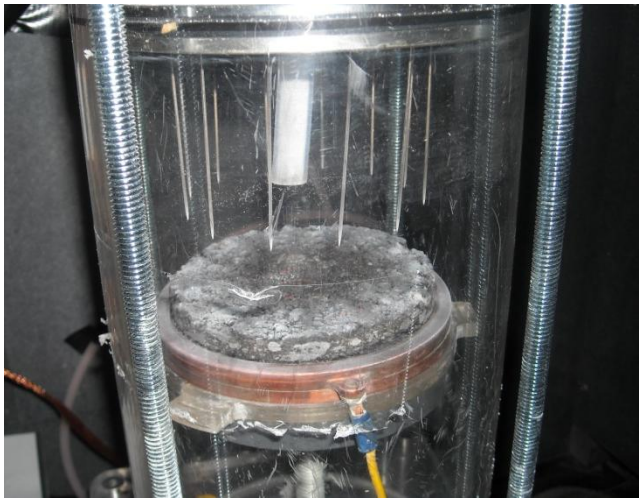


Figure 4.1 TiO_2 and APCP coated sample in the APCP generator

Test A3: Then the same samples were put back into the APCP generator and coated with APCP only (No TiO_2) for 20 minutes to see if plasma deposition would reduce the environmental effectiveness of the TiO_2. After coating in the APCP generator samples were ran in the environmental chamber and showed a NO reduction 9.44%. The samples were further washed and ran in the environmental chamber again showing a NO reduction of 4.49%. Figure 4.2 compares the NO reduction for this group of experiments.

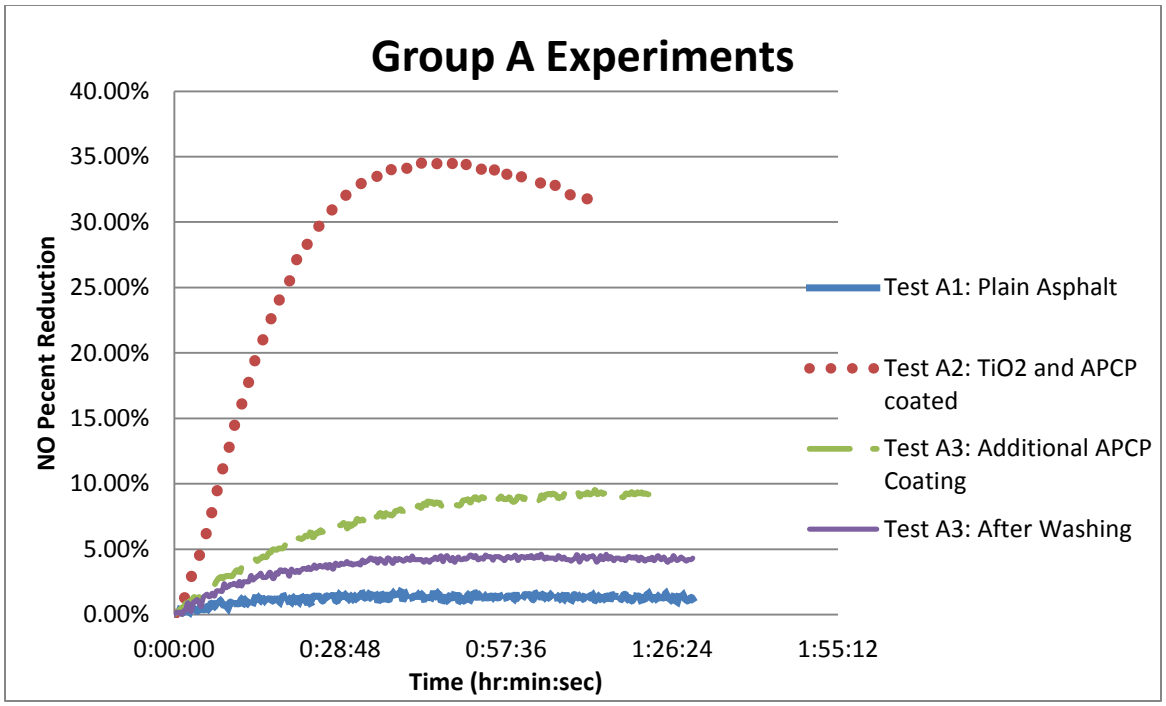


Figure 4.2 NO reduction for Group A experiments with respect to time

Figure 4.2 shows that when the samples were coated with TiO_2 and APCP simultaneously for 5 minutes a high NO reduction (34.80%) was observed. Then when these samples were coated with APCP only for an additional 20 minutes the photocatalytic activity dramatically decreased to 9.44%. These samples were then washed and scrubbed and the NO reduction decreased to 4.49%, but it is still greater than the 1.63% NO reduction for samples with no coating.

4.2 GROUP B EXPERIMENTS

Since the samples tested in Group A showed low NO reduction after washing the same six asphalt samples were coated with TiO_2 and APCP four more times. Each time a different parameter was changed to try to increase the NO reduction. Table 4.1 shows the APCP generator parameters that were used for all the tests.

TABLE 4.1 APCP Generator Parameters for Each Test

Parameters	Test A2	Test A3	Test B1	Test B2	Test B3	Test B4	Test 6
Distance from sample to needle tips (cm)	3.5	3	3.5	2.25	2.25	4.5	3.5
Distance from needle tips to ground ring (cm)	4	3.5	4	2.5	2.5	5	4
Distance from TiO_2 to needle tips (cm)	1	1	1	1	1	1	1
Argon flow rate (sccm)	500	500	500	500	350	600	500
Acetylene flow rate (sccm)	70	70	70	70	70	55	70
TiO_2 flow rate in argon (lpm)	1.7	0	1.3	1.3	0.9	1.7	1.4
TiO_2 application rate: Frequency of pulling the trigger (seconds)	12	0	15	15	15	17	15
TiO_2 duration for each time pulling the trigger: (seconds)	3	0	4	4	4	2	4
Applied Voltage (KV RMS)	7.7	7.7	8.3	6.5	6.5	6.5	0
Coating Time (minutes)	5	30	10	10	10	10	12

Test B1: For this test the TiO_2 rate was decreased to be able to increase the APCP processing time because with less TiO_2 the APCP generator can run longer before it has a tendency to spark. After coating in the APCP generator these samples were immediately ran in the environmental

chamber and showed a NO reduction of 44.60%. Then the samples were washed and ran in the environmental chamber again showing a NO reduction of 4.36%.

Test B2: For this test the gap distance between the needle tips and substrate was decreased to see if this would help the TiO_2 immobilize to the surface. After coating in the APCP generator these samples were immediately ran in the environmental chamber and showed a NO reduction of 48.24%. Then the samples were washed and ran in the environmental chamber again showing a NO reduction of 5.07%

Test B3: For this test the argon and TiO_2 flow rate were decreased to see if this would help immobilize the TiO_2 to the surface. After coating in the APCP generator these samples were immediately ran in the environmental chamber and showed a NO reduction of 19.24%. Then the samples were washed and ran in the environmental chamber again showing a NO reduction of 5.30%.

Test B4: For this test we increased the argon and TiO_2 flow rate, increased the gap distance, and decreased the acetylene flow rate to see what effects these parameters would have on the surface coating. We also coated two more samples in addition to the original six to increase the treated surface area in the environmental chamber. After coating in the APCP generator these samples were immediately ran in the environmental chamber and showed a NO reduction of 42.15%. Then the samples were washed and ran in the environmental chamber again showing a NO reduction of 5.92% Figure 4.3 compares the NO reduction for the experiments in Group B. For all experiments the NO reduction before washing was a lot higher than after washing and scrubbing.

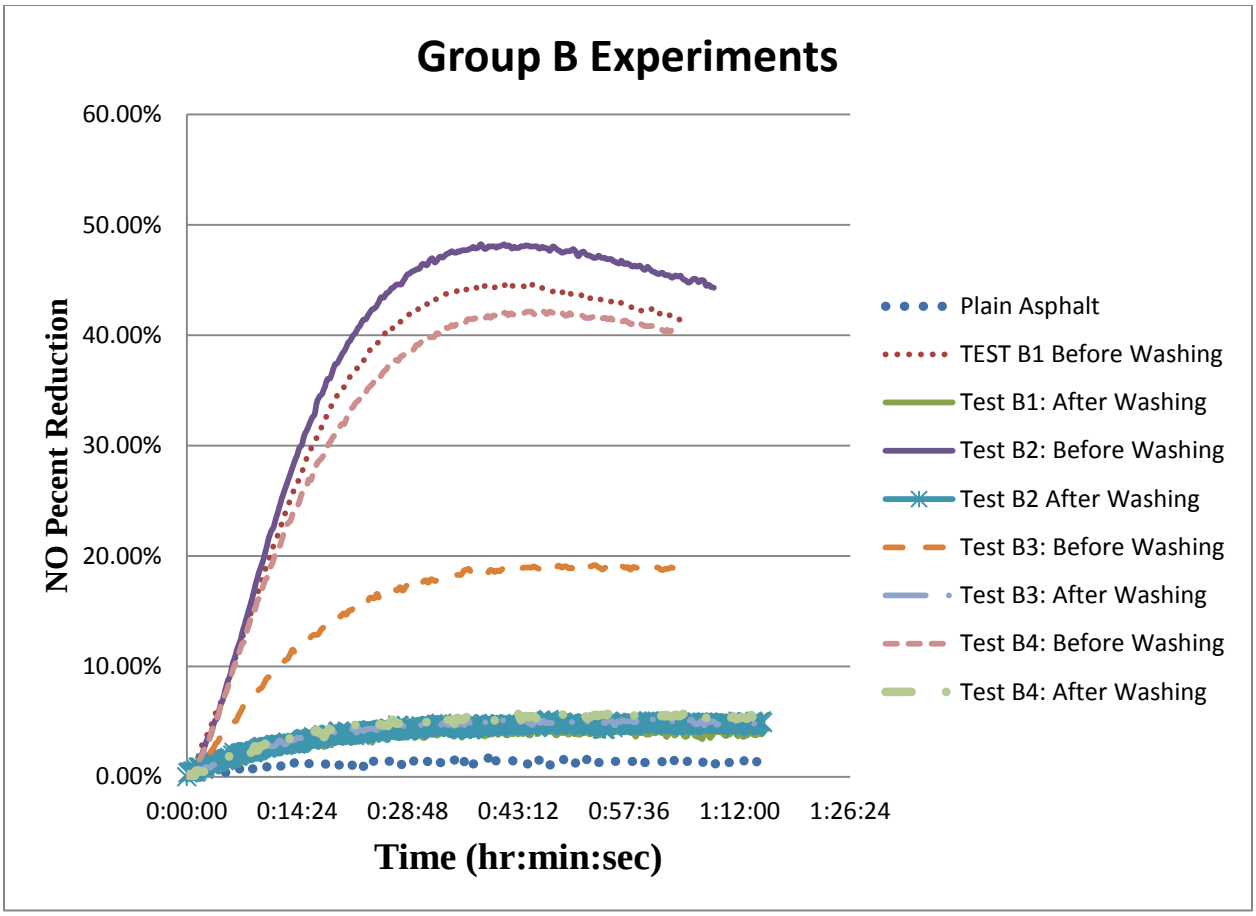
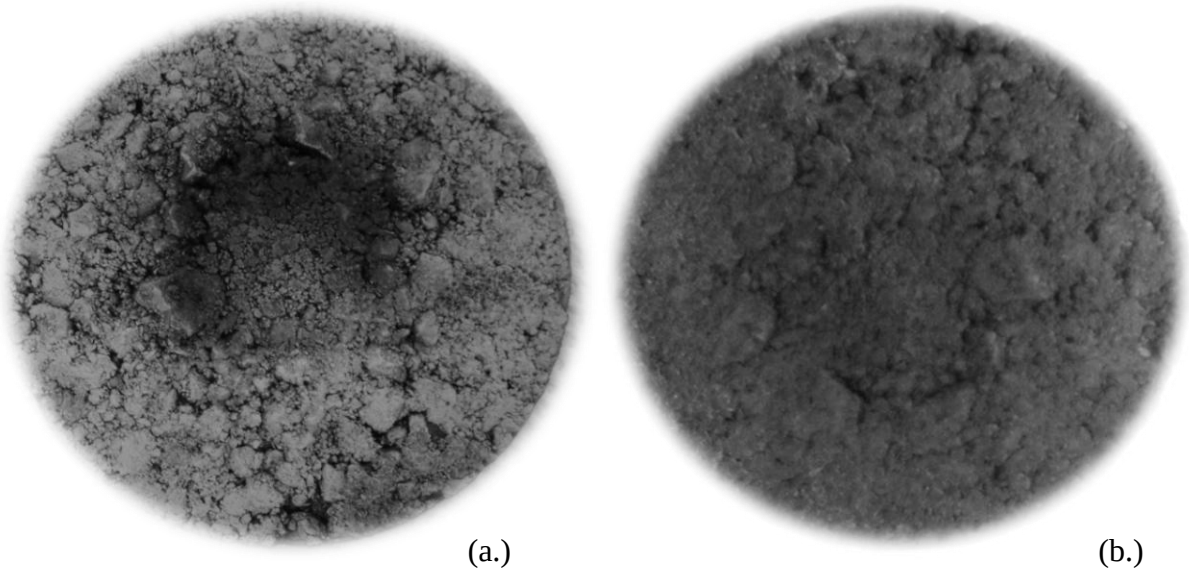


Figure 4.3 NO reduction for Group B experiments with respect to time

Figure 4.4 shows the results for one of the 6 samples that had been ran in all of the group B experiments. Before washing the sample is covered with loose TiO_2 and after washing the sample does not appear white any more, but it still has a gray tint especially around the edges.



(a.) (b.)

Figure 4.4 Comparison of TiO_2 using APCP before washing (a), and after washing (b.)

So, to see if there is some immobilized TiO_2 after washing a Field Emission Scanning Electron Microscope (FE SEM) was used. Figure 4.5 shows and FE SEM image of TiO_2 immobilized on asphalt by APCP after step 4.

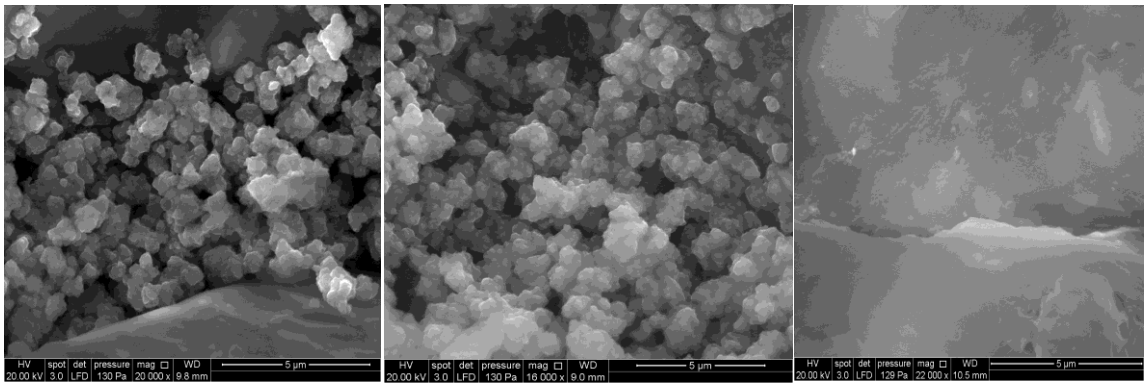


Figure 4.5 FE SEM image of immobilized TiO_2 on asphalt (Left: before washing and scrubbing; Center: after washing and scrubbing; Right: control with no TiO_2)

4.3 GROUP C EXPERIMENTS

To compare the TiO_2 coating using APCP two commercial photocatalytic TiO_2 products were acquired. One product was a photocatalytic TiO_2 sol called S5-300B from Cristal Global. It is a stable aqueous dispersion of anatase TiO_2 in water. The sol composition is approximately 18% TiO_2 by weight, approximately 78% water, and less than 5% diethylamine. Diethylamine is a secondary amine that is miscible in water and is used as a corrosion inhibitor. The photocatalytic TiO_2 sol has a dry surface area of about 300 m^2/g and pH of 11. Also asphalt samples were sent to Pureti Inc. and coated with their TiO_2 surface treatment technology. This a patented technique that uses an electrostatic spray gun to apply a TiO_2 based surface treatment.

Test C1: Six Pureti samples were run with the environmental chamber and showed 23.51% NO reduction. These samples contain 4 gm/m^2 of TiO_2. This was used to compare to the amount of TiO_2 in APCP coatings and the commercial liquid TiO_2 sol. This application rate is equal to 0.03 grams of TiO_2 on each of the 6 samples. After washing the Pureti samples showed a NO reduction of 28.23%

Test C2: Six asphalt samples were coated with the liquid TiO_2 sol to compare with the other treatment methods. The liquid TiO_2 is 18% TiO_2 so it was calculated that 0.167 grams of the product needs to be applied to each sample to have a dry TiO_2 concentration of 4 gm/m^2. The liquid sol was applied with a hand held plastic spray bottle. Table 4.2 showed the sample weights before and after coating. It is noted that this concentration of TiO_2 is greatly higher than the concentration for APCP coated samples. The actual average TiO_2 concentration on these

samples is 3.55 gm/m^2 by weight. The Liquid TiO_2 sol showed a NO reduction of 58.08%. After washing and running in the chamber a NO reduction of 56.12% was recorded.

TABLE 4.2 Sample Weights Before and After Liquid Sol

Sample	Weight before coating with liquid sol (grams)	Weight after coating with liquid sol (grams)	Weight Difference (grams)
L1	213.52	213.7	0.18
L2	119.03	119.17	0.14
L3	214.28	214.43	0.15
L4	204.67	204.83	0.16
L5	260.95	261.06	0.11
L6	182.54	182.76	0.22

Test C3: In this experiment TiO_2 was applied to six asphalt samples without using APCP. The samples were placed in the APCP generator with all of the same parameters; except the power was not turned on and the TiO_2 was allowed to fall onto the samples. The purpose was to show that none of the TiO_2 will immobilize to the sample, and that it will all wash off. We put on the same amount of TiO_2 on these samples as the Pureti and liquid TiO_2 samples contain. Table 4.3 is the weights before and after applying the TiO_2 to the samples.

TABLE 4.3 Sample Weights Before and After TiO_2

Sample	Weights before coating with TiO_2 only (grams)	Weight after coating with TiO_2 only (grams)	Weight Difference (grams)
51	122.14	122.18	0.04
52	139.11	139.14	0.03
53	112.31	112.33	0.02
54	95.44	95.46	0.02
55	195.43	195.47	0.04
56	122.07	122.11	0.04

The average TiO_2 weight on each sample was 0.03 grams making it the same TiO_2 rate as the Pureti samples. The TiO_2 only coating showed a NO reduction of 21.42% compared to 23.51% from the Pureti Samples. This is valuable information because it is difficult to accurately determine the weights of the APCP and TiO_2 coatings because of the harsh plasma environment. Often the TiO_2 APCP coated samples weigh less after being in the APCP generator making it difficult to quantify the amount of TiO_2 applied. After the samples coated with TiO_2 only were washed and ran in the environmental chamber again they showed a NO reduction of 2.28%. Figure 4.6 compares the NO reduction for the experiments in Group C.

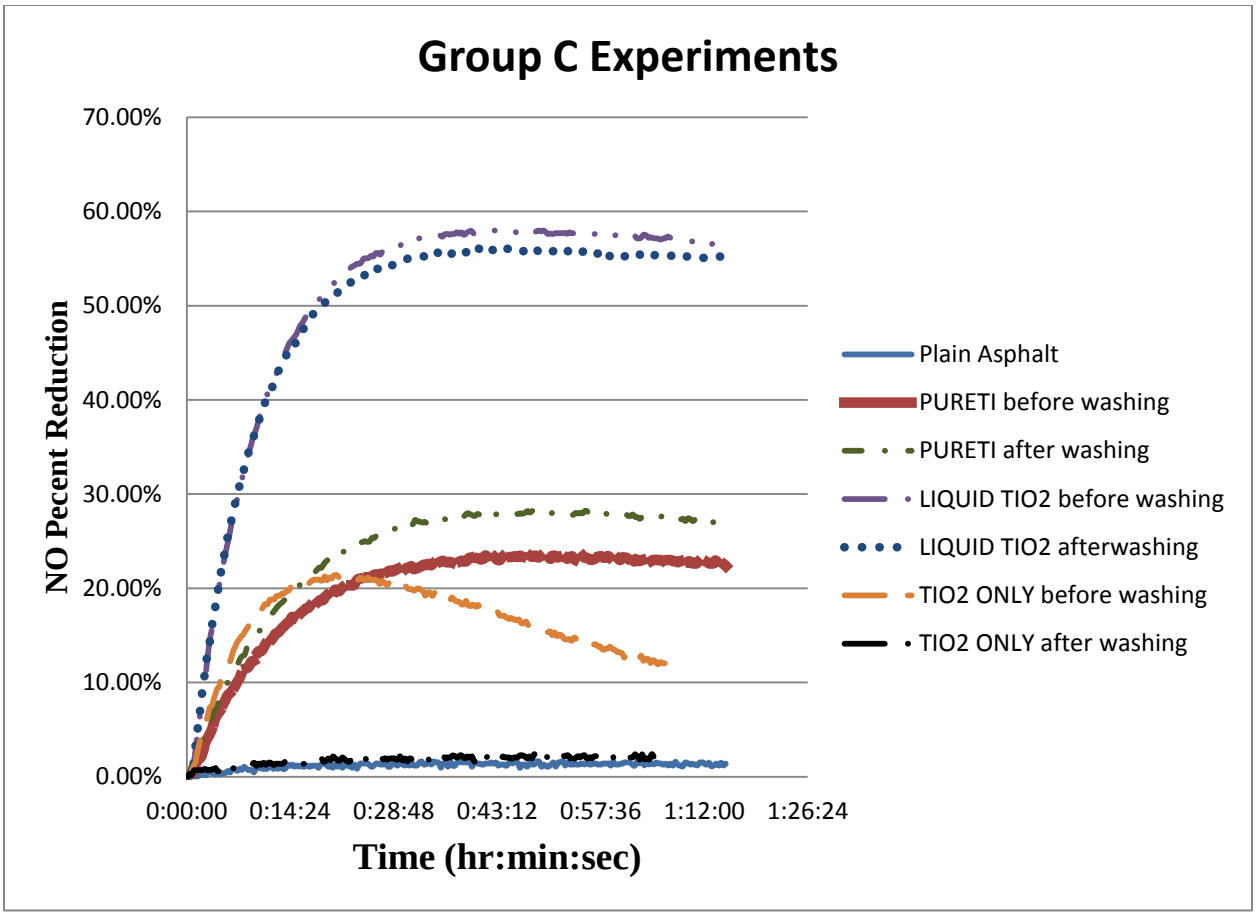


Figure 4.6 NO reduction for Group C experiments with respect to time

4.4 SUMMARY OF EXPERIMENTS

The control asphalt samples with no TiO_2 coating showed minimum NO reduction (<3%) in the environmental chamber. The TiO_2 coated asphalt samples using APCP showed clear NO reduction (approximately 33% on average) before washing and scrubbing. The washed and scrubbed TiO_2 coated asphalt samples using APCP, however, showed limited NO reduction (5%). These results showed a dramatic decrease after the samples were washed, which could be due to the low efficiency of the plasma immobilization. For the existing design and needle array

with a diameter of 3.5 inches and 12 needles, most of the plasma polymerized film could only be deposited on the outer ½ inch of the samples resulting in a low deposition rate. Based on this research hypothesis, we redesigned the APCP generator electrode plate to hold 40 needles to create a larger plasma deposition area. This new design and the testing results based on the modified APCP generator will be described in chapter 5.

CHAPTER 5: EXPERIMENTS WITH 40-NEEDLE APCP GENERATOR

Based on the preliminary results in chapter 4, the APCP generator was modified with an increased number of needles to increase the APCP processing region and improve immobilization of TiO_2. Holes were drilled in the electrode plates to fill in the previous 12 needle circular array with 28 additional needles. For each of the 28 needles 5 small holes were drilled using the same pattern described in chapter 3, one hole for the needle and 4 holes around each needle for the gases to pass through. This design is illustrated in Figure 5.1.

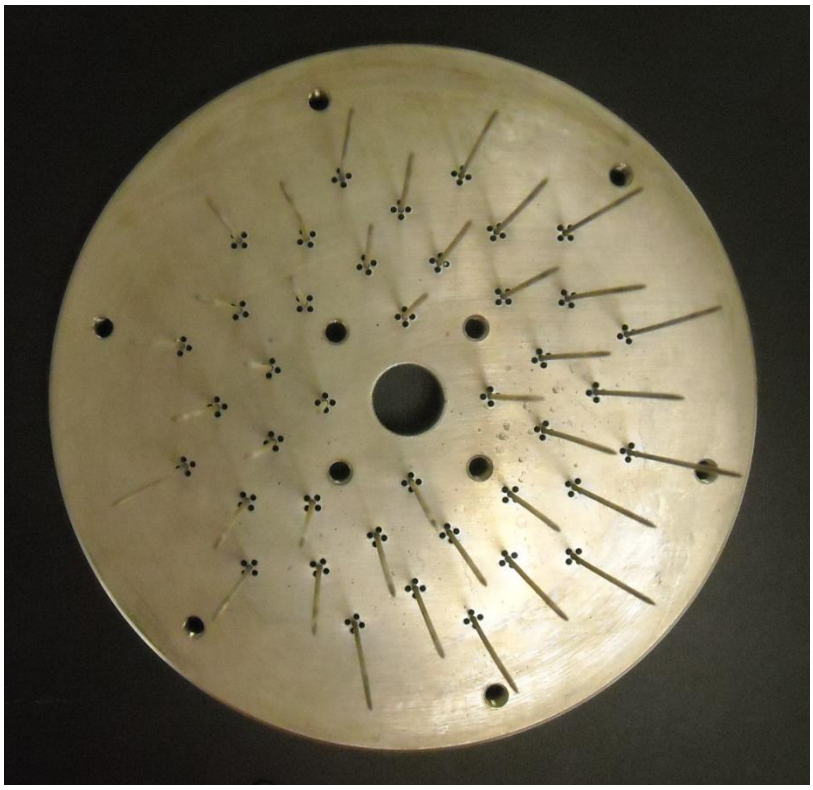


Figure 5.1 Electrode plate with 40 needles

To fire all the needles evenly and effectively each needle needs to be the same distance from the ground ring. So, the ground ring was upgraded to a stainless steel ring that holds a stainless steel mesh screen as shown in Figure 5.2.

Figure 5.2 Stainless steel ground ring and mesh

This creates a flat plane that is equal distances from all the needle tips, which allows all the needles to fire as shown in Figure 5.3. The concept is that the 16 mesh screen collects the charged species in the plasma region and allows the free radicals to flow through the mesh and deposit a thin plasma polymerized film on the substrate downstream of the plasma region. When the sample was placed below the ground screen it was no longer feasible to have the TiO_2 enter from the top of the APCP generator because the powder cannot efficiently flow through the

screen. A ½ inch opening was therefore drilled in the side of the APCP tube below the stainless steel ground ring for the TiO_2 to enter horizontally below the mesh.

Figure 5.3 APCP streamers in 40 needle design

5.1 EXPERIMENTS WITH SAMPLE BELOW THE SCREEN

The goal for the new 40-needle APCP generator design was to have the sample below the mesh, and allow the generated APCP free radicals to flow through the mesh and mix with the TiO_2 that entered horizontally to form a surface treatment composed of APCP and TiO_2 on the asphalt surface. To try to create a TiO_2 coating using APCP with this new APCP generator design, three different application methods were tried.

5.1.1 TiO_2 and APCP Applied Simultaneously

The first application method consisted of applying TiO_2 and APCP simultaneously through the APCP generator. The goal was to have a flux of free radicals going through the screen towards the substrate, and while these free radicals were traveling to the substrate to add TiO_2 so the plasma radicals can attach to the individual TiO_2 granules. Then these plasma radicals surrounding the TiO_2 can adhere to the substrate surface as illustrated in Figure 5.4.

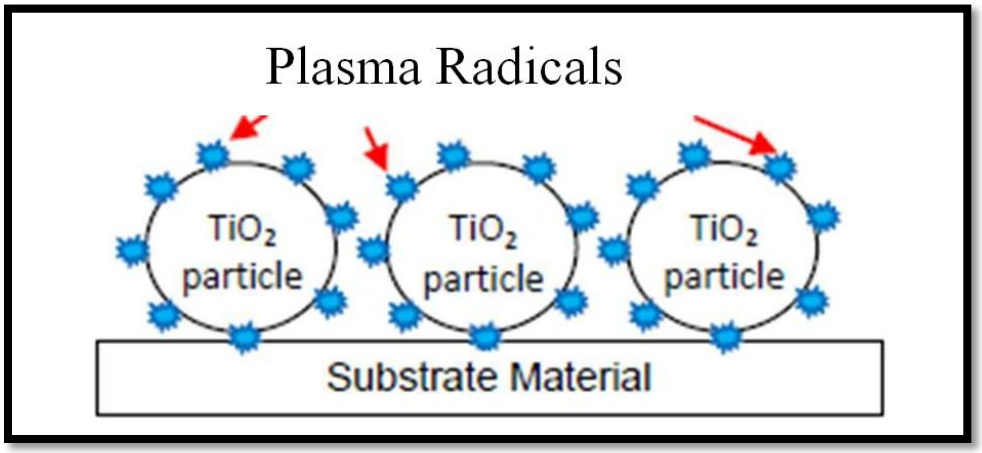


Figure 5.4 Schematic sketch of TiO_2 coating on asphalt through APCP activated radicals

To test this concept first six plain asphalt samples (1-6) were tested in the environmental chamber and showed a NO reduction of 2.93%. Then these six samples were coated with APCP and TiO_2 simultaneously. Each sample was ran in APCP generator for 25 minutes at 8.3 kV RMS. The procedure consisted of applying APCP only for 5 minutes, then applying TiO_2 and APCP to the samples for 20 minutes. The powder coating gun trigger was pulled approximately 50 times during the coating period. After treatment in the APCP generator the six samples were ran in the environmental chamber and showed a NO reduction of 13.50%. Then the samples

were washed and ran in the environmental chamber and showed a NO reduction of 1.84%. With this technique it was challenging to get enough TiO_2 onto the sample to see high NO reduction rates either before or after washing. Also there was concern that the plasma radicals were quenching as soon as they were hitting the TiO_2 granules upstream of the substrate, which could by why the TiO_2 was not bonding to the substrate. The second technique was thus tried to improve the effectiveness of the photocatalyst APCP TiO_2 coating on asphalt.

5.1.2 TiO_2 on Samples by Hand; Then APCP Generator Coating

Since it was difficult to get enough TiO_2 onto the sample with the horizontal TiO_2 inlet the second approach was tried. In this experiment the same six samples (1-6) were coated by hand with TiO_2 using a salt shaker to apply TiO_2 to the sample. After running the environmental chamber test, a total NO reduction of 71.56% for six samples were achieved. These samples were then put into the APCP generator and coated with APCP for 20 minutes each to try to immobilize the TiO_2 powder onto the asphalt, and to attempt to identify if enough free radicals were getting through the mesh to cover the TiO_2 particles. The six samples were run in the environmental chamber and showed a NO reduction of 58.96%.

These six samples were further divided into two groups: Samples 1-3 were ran in the environmental chamber and showed a NO reduction of 38.37% and 13.68% before and after washing, respectively. Samples 4-6 were ran in the environmental chamber and showed a NO reduction of 32.35%. Then samples 4-6 were coated in the APCP generator with APCP only for an addition 40 more minutes each, and showed a NO reduction of 20.28% before washing and 10.39% after washing.

To compare with this coating method three new samples were prepared using the same procedure, but no APCP coating. First three different plain samples (7-9) were ran in the environmental chamber and showed NO reduction of 4.60%. Then these samples were sprinkled with TiO_2 by hand using a salt shaker and showed a NO reduction of 49.31% and after washing a NO reduction of 14.54% was reported. Figure 5.5 summarized the NO reductions obtained from this coating method. When comparing the samples it was difficult to distinguish what, if any, effects the plasma coating had on these samples that had been pretreated with TiO_2. This lead to the third technique, which involved trying to apply an APCP film followed by TiO_2 being deposited.

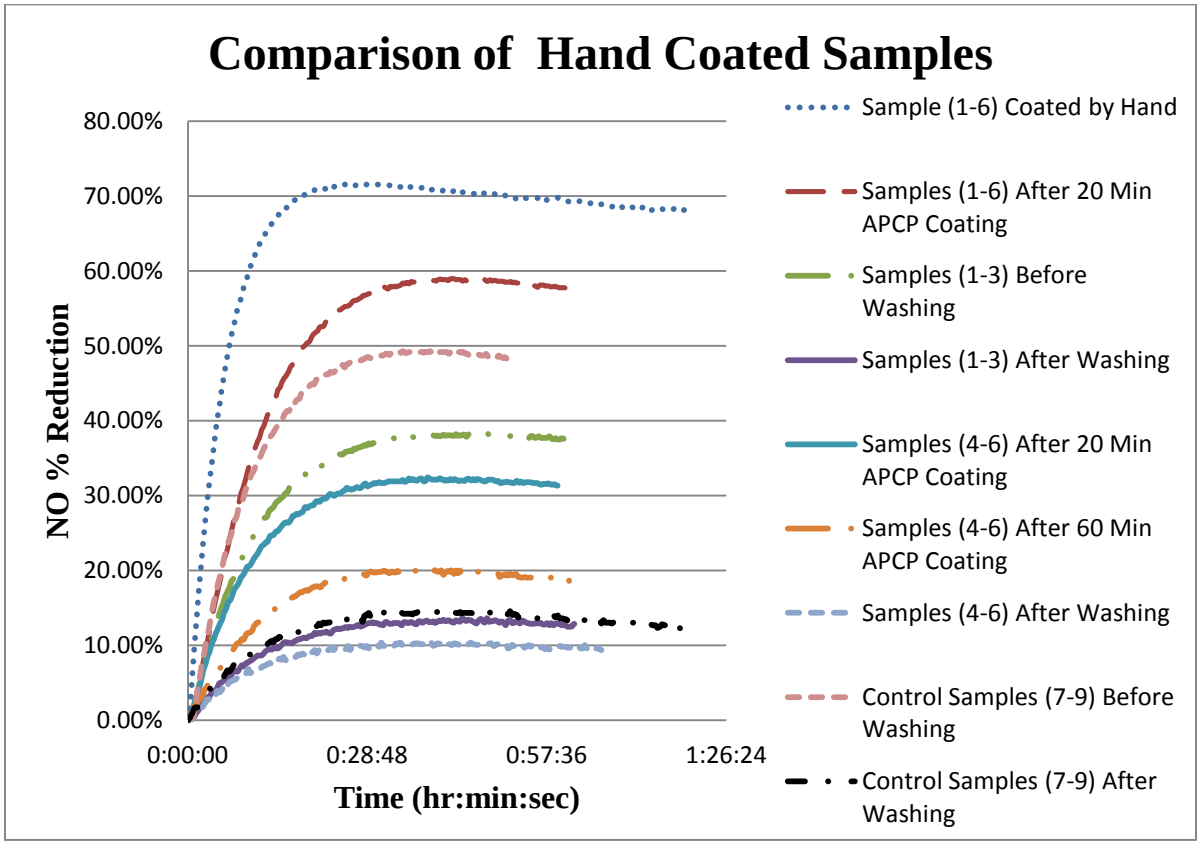


Figure 5.5 Samples coated by hand then with APCP

5.1.3 Duty Cycle: APCP Only Then Power Off and TiO_2 Applied

The third application method consisted of using a duty cycle to try to improve adhesion of TiO_2 to asphalt using APCP, which is imposed by turning the plasma on and off in a known pattern with respect to time. This on/off pattern allows the radicals to arrive at the growing film, followed by a flux of the original unmodified material (TiO_2). The reason for trying this technique was when the power is turned off it is easier to control the flow of the TiO_2 because there will not be charged items in the APCP generator. Also we hypothesized a plasma polymerized film would be growing on the substrate that would incorporate and immobilize the falling TiO_2 granules. For this experiment three samples (10-13) were tested before any treatment and showed a NO Reduction of 4.60%. Then the three samples were coated with APCP immediately followed by TiO_2. For each sample APCP was ran for 12 minutes, followed by the power turned off and TiO_2 immediately added. After coating a NO reduction of 7.71% was observed. After washing a NO reduction of 6.01% was observed.

Then this same duty cycle technique was used on three new samples with different coating parameters to try to increase the NO reduction rate. The three new samples (14-16) were tested in the environmental chamber before treatment and show a NO reduction of 4.80%. Then the samples were coated with the following procedure: APCP only for 10 minutes, then power off and TiO_2 only for 2 minutes to complete one cycle. This was repeated for three cycles for each sample giving a total APCP generator treatment time of approximately 36 minutes. Then these samples were immediately ran in the APCP generator and showed a NO reduction of 6.62% before washing, and a NO reduction of 6.77% after washing.

Then the APCP duty cycle technique was conducted again with different coating parameters. We ran out of new plain asphalt samples so six samples that appeared to have low concentrations of TiO_2 coating on them were gathered and tested in the environmental chamber and showed a NO reduction of 7.31%. These six random samples were coated with APCP only for 15 minutes, then power was turned off and TiO_2 was immediately added for 2 minutes. The NO reduction before washing was 6.90% and 7.37% after washing.

5.1.4 Discussion of Below Screen Techniques

These low NO reduction rates lead to the hypothesis that possibly efficient immobilization of TiO_2 requires charged APCP species to arrive at the substrate along with radicals and nano TiO_2 powder, and efficient immobilization requires the powder to pass through the gap where some activation process happens to allow it to be immobilized at the substrate.

5.2 SMALL SAMPLE EXPERIMENTS ON TOP OF SCREEN

After trying a variety of techniques to immobilize TiO_2 particles to a substrate material below the screen but not successful, a different design with the substrate exposed to gap conditions was evaluated. For this experiment asphalt samples were broken up into 40 small samples with an average diameter of approximately ½ inch. These samples were placed on top of the screen, 6 to 8 samples were placed on the screen and coated at a time. The goal was to get maximum exposure of each sample to the plasma region. TiO_2 was inserted from the top of the APCP generator. The TiO_2 inlet was even with the needle tips to get maximum dispersion of TiO_2. For this experiment first APCP only was ran for 5 minutes and then TiO_2 and APCP were

ran for 5 minutes. The APCP generator power was approximately 8 kV RMS. When the power was on at the same time as the powder coating gun trigger was pulled it would generate a spark. So, during the five minutes when the powder was being applied a fast on/off duty cycle was conducted every 10 seconds so powder could be distributed onto the samples safely. The small asphalt samples were placed on a metal pan for testing in the environmental chamber as shown in Figure 5.6.

Figure 5.6 Pan containing APCP TiO_2 coated samples for Environmental Chamber

Before treatment a NO reduction of 7.43% was observed. After treatment, a NO reduction of 11.15% was observed before washing and 5.28% after washing.

Visually the samples showed evidence of having TiO_2 on the surface as illustrated in Figure 5.7. The samples appear gray before washing and still grayish after washing. Based on this

experiment it was hypothesized that a larger asphalt surface area needs to be treated so see better NO reduction.

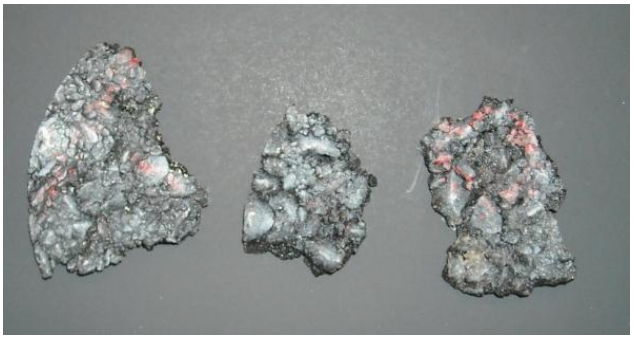


Figure 5.7 Small asphalt samples after APCP TiO_2 coating

Then this method was tried again with more broken samples, a total of approximately 60 samples, but the pollution removal efficiency did not improve. For this test APCP only was applied to the samples at approximately 8 kV RMS for 10 minutes. Then the power was turned off for 10-15 seconds so TiO_2 could be incorporated in the APCP generator. Then the power was turned back on for 2 minutes and this on/off duty cycle was repeated for a total coating time of 25 minutes. Before testing the NO reduction was 5.32%, after coating the NO reduction was 10.28%, after washing the NO reduction was 4.52%.

5.3 SUMMARY OF 40 NEEDLE DESIGN EXPERIMENTS

This chapter described the tests that were conducted with the 40-needle APCP generator design to try to create an air purifying surface layer on asphalt composed of TiO_2 and APCP.

Different application methods were tested. The results indicated that this design has difficulty in getting TiO_2 onto the substrate because of the different flow characteristics that are created by the addition of the stainless steel mesh. Low NO reductions were seen before and after washing for most application methods, except applying TiO_2 by hand. The problem with applying TiO_2 by hand is there was no conclusive evidence that APCP can help in the immobilization process if the TiO_2 is already on the sample. Chapter 6 will describe the preliminary findings of this study and make recommendations for future work that will address the challenges encountered during testing.

CHAPTER 6: PRELIMINARY FINDINGS AND RECOMMENDATIONS FOR FUTURE WORK

Utilizing TiO_2 as a photocatalyst for self-cleaning and air purifying applications is becoming common practice all over the world. TiO_2 has shown promising air purifying abilities when applied to transportation infrastructure. Most of the methods have involved mixing TiO_2 into concrete slurries, paints and other materials, or applying TiO_2 as a liquid coating. Mixing TiO_2 into products is not the most effective method because direct sunlight is required for the photocatalytic reaction, and a lot of the applied TiO_2 will not be utilized. Liquid and other thin surface coatings are more efficient, but most of these coatings are not durable when exposed to weathering and traffic conditions. So this research investigated an innovative concept to try to create a more durable and efficient surface coating by using APCP to bond TiO_2 to asphalt. This chapter will summarize the findings from this research, describe the challenges with using APCP to immobilize TiO_2, and discuss recommendations for future work on this topic.

6.1 PRELIMINARY FINDINGS

This is the first time APCP has been used with the intent to immobilize nano TiO_2 powder onto asphalt. The objective of this study was to use APCP to adhere TiO_2 to infrastructure surfaces to improve pollutant removal efficiency and coating durability. This research developed an APCP generator, and successfully generated APCP in a mixture of argon and acetylene. Plasma polymerized acetylene was shown on glass with the use of a scanning

electron microscope (SEM) and atomic force microscope (AFM). Then TiO_2 was safely mixed into an argon and acetylene APCP environment at a controlled rate with a powder coating gun. Different TiO_2 application methods were tested and evaluated for the ability of the TiO_2 coating in APCP to remove nitrogen oxides (NO) in an environmental chamber. Then the durability of the coating was tested by washing and scrubbing the sample to remove any TiO_2 that was not strongly immobilized.

The plasma radicals generated by the APCP generator were found to be able to adhere TiO_2 granules to asphalt. Signs of immobilization of TiO_2 were shown in field emission scanning electron microscope (FE SEM) images. TiO_2 was identified on the asphalt samples both before and after washing and scrubbing; indicating a strong bond between the TiO_2 particles and the substrate asphalt sample was achieved. Through this research acetylene was found to be an appropriate precursor gas for coating TiO_2 onto asphalt.

Some reduction of NO was observed for TiO_2 coated asphalt specimens using APCP. Although, the rates were lower than desired. With the 12 needle APCP generator design a NO reduction of 33% on average was shown before washing, and a NO reduction of 5% on average was shown after washing and scrubbing. The NO reduction for plain asphalt samples was less than 3% so the TiO_2 coating in APCP is showing some signs of being photocatalytic.

To try to improve this pollution removal efficiency the APCP generator was modified to hold 40 needles. For this APCP generator design different application methods were tried. The method applying TiO_2 simultaneously with the APCP the samples showed a 13.5% NO reduction before washing and a 1.84% NO reduction after washing and scrubbing. For the Duty Cycle technique (applying APCP only then power off and TiO_2) the samples showed a NO reduction of

8.7% before washing and 5.5% after washing on average. The new APCP generator design provided new challenges that were not able to be studied in detail in this preliminary research. It is recommended to complete more experiments with the 40 needle APCP generator design, because it is showing promising signs towards being an effective tool to immobilize TiO_2 to asphalt. Visual inspection and FE SEM studies show signs of immobilization, but more work is necessary to increase the concentration of TiO_2 that is immobilized after washing and scrubbing.

The APCP method of applying TiO_2 by hand first and then coating with APCP did not show promising results for immobilization of TiO_2 and this method is not recommended for future work.

6.2 CHALLENGES AND FUTURE WORK

This work was very innovative and exploratory, and with that came many challenges. One large challenge was controlling the powder flow through the APCP. This was especially challenging because TiO_2 is a semiconductor and was attracted to the needle electrodes and any other charged items in the APCP generator. A detailed study needs to be conducted on how to control the TiO_2 in the APCP generator. This could possibly include installing barriers to prevent the powder from accumulating on the needles and ground ring. The fact that TiO_2 is a semiconductor helped disperse the particles. When the TiO_2 entered vertically in the center of the APCP generator it was pulled outwards towards the needles. This could be used to help make an even coating of TiO_2 in APCP if the interaction was better understood.

There are still some unanswered questions about how the plasma deposition is forming. It is believed that the plasma polymerized film is growing from nodules on the substrate. Although, there is still a possibility that some of the plasma polymerized nodules are growing in the gas phase and then falling on the substrate in the form of a plasma dust. Studying more precursor molecules will help determine the nature of the growing nodules. There needs to be a more in depth study of the plasma film. Some questions that need to be answered include: Does the plasma film cover the TiO_2 particles? If so, how thick is the plasma film on top of the TiO_2 particles? Does the plasma film prevent or hinder the photocatalytic reaction?

Another challenge is the TiO_2 surface coating should be hydrophilic so that the surface can be self-cleaned by water. The problem is plasma polymerized acetylene films are usually used to create hydrophobic properties. A more in depth study of the properties of the TiO_2 and APCP coating need to be studied to determine what effects the APCP had on the asphalt and TiO_2. The coating could be compared on a microscopic level to the Pureti surface treatment and other proven photocatalyst coatings to better understand if the APCP is reducing the ability of the TiO_2 to be used as a photocatalyst. Also it was difficult to quantify the APCP TiO_2 loading that was immobilized to a substrate sample given the low deposition rate.

For further APCP generator optimization the recommendation would be to use COMSOL to model the flow dynamics within the APCP generator. Also a more detailed study on the microscopic level would be useful to optimize the APCP generator and coating. The FE SEM could be used to get a qualitative concentration of TiO_2 at different locations within the APCP generator.

Eventually after the APCP generator has been modified to improve efficiency and produce a durable photocatalytic coating the coating can be studied for resistance to traffic load, deicing chemicals, freeze/thaw conditions, and other conditions that road surfaces must withstand. Also it will eventually be critical to make necessary modifications to the APCP generator design to ensure it is adaptable to an outdoor environment and can be implemented into engineering field applications.

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