Environmental Impacts of Pavement Rejuvenators

A Major Qualifying Project Submitted to the Faculty of WORCESTER POLYTECHNIC INSTITUTE in partial fulfilment of the requirements for the Degree of Bachelor of Science

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Abstract

Pavement rejuvenators are used as a cost-effective method for maintaining roadways. This project examined asphalt-based, bio-based, and coal-tar-based rejuvenators to determine rejuvenator effectiveness and the concentrations of polycyclic aromatic hydrocarbons (PAHs) in particulate material detached from pavement surfaces treated with each rejuvenator. Through testing using a Model Mobile Load Simulator (MMLS) and Gas Chromatography analysis, we observed that rejuvenators qualitatively appeared to improve pavement surface appearance, and determined PAHs were present in particulate material detached from pavement samples treated with the rejuvenators. Based on our results, we recommend the use of bio-based rejuvenators because of the improvement in surface appearance and that the particulate material detached from bio-based rejuvenators do not contain high levels of PAHs.

Executive Summary

The research and testing conducted in this project investigated the effectiveness and potential environmental impacts of three types of pavement rejuvenators. A pavement rejuvenator is a substance that is applied to pavement surfaces to revitalize old asphalt, thereby extending its life. Applying rejuvenators allows municipalities to improve roadway pavements at a lower cost than completely renovating and repaving roads. There is a lack of published research on rejuvenators and as a result, little is known about how rejuvenators may affect the environment. This project investigated the performance of three types of pavement rejuvenators and analyzed the chemicals present to determine any potentially harmful environmental impacts. The three rejuvenators tested were an asphalt-based rejuvenator, a coal-tar-based rejuvenator and a bio-based rejuvenator.

To assess the environmental impacts, particulate matter that had detached from pavements treated with each type of rejuvenator was collected, extracted with methylene chloride, and injected into a gas chromatograph to quantify polycyclic aromatic hydrocarbons (PAHs) present in the particulate matter. PAHs are carcinogenic and are a concern to public health and aquatic life. If PAHs are present in this particulate matter during testing, it can be inferred that they are present in particulate matter released from pavements on roadways. The mobilization of this particulate material could cause problems in the environment because of the presence of PAHs.

To conduct our tests, a PaveTesting Model Mobile Load Simulator machine (MMLS) was used. Pavement disks coated with the different types of rejuvenators were cycled through the MMLS machine to simulate roads being driven on through repeated tire-pavement contacts. The

MMLS simulation dislodged particulate matter that was then chemically analyzed through GC analysis. Concentrations of PAHs in each sample were reported.

Results indicated that the coal-tar-based rejuvenator performed well with respect to limiting the mass of particulate that was mobilized from the car tire abrasion. The asphalt-based rejuvenator had the worst performance in this comparison in that the greatest mass of particulate matter was released. The particulate from the coal-tar-based rejuvenator coated asphalt disks however, contained a high concentration of PAHs. The data confirmed our hypothesis that coal-tar-based rejuvenator would have more PAHs in particulate than the asphalt-based rejuvenator or the bio-based rejuvenator. The PAH total for the detached material from the coal-tar-based rejuvenator run was $3,440 \pm 380$ mg PAH/kg sample. In contrast, the detached material from the bio-based rejuvenator run contained 582 ± 57 mg PAH/kg sample and the detached material from the asphalt-based rejuvenator run contained 364 ± 26 mg PAH/kg sample.

Based on our findings, we recommend bio-based rejuvenators for use on roadway pavements based on their low PAH concentrations and good performance in our visual assessment of the pavement surfaces. We do not recommend using coal-tar based rejuvenators due to environmental concerns despite their favorable performance in a visual surface assessment, as the particulate matter contained a greater concentration of total PAHs than the other two types of rejuvenators evaluated in this work. We also recommend further testing of rejuvenators due to the lack of available data on performance and environmental impact.

Statement about Professional Licensure

The reason for obtaining a professional license is to ensure that projects that involve the public can be completed and approved by professional engineers. This protects the public from any potential mishaps that could occur without the direct involvement of a professional engineer. The process to gain a professional license is demanding to ensure the engineer is qualified and competent in their field of work. Many companies now limit their work to be with professional engineers, and projects involving the public are required to have oversight by professional engineers. In addition, licensure allows for the engineer to get proper recognition for the quality work that they accomplish.

Obtaining a professional engineering license is not an easy process, it first requires an engineering degree from an ABET accredited university. Before obtaining the license, you also must take the Fundamentals of Engineering exam (FE). After passing the FE exam, the engineer then must complete four years of qualified professional experience, and then take and pass the Professional Engineering exam.

Capstone Design Statement

The design requirements for this project were satisfied in two ways:

- 1. Experimental protocol was designed to obtain our data and analyze our results.
- 2. A solution for a containment and monitoring method was designed for preventing the spread of PAHs from pavements treated with coal-tar-based rejuvenators.

The Major Qualifying Project at WPI includes a capstone design requirement set forth by the Accreditation Board of Engineering and Technology (ABET). ABET General Criterion 4 states: "Students must be prepared for engineering practice through the curriculum culminating in a major design experience based on the knowledge and skills acquired in earlier course work and incorporating engineering standards and realistic constraints that include most of the following consideration: economic; environmental; sustainability; manufacturability; ethical; health and safety; social; and political."

Experiments were designed intended to determine the chemical composition of detached particulate from pavement that had been treated with different types of rejuvenator in a laboratory setting. Previous tests of this nature performed with detached pavement samples collected from roadways, however this method allows for a greater range of variables to affect the experiment. This experiment used a Model Mobile Load Simulator (MMLS) to produce detached pavement samples in a laboratory setting, with limited external variables. The MMLS was operated for 24 hours for each rejuvenator run and any detached material was collected. Methylene chloride was used to solvate the detached material, so it could be analyzed through gas chromatography. The experimental design considered environmental impacts.

The second design completed in this project was a solution for roadways with high PAH concentrations from rejuvenator application. Containment, removal, and treatment solutions were

considered, and containment was chosen because it would greatly reduce the risk of initial exposure to PAHs. The design solution consisted of painting over the contaminated surface in high traffic areas and sealing the paint layer with fresh asphalt. Over time, the top asphalt layer will wear away and when the paint is revealed it would signal that the road should be resealed to continue the containment of the PAHs. The paint would only be applied in high traffic areas because these areas would wear away first and painting the entire roadway would be more expensive. Through cost analysis, standard highway paint used by municipalities was determined to be the most economically viable. This solution design considered environmental, sustainability, economic, and health and safety factors.

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Chapter 1: Introduction

In order to maintain roads and extend pavement life, there have been different approaches and products developed. Pavement rejuvenators may be a promising alternative to removing and repaving end-of-life road pavements. Research is ongoing to determine the effectiveness of different types of rejuvenators for extending the service life of asphalt pavements. Municipalities are leaning towards the use of rejuvenators due to the possible significant cost savings. Some rejuvenation products have been around for several decades; but recently the use of some of these products has come into question due to the possible negative environmental and health effects.

Many studies have been completed looking at the effectiveness and environmental implications of various pavement sealers and binders, however, not many studies have been conducted looking at pavement rejuvenators. Rejuvenator products function by penetrating the surface of pavement and replenishing chemicals restoring flexibility. This prevents roads from becoming brittle and eventually cracking. Rejuvenators are available with asphalt base, coal-tar base, and environmentally friendly bio-based products (such as soybean oil). Recently, studies have shown that coal-tar-based pavement rejuvenators contain polycyclic aromatic hydrocarbons (PAHs), some of which are known carcinogens. Since these chemicals are being applied directly to road surfaces, wear and tear can cause these potentially harmful chemicals to be released into the environment.

The goal of this project was to (1) qualitatively evaluate the effect of different rejuvenators on pavement surface appearance after repeated tire loading experiments, and (2) quantify contaminant mobilization via detached particulate material from rejuvenated pavement samples subjected to repeated tire loading. The PAH contaminants in the dust mobilized from

pavements treated with coal-tar-based rejuvenator, asphalt-based rejuvenator and bio-based rejuvenator were quantified and compared. This material was analyzed via gas chromatography for sixteen priority PAHs.

Chapter 2: Background

2.1 Asphalt Rejuvenation Techniques

There are multiple techniques to revitalize asphalt surfaces. Different regions require different products to make roads and other asphalt surfaces last as long as possible and minimize repair costs. Pavement rejuvenators and sealers are among the most commonly used products for road revival. Pavement rejuvenators are used as preventative maintenance; they are applied to the surface of a new road to protect it and strengthen the binder in the asphalt base (Standard Practice for Pavement Recycling, 1988). Pavement rejuvenators can also be incorporated into recycled pavement that will re reapplied to the road. There are products on the market, such as *Revive*, that are specifically designed to be incorporated into recycled asphalt to help control the flexibility and stiffness of the recycled asphalt (ArrMaz, 2018). Applying rejuvenators to a new road has the potential to make the pavement last between two and five years longer. Pavement sealers can be applied after years of use to fill cracks and repair imperfections on the surface of the asphalt. Pavement sealers also prevent liquids like gasoline and oil from entering the asphalt, so the degradation of the asphalt surface happens at a slower pace (Crenson, 2010).

Rejuvenators are typically applied to the road in warm weather so they cure better. In order to apply the rejuvenator to a pavement surface, the surface must first be cleaned using a power broom. A truck containing rejuvenator will then apply the rejuvenator by spraying it onto the pavement surface as the truck drives over the roadway. To ensure of complete coverage, workers will take manual sprayers and apply the rejuvenator to difficult-to-reach areas. After the rejuvenator is applied, sand may be applied to the pavement surface and left to sit for 24 hours. This is done as another step to help the rejuvenator cure. After this period, the sand will be swept

off the area (Metropolitan Government of Nashville and Davidson County, n.d.). Rejuvenating the pavement when the asphalt is initially applied is claimed to reduce the cost of maintenance of the pavement. Since the rejuvenator is expected to extend the life of the pavement, roads do not have to be repaved as often.

2.2 Asphalt-Based Rejuvenators and Sealants

The first type of rejuvenator developed was an asphalt-based rejuvenator. It was created in 1960 by the Golden Bear Oil Company and named *Reclamite*. The main reason Golden Bear Oil Company decided to create a rejuvenator was to restore roadways without having to completely re-pave the entire surface. *Reclamite's* main purpose is to soften the surface of oxidized pavement. The rejuvenator is partially absorbed into the asphalt binder to increase pavement life (Brownridge, 2010). This is done by adjusting the properties within the pavement mixture. For asphalt rejuvenators, it is best for them to be sprayed on the pavement surfaces during hot weather because the heat increases the absorption rate of the rejuvenator.

Asphalt-based rejuvenators are made up of two main materials. First, there are the asphaltenes which are a group of large molecular sized chemicals that are insoluble in *n*-pentane. The asphaltenes precipitate out when combined with *n*-pentane and what remains (doesn't precipitate) are maltenes, the other main material in asphalt rejuvenators. Maltenes have four identified components, which are first acidiffins, second acidiffins, nitrogen bases, and saturated hydrocarbons. The maltenes are important compounds that help rejuvenators incorporate into pavement. These are the components of the rejuvenator that revitalize the road surface (Boyer, 2000). For the rejuvenator to properly function, there needs to be a balanced blend of maltenes in

an oil-in-water emulsion tailored to the specific properties of the maltenes in the mix (Brownridge, 2010).

In order to test specific ratios in the asphalt-based rejuvenators, the Rostler Analysis is used. The test, named after its developer Fritz Rostler, assesses the relationship of the maltenes as compared to the asphaltenes. The equation used for the analysis is:

$$\frac{PC+A1}{S+A2}$$
 (Equation 1)

PC=Polar Compounds A1=First Acidiffins

A2=Second Acidiffins S=Saturated Hydrocarbons

The range for this value should fall somewhere between 0.3 and 0.6.

The specific ratios in the asphalt-based rejuvenator are used for changing properties of the actual rejuvenator. The rejuvenator needs to have a high insolubility in water, so it will not be washed away. The ideal viscosity at 25 °C is between 15-40 SFS (saybolt furol seconds)

(Brownridge, 2010). This makes the rejuvenator able to be absorbed without being too runny.

Skid resistance is a concern when applying asphalt-based rejuvenators to roads. When the rejuvenators are applied, they can reduce the skid resistance of the road for up to a year. A lack of skid resistance can be particularly dangerous in areas where the weather affects road conditions. Drivers would need to account for the compromised weather conditions and for the presence of a new rejuvenator on the road. If a newly sprayed rejuvenator is not absorbed within 24-48 hours, it should be scraped off to prevent safety concerns like this (Brown, 1988). Another concern about applying asphalt-based rejuvenators are their chemical properties. Rejuvenators are typically composed of asphaltenes which are insoluble in water, not affected by oxidation,

and they have highly reactive sub-fractions (Brownridge, 2010). These properties, while making these rejuvenators good at reviving the roads, would make it difficult for clean up if the need should arise. The insolubility of the rejuvenator in water would make it easy to separate in case of a spill because they would not dissolve in the water, but since some of these compounds do not oxidize, clean up would still be difficult.

Asphalt-based sealants have been around for longer than rejuvenators. Their chemical composition is similar and with that similar environmental concerns exist. Many asphalt-based sealants use a mixture of aliphatic and aromatic hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs). This is of concern because some PAHs are known carcinogens. Since they are prominent in asphalt-based sealers, this runs the risk of these PAHs getting into waterways if any particulate matter was released from the road coated with this sealant (Simon, 2006).

2.3 Coal-Tar-Based Rejuvenators and Sealants

Coal-tar is a viscous, black, oily substance that is a by-product of coke production. This substance is found in many products, including soaps, dandruff shampoos, and roofing materials. Coal-tar or coal-tar pitch also constitutes 20-40% of coal tar sealers. Unfortunately, coal-tar is a source of polycyclic aromatic hydrocarbons (PAHs), which if consumed can lead to the possibility of skin, bladder, lung, or respiratory cancer (Thibeault Jr., 2016). PAHs are also toxic to aquatic organisms.

Coal-tar-based rejuvenators represent a large portion of rejuvenator products that are used on pavements. In a general sense, they provide the same benefits as other product types, but are also known to provide protection from fuel spills. Coal-tar-based materials provide a higher level

of fuel resistance because there is a residual amount of coal-tar left on top of the pavement. The rejuvenator's thickness allows it to last longer and maintain its fuel resistant characteristics until cracks develop in the road surface or it is worn off from traffic (Shoenberger, 2003).

While there has not been a significant amount of research done on coal-tar-based rejuvenators, there has been more research done on coal-tar-based sealants. In 2016, the U.S. Geological Survey (USGS) and Milwaukee Metropolitan Sewerage District performed a study on 40 different streambeds. The results of this study indicated that the primary transport method of toxic PAHs in the sampled streambeds was stormwater runoff. These toxic PAHs originated from pavement surface debris that had been treated with coal-tar-based sealants. In Milwaukee, scientists collected sediment samples from streambed sites and dust samples from parking lot sites. According to their results, dust from coal-tar-based sealant was the source of on average 77% of the PAHs in the sediment samples (Baldwin et al., 2016). Coal-tar-based sealants contain an average concentration of sixteen PAHs about 1,300 times greater than asphalt-based sealants (Weinhold, 2012). Unfortunately contact with tires, wind, and stormwater can disperse PAH-laden particles. Other studies have shown that there are risks involved when tracking particles of coal-tar sealant into homes (Baldwin et al., 2016).

2.4 Bio-Based Rejuvenators

Bio-based pavement rejuvenators were developed in the early 2000s as an eco-friendly alternative to the coal-tar and asphalt-based rejuvenators that were on the market. Bio-based rejuvenators work the same way as the other rejuvenators, except the medium that transfers the polymers to the pavement surface is an agricultural product, usually 70-85% soybean or vegetable oil. Currently, the market for this alternative is dominated by two products, *RePLAY*

(manufactured by BioSpan) and *Biorestor* (manufactured by BioBased Spray Systems).

However, other products are starting to surface on the market such as Cargill's Anova 1900 rejuvenator. Overall, bio-based products have yet to be widely adopted and are still being tested to see if they meet the same standards as their coal-tar-based and asphalt-based counterparts. A study conducted by the University of Minnesota and the Minnesota Department of Transportation indicated that the products improved pavement samples in laboratory testing. However, no significant improvement was found in field testing (Marasteanu, 2016).

2.5 Polycyclic Aromatic Hydrocarbon Contamination from Rejuvenators

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds made up of multiple aromatic rings that are fused together. These aromatic rings are benzene rings, which are made up of six carbon atoms and six hydrogen atoms. The carbons are bonded to each other in a ring, with each carbon atom bonded to two others, in a resonant structure. There is one hydrogen atom attached to each carbon atom in the ring. Below are structures for two different common PAHs, phenanthrene and benz(a)anthracene.

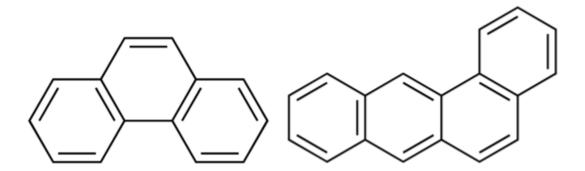


Figure 1: Structures for two Common PAHs, Phenanthrene (left), Benz[a]anthracene (right) (Sigma Aldrich, 2018)

There are over 100 known PAHs in air, food, and water. They are rarely found in nature but are commonly created from man-made processes. PAHs are by-products of natural combustion or high-pressure processes, and are a component to many fossil fuels, coal-tar pitch and creosote (Agency for Toxic Substances and Disease Registry, 2009). They are also found in cigarette smoke and food items that are cooked over charcoal or grilled.

PAHs are typically in a solid form when pure and possess low volatility. They can be photo-oxidized or degraded to similar substances. Their concentrations in water are usually low because of their low aqueous solubilities, however they can be bound to particulate material, thereby mobile. They can accumulate in soil and leach into water from there. Their presence in soil means they can be absorbed by plants (Agency for Toxic Substances and Disease Registry, 2009). Of the 100 known PAHs, there are sixteen that are particularly toxic to mammals and marine life: acenaphthylene, acenaphthene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene, and pyrene (Agency for Toxic Substances and Disease Registry, 2009). All sixteen of these toxic PAHs have between two and six aromatic rings and molecular weights that range from 128-270 g/mol. The solubility of these PAHs range from insoluble to slightly soluble and the vapor pressures range from slightly volatile to non-volatile. The different molecular weights, solubilities and vapor pressures of these PAHs determine their respective fate and transport in the environment. A table of the PAHs studied in this work can be found in Appendix Α.

2.6 Identification and Quantification of Polycyclic Aromatic

Hydrocarbons

PAHs can be identified with different methodologies/instruments. One instrument that can be utilized for detecting PAHs is gas chromatography. In gas chromatography, the contamination must be transferred from its "original" phase (e.g. soil, sediment, water) to a volatile solvent; the original form can be solvated with methylene chloride, and then injected into a heated column where the sample volatizes. Traveling through the column in the gas phase, the different molecules are separated depending on their affinity to the column stationary phase. Following separation, the individual contaminants are quantified with appropriate detectors. This method is an accurate method of measuring and detecting PAHs.

Another method for PAH detection is liquid chromatography. Liquid chromatography works by dissolving the particulate in a solvent, then injecting the liquid into the instrument for separation. The different molecules in the liquid travel at different velocities in the column, causing them to separate.

A third method of testing is using rapid testing PAH indicator strips (DEUROLAB, 2016). They are inexpensive, readily available, and quick at determining whether PAHs are present in the sample. However, the strips cannot indicate which PAHs are present or how much of the material is made up of PAHs.

Chapter 3: Hypotheses

Based on background research, we hypothesized that:

- There is a significant variation in the amount of polycyclic aromatic hydrocarbons
 (PAHs) in the particulate material that is dislodged from pavements treated with
 different rejuvenators. We suspected that the coal-tar-based rejuvenator would have
 more PAHs in detached material from the asphalt samples than those treated with
 asphalt-based rejuvenator or bio-based rejuvenator.
- 2. Less particulate material is dislodged from the pavement samples applied with rejuvenators versus the pavement samples without any rejuvenator.
- The surfaces of the asphalt disks treated with rejuvenator and subjected to repeated tire contacts would have different surface appearance dependent on the rejuvenator used.

Chapter 4: Objectives

The goal of this project was to evaluate different types of rejuvenators used for maintaining asphalt pavement. To address this goal, the following four specific objectives were completed:

Objective 1: Use the Model Mobile Load Simulator apparatus to simulate the repeated contact of tires with pavement, and gather any particulate material detached from the surfaces.

Objective 2: Perform chemical analysis for PAH compounds in the particulate material produced in the MMLS testing by extracting the contaminants from the particulate and analyzing the extract by gas chromatography.

Objective 3: Compare the PAH concentrations in the particulate material produced in the MMLS testing for the different rejuvenators. Make recommendations based on the findings for the best course of action for future pavement treatment.

Objective 4: Observe the effects of different rejuvenators on the pavement surface appearance after repeated tire contacts in the MMLS.

Chapter 5: Methodology

5.1 Research and Supply Gathering

After researching each type of rejuvenator, it was necessary to obtain samples of each type. Each rejuvenator could then be tested in the Model Mobile Load Simulator (MMLS) machine and a chemical analysis of the detached material from the pavements was conducted. Samples of bio-based, asphalt-based, and coal-tar-based rejuvenators were obtained. In addition, road scrapings were supplied from a community where a coal-tar-based product had been applied in North Carolina. The road scrapings were provided solely for chemical testing and were not tested like the other samples with the MMLS, but the same procedure for chemical testing was used on these scrapings as the ones obtained experimentally. It is important to note that the asphalt product used as a rejuvenator in this testing was a product that had the capabilities, ingredients, and characteristics of a typical asphalt-based rejuvenator. The product had other purposes and uses in addition to being a rejuvenator, but this was the closest we could obtain to an actual asphalt-based rejuvenator.

5.2 Model Mobile Load Simulation

The goal of the Model Mobile Load Simulation (MMLS) test was to capture any material (particulate material) detached from pavement samples after different types of rejuvenator had been applied to them. The test was conducted using a Model Mobile Load Simulator (MMLS) testing apparatus.



Figure 2: Model Mobile Load Simulator.

The MMLS testing machine has four tires that travel on a belt at various speeds, with adjustable force, contacting disks of asphalt pavement or other materials. Each asphalt disk was a 4-inch-tall cylinder with a 6-inch diameter. To fit them into the machine, the disks were cut on two of the sides in parallel, resulting in a width of 4 inches (Figure 3).



Figure 3: Photographs of the asphalt disks used in the MMLS.

For each run, six asphalt disks were placed into the machine in designated spots. The space where the final three disks would go was left empty to capture detached material.

Aluminum foil was used to collect this debris in the final section; the foil lined the bottom, sides and back of the section (Figure 4).



Figure 4: MMLS with Six Disks and Aluminum Foil to Catch Detached Material.

Four runs were conducted, one for each type of rejuvenator (bio-based, asphalt-based, and coal-tar-based) and a control (no rejuvenator). For the control test, the six asphalt disks were placed in the base of the machine after they had been cut to size. In the tests with rejuvenator-applied disks, the specific type of rejuvenator was applied to the surfaces of six asphalt disks per manufacturer's application rate. Using values from the specification sheets for each rejuvenator, the application rate was calculated so that the amount of rejuvenator applied to the surface of the disks was comparable to a typical application rate if the rejuvenator was used commercially. After calculating the application rate for each rejuvenator, the amount of rejuvenator specified per surface area of each disk was applied to the six disks using an automatic pipette. A spatula

was used to spread the rejuvenator over the surface of the disks to ensure that the rejuvenator was evenly coating the surface of the disk.

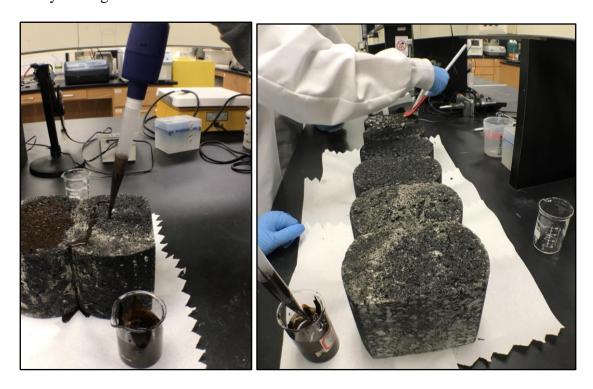


Figure 5: Applying Rejuvenator to Asphalt Disks.

Next, the rejuvenator was allowed to cure for 48 hours. Subsequent to the curing step, the six disks and aluminum foil were put into the MMLS. The machine was operated for 24 hours, with each tire completing a cycle approximately 81,000 times over the test period, about 3,375 cycles per hour. At the end of the 24 hours, the machine was stopped and a small hand vacuum (Dirt Devil Quick Flip Cordless Hand Vacuum) was used to collect all the particulate matter that accumulated on the machine and on top of the disks. The aluminum foil was removed and the material there was also vacuumed up. After the experiment, the MMLS was cleaned to remove any excess debris that was not picked up by the vacuum and aluminum foil was replaced for each set of new disks.

5.3 Visual Analysis of Asphalt Disk Surfaces after MMLS Test

To qualitatively assess the performance of each rejuvenator on the surface of the asphalt disks after use, a visual comparison was done before and after the rejuvenator treated disks were run through the MMLS testing procedure. Photos of the disks were taken after the rejuvenator was applied to the disks and then again after the disks had gone through 24 hours in the MMLS machine. The visual comparison included looking at the amount of large debris that came off the disks, the total amount of debris that detached from the disks and the surface appearance of the disks.

5.4 Particulate Material Sample Preparation

Once all the particulate material generated in the test was collected, it was removed from the vacuum and weighed on an analytical balance. Next, the particulate material was combined with methylene chloride (Fisher Scientific, 99.999% pure) in a clean 200 mL volumetric glass flask. The detached material was weighed using an analytical balance and added to the volumetric flask, then methylene chloride was added until the flask was filled to the measuring line. The flask was then capped, inverted multiple times to begin mixing, and put into a sonication bath for 10 minutes to fully mix the solution. The solution was then transferred into a clean 250 mL beaker. Using 0.45 micrometer RC-membrane filters and 5 mL syringes with luer-lok tips from Becton Dickinson, the solution was transferred into 1.5 mL vials for gas chromatography (GC) analysis. All waste was disposed of in hazardous waste containers. The glassware used and all parts of the vacuum were thoroughly cleaned using soap and water before the next experimental run. Purified water for rinsing was produced by a Thermo Scientific 7150

water purifying system. Before starting each run the glassware was rinsed with methylene chloride.

5.5 Pure Rejuvenator Sample Preparation

In addition to testing particulate matter sample solutions in the gas chromatography (GC) machine, samples of bio-based, coal tar-based and asphalt-based rejuvenator were also prepared to analyze the GC response of these rejuvenators themselves. For each run, a clean 100 mL volumetric flask was rinsed with methylene chloride. 0.5 microliters of each rejuvenator was measured and pipetted into the flask with an automatic pipette. The flask was then filled to the 100 mL line with methylene chloride and inverted multiple times to mix the rejuvenator with the methylene chloride. The solution was transferred into a clean 200 mL beaker to make transferring the solution into GC vials easier. A 5 mL syringe was used to fill 1.5 mL GC vials with the solution. The vials were capped and stored until they could be tested in the GC.

5.6 Gas Chromatography Analysis

Before running the experimental samples in the GC, PAH standards were prepared. Using a 1 mL vial of sixteen concentrated PAHs, (exact concentrations can be found in Appendix D), a serial dilution from PAH standard solution (Ultra Scientific) was conducted using methylene chloride to produce five increasing concentrations.

Gas chromatography with an Agilent Technologies (6890 Series GC System) with flame ionization detector (FID) was utilized for chemical analysis to determine PAH concentrations in the extracted samples. The 1.5 mL sample vials, once prepared, were loaded into the sampler tray on the 7683 series Agilent Technologies autosampler unit. The GC oven was initially set to

35 °C for 4 minutes and temperature increased to 50 °C at a rate of 3 °C/minute. Then, the oven temperature was increased to 290 °C at a rate of 8 °C/minute and held at that temperature for 3 minutes. The detector (FID) temperature was 300 °C. 2.0 µL of sample was injected. Helium was the carrier gas. A photo of the GC can be seen in Figure 6.

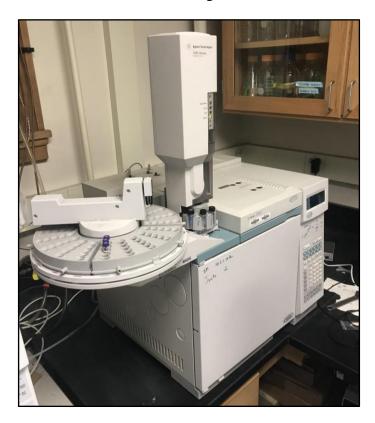


Figure 6: Gas Chromatography Instrument.

To find the concentrations of PAHs in the experimental samples, the GC response (peak area) for each sample (experimental data) was compared with the standard curves. Figure 7 shows the response curve for the sixteen PAH standards.

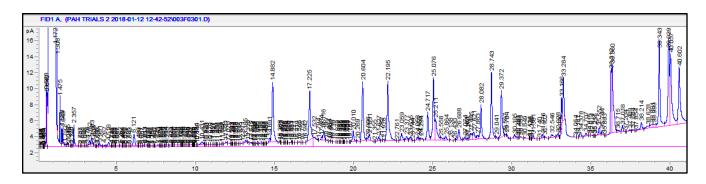


Figure 7: Example PAH Standards Chromatogram.

A calibration curve was obtained with each concentration of the PAH standards represented, and all the experimental samples were calibrated to account for any variation in the GC. Once all the samples were calibrated, the amount of PAHs in each sample were compared to the relative weight of material that detached from the disks for each individual run. Using this information, ratios of PAHs present in the detached material for each type of rejuvenator were compared and analyzed.

Chapter 6: Results and Discussion

6.1 Visual Assessment

When assessing the functionality and environmental impact of each rejuvenator, the first assessment was a visual one. After each run of the asphalt disks in the MMLS machine, a photo was taken of the disks in the machine and the foil that was placed there to collect any particulate. The photos were visually assessed to ascertain the amount of particulate that came off the disks. We performed two runs for the control on the MMLS machine. The first run had a significant amount of particulate come off of the asphalt disks. The second run had about half or less the amount of particulate visually as the first run and weighed 0.2259 g (Figure 8). The run for the control was conducted twice in the MMLS because accurate measurements of the weight of the particulate were not taken before the chemical analysis was conducted.



Figure 8: Second Control Run. Left is a Photograph of the Pavement Samples Before MMLS.

Middle Image is Particulate Detached During the Testing. Right is a Photograph of the

Pavement Samples after MMLS.

After the control tests, disks that had been coated with the asphalt-based rejuvenator were tested. This run produced less particulate than the first control run. The recorded weight of the

particulate from this test was 0.8315 g. The amount of particulate that came off of the disks during this run was much higher than the control. It did prevent some larger pieces on the surface of the asphalt disks from breaking off that would have come off of the disks without any rejuvenator but compared to the runs with the other two rejuvenators it was much less effective in keeping the disks from releasing dust and preventing larger pieces of the asphalt from breaking off of the disks.



Figure 9: Asphalt-Based Rejuvenator Run. Left is a Photograph of the Pavement Samples

Before MMLS. Right is a Photograph of the Pavement Samples after MMLS.

The disks coated with bio-based rejuvenator were run in the MMLS machine next. The disks coated with this rejuvenator had visually about the same amount of particulate as the second control run. This rejuvenator helped the surface of the disks remain intact better, unlike the asphalt-based rejuvenator. The weight of the particulate that was detached from the disks treated with the bio-based rejuvenator was 0.5559 g (Figure 10). This is slightly more than half the weight of the particulate that came off during the asphalt-based rejuvenator run. All in all, the bio-based rejuvenator worked well to keep the disk surfaces in good condition after being

subjected to large amounts of force and lessened the amount of particulate released from the disks compared with those not coated with rejuvenator or disks treated with the asphalt-based rejuvenator.



Figure 10: Bio-Based Rejuvenator Run. Left is a Photograph of the Pavement Samples Before MMLS. Middle Image is Particulate Detached During the Testing. Right is a Photograph of the Pavement Samples after MMLS.

The last run was conducted with disks coated with coal-tar-based rejuvenator. The visual amount of the particulate that detached from the disks was comparable to the amount that was obtained from the second control run or the bio-based rejuvenator run. The detached particulate weight from the disks coated with coal-tar-based rejuvenator was 0.2458 g (Figure 11). This particulate weight is about half that of the bio-based rejuvenator run, and significantly less than the first control run's particulate amount. This indicates that the coal-tar-based rejuvenator held the asphalt disk surface material together better than either of the other two rejuvenators.



Figure 11: Coal-Tar-Based Rejuvenator Run. Left is a Photograph of the Pavement Samples

Before MMLS. Middle Image is Particulate Detached During the Testing. Right is a

Photograph of the Pavement Samples after MMLS.

Based on visually assessing the rejuvenator performance (see photos in Figures 8, 9, 10 and 11) and mass of particulate material released (Table 1), the coal-tar-based rejuvenator was the most effective at reducing the amount of particulate that was released from the asphalt disks during the testing. The bio-based rejuvenator allowed somewhat more material to be released from the surfaces, and the asphalt-based rejuvenator produced the greatest amount of detached material.

Table 1: Mass of the particulate matter from MMLS runs.

Run	Particulate Mass
Control 1	Unknown
Control 2	0.2259 g
Asphalt Binder	0.8315 g
Bio-based	0.5559 g
Coal-tar-based	0.2458 g

6.2 Analysis of Polycyclic Aromatic Hydrocarbons (PAHs) Present in Detached Material

To analyze and quantify the amount of PAHs in each sample, the contaminants associated with the particulate material that was released from the asphalt disks during the MMLS test was transferred into solutions using methylene chloride as a solvent according to the procedure outlined in the methodology chapter. The following figures show the concentration of PAHs present in each sample of particulate matter collected from each experimental run with units of mg PAH/kg particulate matter. There are also graphs that represent the total number of PAHs in each type of rejuvenator, a graph showing the mass of PAHs per unit area with units of mg PAH/m², and graphs highlighting the carcinogenic PAHs separately.

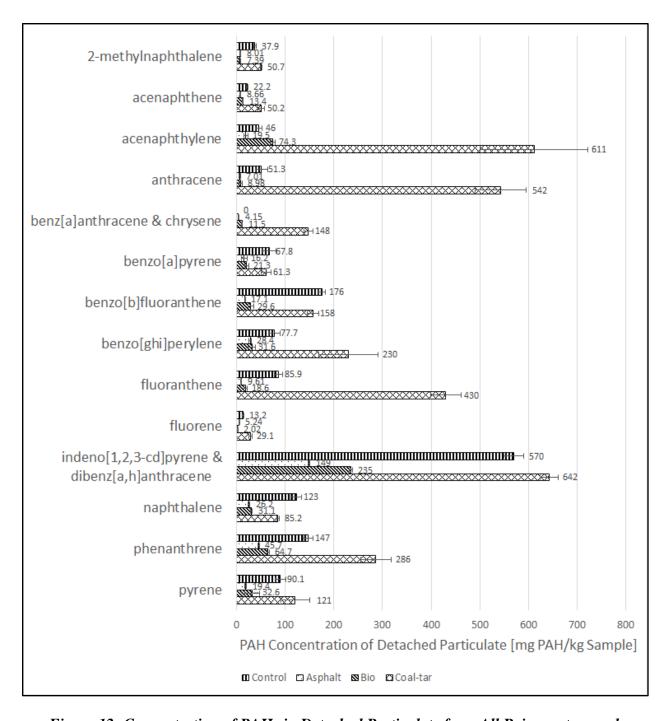


Figure 12: Concentration of PAHs in Detached Particulate from All Rejuvenators and Control.

A greater total concentration of PAHs was mobilized from the control than the asphaltbased or bio-based rejuvenators. The results from the control indicated the asphalt disks themselves had significant PAH levels which were present in detached material, and that the rejuvenators performance evaluation, in terms of PAHs mobilized, would have to be discussed with how the rejuvenators compared to the PAH concentrations for the control run.

The bio-based rejuvenator performed well in terms of sum of the concentration of PAHs mobilized from the MMLS, as the sum of the concentration of PAHs was 928 mg/kg of sample lower than the control. When looking at the data in Figure 12, all the PAH levels were lower in the bio-based rejuvenator compared to the control except for acenaphthylene and the combined concentrations of benz[a]anthracene and chrysene. The sum of the concentration of benz[a]anthracene and chrysene in the bio-based rejuvenator are similar to the levels found in the asphalt-based rejuvenator. The concentration of acenaphthylene is considerably higher (54.8 mg per kg of sample) in the bio-based rejuvenator compared to the asphalt-based rejuvenator but is only 28.3 mg per kg of sample higher than the control.

The asphalt-based rejuvenator had the lowest sum of the concentration of PAHs mobilized from the MMLS as the sum of the concentration of PAHs was 1,146 mg per kg of sample lower than the control. Looking at Figure 12, all the PAH levels were lower in the asphalt-based rejuvenator compared to the control except for the combined concentrations of benz[a]anthracene and chrysene. Since benz[a]anthracene and chrysene peaks overlapped in the chromatogram as a co-eluting peak in our method, the concentrations of benz[a]anthracene and chrysene cannot be individually determined. However, the combined total concentration for benz[a]anthracene and chrysene in the asphalt-based rejuvenator of 4.15 mg/kg of sample, which while a higher concentration, is not statistically greater than the control where no PAHs were detected in the samples. Additionally, the total sum of the concentration of PAHs mobilized from

the testing with the asphalt rejuvenator applied was 928 mg per kg of sample less than the control.

The coal-tar-based rejuvenator had the highest sum of the concentration of PAHs mobilized from the MMLS machine as the sum of the concentration of PAHs was 1930 mg per kg of sample higher than the control. This is alarming because not only is a high concentration of the coal-tar-based rejuvenator mobilizing from the disk, but because this is the only rejuvenator that fails to reduce the sum of the concentration mobilized from the disk during the tests. When comparing the coal-tar-based rejuvenator to the control, illustrated in Figure 12, there were three PAHs that the concentrations were lower than the control, benzo[a]pyrene, benzo[b]fluoranthene, and naphthalene. However, the concentrations of the PAHs were only slightly lower compared to the control, with naphthalene being the lowest compared to the control by 37.8 mg per kg of sample.

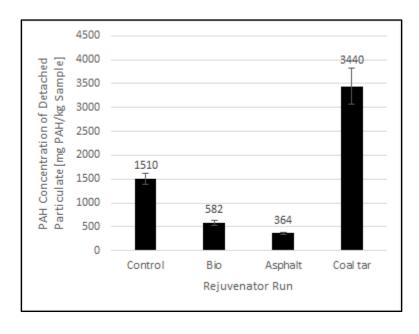


Figure 13: Total Amount of PAHs Present in Trials with Each Rejuvenator.

The graph above shows the total amount of PAHs found in each type of rejuvenator. All sixteen PAHs were added together to calculate the total concentration of PAHs. As seen in Figure 13, the trial with the coal-tar-based rejuvenator had the highest total amount of PAHs in the particulate matter that was released from the asphalt disks. The amount of PAHs in the coal-tar-based rejuvenator material was almost ten times greater than the amount of PAHs found in the asphalt-based rejuvenator material.

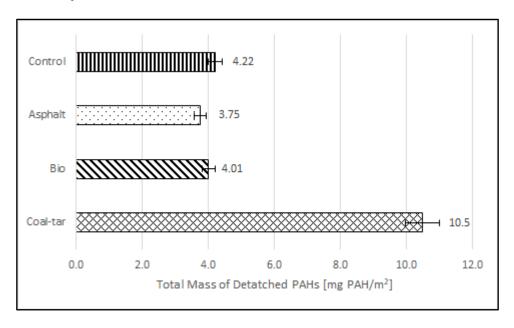


Figure 14: Mass of Detached PAHs per Area of Rejuvenator Application.

Figure 14 shows the mass of PAHs detached per area. The calculations to find this information adjusted the data to normalize the amount of particulate material that detached from the asphalt disks, because each trial had a different amount of particulate material released. The values in this graph represent the mass of PAHs, in mg, that was released per m². These values were calculated to definitively quantify which rejuvenator released the greatest PAH mass, as it takes both the concentration of PAHs and the mass of detached material into consideration. As seen in Figure 14, the control, asphalt-based rejuvenator and the bio-based rejuvenator all have

similar amounts of PAHs that would be released per surface area. The coal-tar-based rejuvenator resulted in over 10 mg of PAHs that were released per surface area, more than double the amount of PAHs released from any other rejuvenator.

PAHs that are known carcinogens were separately reported in Figure 15. When comparing the asphalt-based, bio-based, and coal-tar-based rejuvenators to each other and the control, there are trends that appear when looking solely at the PAHs that are known carcinogens. These trends can be visualized in Figure 15.

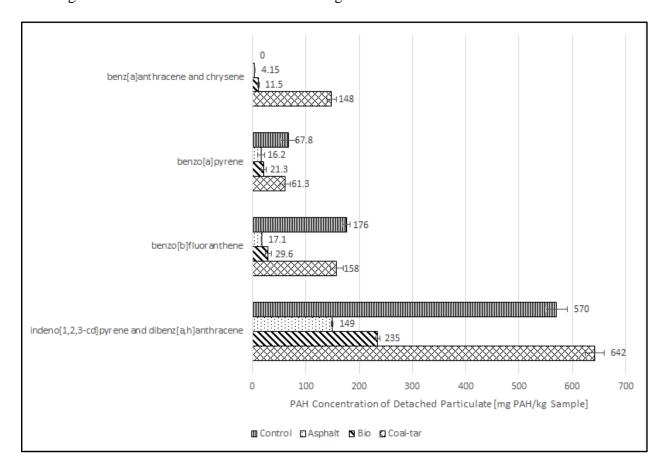


Figure 15: Concentration of Carcinogenic PAHs in Detached Particulate for All Tests.

The coal-tar-based rejuvenator consistently resulted in elevated concentrations of the carcinogenic PAHs released from the pavement samples. The concentrations of the carcinogenic

PAHs in the material detached from the coal tar-treated samples are 2.5 to over 10 times greater than both the bio-based and asphalt-based rejuvenators. The control run tends to have similar concentrations as the samples treated with coal-tar-based rejuvenators except for indeno[1,2,3cd]pyrene & dibenz[a,h]anthracene; the coal-tar-based rejuvenator is slightly elevated in these compounds when compared to the control. The sum of the carcinogenic PAH concentrations in the coal-tar-based rejuvenator was 1010 mg per kg of sample, the sum of the carcinogenic PAH concentrations in the control was 814 mg per kg of sample, the bio-based rejuvenators sum was 297 mg per kg of sample, and the asphalt-based rejuvenators sum was 186 mg per kg of sample. Both the asphalt-based and bio-based rejuvenators were able to reduce the sum of the carcinogenic PAHs mobilized from the tests by 627 mg per kg of sample and 516 mg per kg of sample respectably. The asphalt and bio-based rejuvenators were able to reduce the sum of carcinogenic PAHs in the detached material from the control because the rejuvenators reduced the amount of the material mobilized from the disk and because their chemical makeups contain lower levels of carcinogenic PAHs compared to the coal-tar-based rejuvenators. Lastly, an interesting trend from Figure 15 shows that every rejuvenator and the control run had indeno[1,2,3-cd]pyrene and dibenz[a,h]anthracene as the PAH with the highest concentration in the detached material for each test.

6.3 Analysis of Pure Rejuvenator Samples

In addition to testing particulate material from asphalt disks treated with rejuvenators, GC analyses of pure rejuvenator samples were also done. The rejuvenators were diluted with methylene chloride and analysis of the samples was conducted in the same manner as the

particulate samples. Figure 16 shows the results for the concentrations of PAHs in the asphalt-based, bio-based and coal-tar-based rejuvenators.

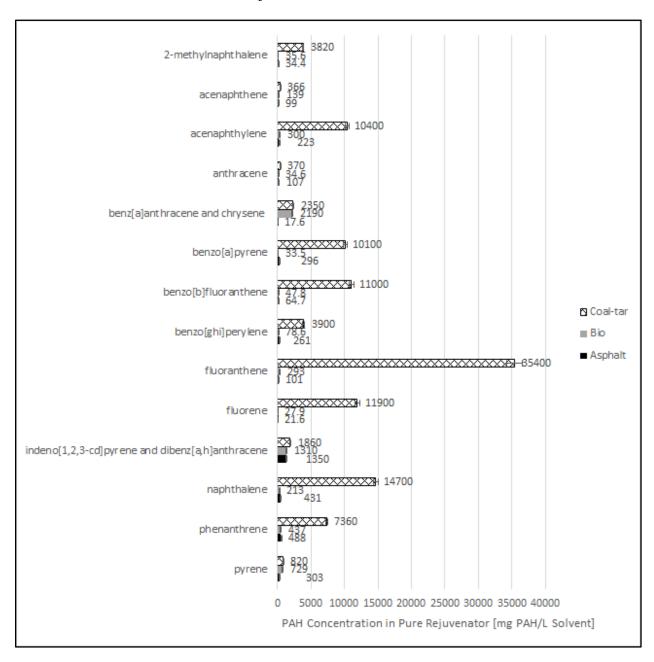


Figure 16: PAH Concentrations in All Rejuvenators.

The results show that the coal-tar-based rejuvenator had significantly greater amounts of PAHs than the bio-based rejuvenator or the asphalt-based rejuvenator. The asphalt-based

rejuvenator had the smallest concentration of PAHs overall as seen in Figure 16. The bio-based rejuvenator has a slightly greater concentration of PAHs than the asphalt-based rejuvenator, but the coal-tar-based rejuvenator had PAH concentrations that were much higher than those of the other two rejuvenators. The data from the coal-tar-based rejuvenator indicates that if particulate matter containing this rejuvenator was mobilized into the environment, it could have serious effects on public health and aquatic life. One of the PAHs that is known to be carcinogenic is benzo[b]fluoranthene. Based on the data shown in Figure 16, the bio-based rejuvenator has only 47.8 mg PAH/ L solvent, the asphalt-based rejuvenator has 64.7 mg PAH/ L solvent, and the coal-tar-based rejuvenator has 11,000 mg PAH/L solvent. The concentration of benzo[b]fluoranthene alone in the coal tar rejuvenator is three orders of magnitude higher than in both the bio-based and asphalt-based rejuvenator.

6.4 Comparisons with Other Data

Our final assessment regarding the data was comparing them to past experiments. In April 2017, a senior project similar to ours was completed by students in the Civil & Environmental Engineering Department at WPI (MacDonald & Meyer, 2017). Like this project, they sought to test coal-tar-based pavement rejuvenators for PAHs. The main difference was that they collected their samples from road scrapings and material detached from roadways as opposed to in the laboratory setting using the MMLS machine. The 2017 project only collected samples from pavement treated with coal-tar-based pavement rejuvenators.

In comparing the field data from 2017 from pavement surfaces treated with coal-tar-based rejuvenators to our laboratory data from 2018 from the detached material from the MMLS run with the coal-tar-based rejuvenator, the main inference that can be drawn is that PAH

concentrations were for the most part greater in the 2017 field data. In terms of the carcinogenic PAHs, all were higher in the field sample except for the co-eluting indeno[1,2,3-cd]pyrene & dibenz[a,h]anthracene.

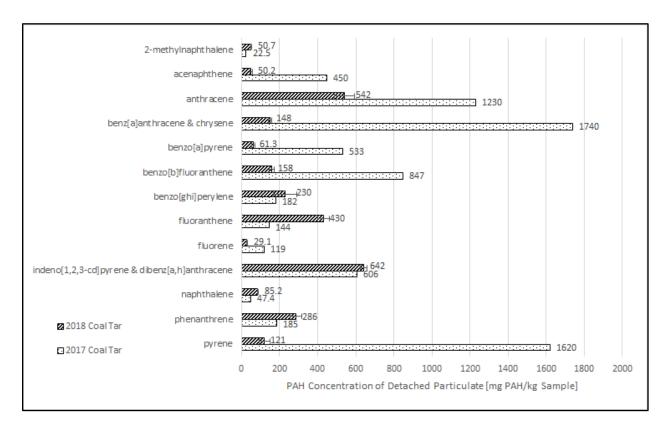


Figure 17: Comparison of 2017 Coal-Tar-Based Rejuvenator Average PAH Concentrations and 2018 Coal-Tar-Based Rejuvenator Average PAH Concentrations.

Reasons for the significant differences in PAH concentrations could have to do with the composition of the rejuvenator itself. Second, it could have something to do with the composition and age of the roadway.

In addition to the particulate recovered from the MMLS runs, we also analyzed a road scraping that was sent to us from a road that has been treated with coal-tar-based rejuvenators in

North Carolina. This road sample was analyzed using GC analysis and compared to the field data from 2017, since both samples were road scrapings instead of the detached material from MMLS runs. The comparison can be seen below in Figure 18.

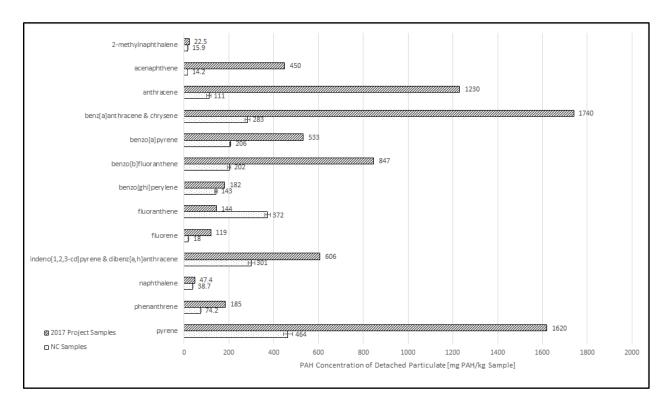


Figure 18: Comparison of 2017 Coal-Tar-Based Rejuvenator Average PAH Concentrations and 2018 North Carolina Coal-Tar-Based Rejuvenator Average PAH Concentrations.

The sample contained lower concentrations of PAHs than the road scrapings from last year's project. However, both road scrapings did contain higher concentrations than the laboratory tests, further inferring that external factors such as roadway composition play a role in PAH concentration.

6.5 Limitations in Testing

In the tests conducted, the conditions were carefully controlled. The MMLS machine ran for 24 hours for each test, with only dry tires in a constant loop. This test is not representative of every road or pavement surface in the United States. Different regions have different weather patterns every season, all of which affect the wear and tear on road surfaces. Since the tests conducted were in such a constant and controlled environment, any variation in performance due to weather or changes in conditions could not be observed. In future testing, a longer duration of testing would be recommended, on multiple different pavement surfaces that are exposed to different weather conditions.

Chapter 7: Conclusions and Recommendations

7.1 Overall Conclusions

The potential for mobilization of PAHs in each type of rejuvenator was determined by testing rejuvenator treated pavement samples in the MMLS testing machine and collecting the detached particulate matter for gas chromatography analysis. A visual assessment of the asphalt sample surfaces after the MMLS testing was also conducted to observe how effective each type of rejuvenator was at accomplishing the goals of a rejuvenator: reviving the pavement surface and minimizing surface damage and cracking. The results showed that the bio-based rejuvenator performed the best in terms of the combination of least PAHs present in the particulate gathered from the pavement surface and the appearance of the asphalt surfaces after the MMLS test. The bio-based rejuvenator had a minimal amount of particulate detached from the pavement samples, and after the test, the surfaces did not appear as worn down as the control tests.

The particulate detached from the asphalt-based rejuvenator was low in PAH concentration, but more particulate was detached than in any other test. This shows that this particular asphalt product did not perform as well as a rejuvenator when compared to the biobased and coal-tar-based products. The asphalt-based rejuvenator that was used in testing was a product that had the characteristics of a rejuvenator, but that was not the product's sole purpose. An asphalt-based rejuvenator intended only for being a rejuvenator could not be obtained for testing, so the asphalt product that we used was the best option for the tests that we conducted. In future testing, we recommend obtaining a product that is solely used as a rejuvenator.

The coal-tar-based product performed well in the visual assessment and served its intended purpose as a rejuvenator in our qualitative evaluation, but the amount of PAHs

mobilized during MMLS testing was higher than for the other tests. In the visual assessment, the disks treated with the coal-tar-based rejuvenator looked the best after testing and produced the least amount of detached particulate matter after the MMLS test. The coal-tar-based rejuvenator test exhibited the greatest amount of PAHs mobilized of any of the tests conducted. For this reason, we do not recommend the use of coal-tar-based pavement rejuvenators. The particulate matter that could be produced from pavement treated with coal tar rejuvenators and mobilized into the environment would contain these PAHs. Therefore, the potential exists for releasing PAHs into the environment in areas close to where these rejuvenators are applied. A suggested alternative to the coal-tar-based products would be using the bio-based or asphalt-based products, because both of these options had fewer PAHs in their particulate matter than the coal-tar-based, or even the control sample.

7.2 Recommendations

As mentioned in the previous section, we do not recommend the use of coal-tar-based products on pavement surfaces because the PAHs found in the rejuvenator can be mobilized into the environment. Instead of using coal-tar-based products, we recommend the use of bio-based or asphalt-based products, because they reduced the amount of PAHs that were mobilized in our MMLS testing. They also perform similarly to the coal-tar-based products in terms of the purpose of a pavement rejuvenator, that is to restore components in the pavement that preserve flexibility. No significant difference in the visual analysis of the bio-based rejuvenator versus the coal-tar-based rejuvenator was observed, so similar results should be expected while using a product that is more environmentally friendly. We would especially not recommend using coal-tar-based products in the northern United States, or other areas that receive lots of precipitation

because we believe that the weather would mobilize the PAHs at a higher rate due to rainfall, snowfall, abrasion from snow plows moving the snow and scraping against the road and sand or ice-melt. We hypothesize that these factors would cause faster and greater mobilization of the particulate containing PAHs, but we would recommend further testing to evaluate this hypothesis.

As a way of managing PAH exposure, we have considered a method of containment of PAHs if coal-tar-based rejuvenators have been applied to a road. To prevent the PAHs from moving into the environment via the particulate matter that would be released from road use, we propose a two-layer solution. First, a robust paint can be applied to the road surface that has already been treated with the rejuvenator. After this paint has been applied to the treated pavement surface, the road can be resealed with a new layer of asphalt. Once the pavement surface is worn down enough to expose the paint underneath the top asphalt layer, parties responsible for roadway maintenance would know when to replace or reseal the top asphalt layer. This should prevent the coal tar treated pavement located underneath the paint from becoming exposed and releasing PAHs into the environment. Other treatment methods we would recommend include using catch basins to capture the particulate matter that would go into runoff from rainwater or placing bioretention basins near water sources to filter out PAHs.

7.3 Design of Pavement Rejuvenator Scheme: Two Rejuvenation Coating Layers

To treat pavement surfaces that have been treated with coal-tar-based rejuvenators, a design was developed for a containment method involving road paint and covering the affected surface with a sealant on top of the paint. This method would entail applying colored road paint

to the entirety of the affected surface. After the paint is applied to the pavement surface, the road could be repaved over the paint layer. As the repaved asphalt surface wears down as the road is used, the paint will be exposed. The application would both prevent particulate material containing the coal-tar-based rejuvenator from mobilizing into the environment, and the paint would act as an indicator to show when the asphalt layer would need to be reapplied to further prevent the mobilization of PAHs. Figure 19 shows a simple sketch of the proposed design.

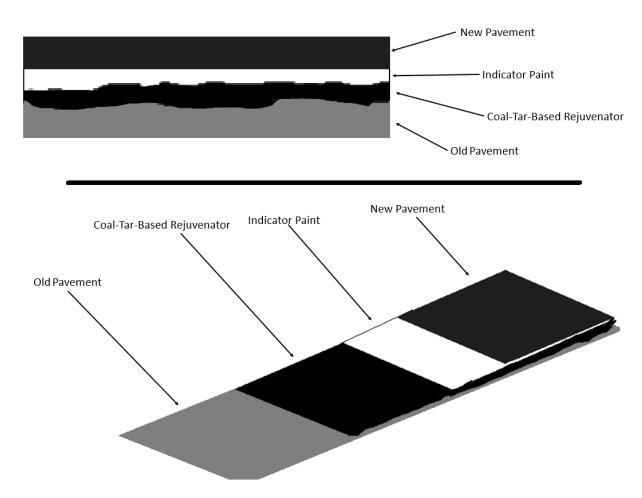


Figure 19: Sketch of Proposed Containment Design, Cross-Section View (Top) and Side-Angle View (Bottom).

Two types of road paint were researched for this method: standard road paint and thermoplastic paint. Standard road paint is the cheaper option; however, it is only estimated to last on frequently used roads for one year. (Federal Highway Administration (FHA), 2005) This estimate takes into consideration the weather elements and how that affects the lifespan of the road paint, but in this design, the paint will be covered by another asphalt surface. Thermoplastic road paints are more expensive than standard road paint, however, thermoplastic paint has an average lifespan of three years compared to standard road paint's one year. (FHA, 2005) Even though these lifespan estimates are based off of the paints being exposed to weather conditions, we believe that this is still a valid parameter for evaluation for these two paints. After calculating the application costs of both types of paint, it was determined that standard road paint, although it has a shorter lifespan, would be the better choice for this situation as it costs less and does not need to hold up in weather conditions. The cost was calculated based on the surface area of road being painted and the amount of times the paint would have to be redone within a span of 10 years. Calculations for the application costs can be found in Appendix C.

The application of the paint would be done systematically based on the specific site location. In towns where coal-tar-based rejuvenators were used, high traffic areas would need to be assessed to determine where monitoring points could be. The monitoring points would be areas where this containment method is used, meaning that small portions of the pavement surface that are frequently used could represent the entire pavement surface, so paint does not have to be applied to every area that was treated with a coal-tar-based rejuvenator. These monitoring points should be areas in the pavement that would be worn down before the rest of pavement surface. Therefore, when the paint is exposed at one of the monitoring points, that

would serve as an indicator that repaving is necessary because the top layer of pavement has been worn down.

We recommend that monitoring points for highways should be about a quarter of a mile near on ramps and off ramps to the highway, and on long stretches of highway with no exits. This would provide a large amount of sample values at high priority locations. In neighborhoods and smaller communities, we recommend placing more monitoring points than those on the highway, but the monitoring points would not need to be as wide as monitoring points on the highway. Varying the monitoring points depending on the traffic in the neighborhood would ensure an accurate representation of wear on the roads in the area. Since road use in different communities can vary greatly, the local government would need to decide the best location for their specific spacing.

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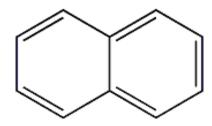
Appendices

Appendix A: PAH information

The following contains information about the sixteen different PAHs the gas chromatography analysis looked for:

Naphthalene

MW: 128.171 g/mol Formula: $C_{10}H_8$

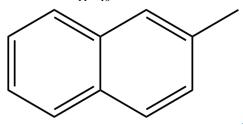


http://www.pherobase.com/database/floral-compounds/floral-

taxa-compounds-detail-naphthalene.php

 $2\hbox{-methyl naphthale ne}\\$

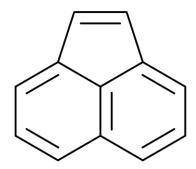
MW: 142.201 g/mol Formula: $C_{11}H_{10}$



methylnaphthalene

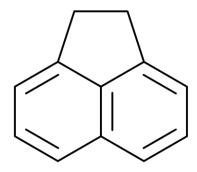
https://wtt-pro.nist.gov/wtt-pro/index.html?cmp=2-

Acenaphthylene MW: 152.20 g/mol Formula: C₁₂H₈



https://www.sigmaaldrich.com/catalog/product/aldrich/416703?lang=en®ion=US

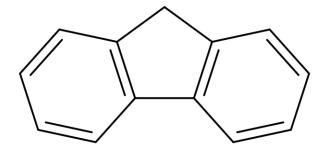
Acenaphthene MW:154.20 g/mol Formula: $C_{12}H_{10}$



https://www.sigmaaldrich.com/catalog/product/aldrich/215376?lang=en®ion=US

Fluorene

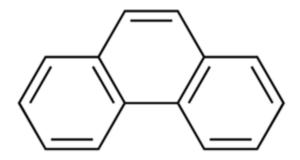
MW: 166.223 g/mol Formula: C₁₃H₁₀



https://www.sigmaaldrich.com/catalog/product/aldrich/128333?lang=en®ion=US

Phenanthrene

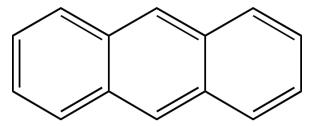
MW: 178.23 g/mol Formula: $C_{14}H_{10}$



https://www.sigmaaldrich.com/catalog/product/aldrich/p11409?lang=en®ion=US

Anthracene

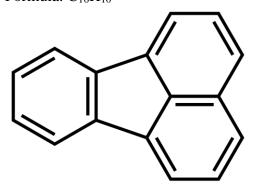
MW: 178.23 g/molFormula: $C_{14}H_{10}$



http://www.chem.ucla.edu/~harding/IGOC/A/anthracene.html

Fluoranthene

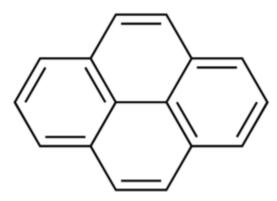
MW: 202.26 g/mol Formula: $C_{16}H_{10}$



https://www.sigmaaldrich.com/catalog/product/aldrich/423947?lang=en®ion=US

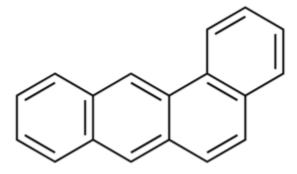
Pyrene

MW: 202.26 g/mol Formula: $C_{16}H_{10}$



https://www.sigmaaldrich.com/catalog/product/aldrich/185515?lang=en®ion=US

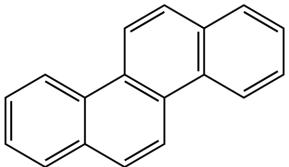
Benz[a]anthracene MW: 228.29 g/mol Formula: C₁₈H₁₂



 $\underline{https://www.sigmaaldrich.com/catalog/product/aldrich/b2209?lang=en\®ion=US}$

Chrysene

MW: 228.29 g/molFormula: $C_{18}H_{12}$



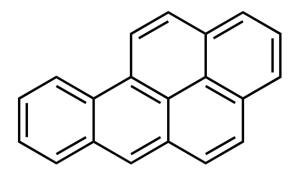
http://www.lookchem.com/Chrysene/

Benzo[b]fluoranthene MW: 252.31 g/mol

Formula: C₂₀H₁₂

https://www.sigmaaldrich.com/catalog/product/aldrich/275336?lang=en®ion=US

Benzo[a]pyrene MW: 252.31 g/mol Formula: C₂₀H₁₂



https://www.sigmaaldrich.com/catalog/product/sigma/b1760?lang=en®ion=US

Indeno[1,2,3-cd]pyrene

MW: 276.33 g/mol Formula: $C_{22}H_{12}$

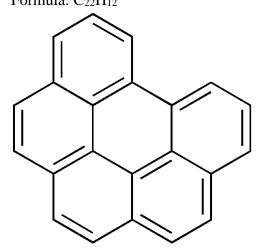
https://www.sigmaaldrich.com/catalog/product/supelco/48499?lang=en®ion=US

Dibenz[a,h]anthracene

MW: 278.35 g/mol Formula: $C_{22}H_{14}$

https://www.sigmaaldrich.com/catalog/product/aldrich/d31400?lang=en®ion=US

Benzo[ghi]perylene MW: 276.33 g/mol Formula: C₂₂H₁₂



 $\underline{https://www.sigmaaldrich.com/catalog/product/aldrich/b9009?lang=en\®ion=US}$

Appendix B: Raw Data

Data Tables for GC Analyses of Rejuvenators

		Area	Area	Area	Area	Area		g/200 mL
								Concentration
time	Coal Tar Scrapings NC	6	7	8	9	10	Peak Avg	Avg g/L
		2.174	2.2593	2.036		2.609		
14.914	naphthalene	3	3	76	1.9098	27	2.197892	0.00011278
		0.718	0.8949	0.809	0.8603	0.910		
17.251	2-methylnaphthalene	443	17	181	64	096	0.8386	4.63E-05
		0.275	0.2371	0.255	0.2964	0.393		
20.017	acenaphthylene	553	13	496	29	126	0.291543	9.92E-05
		0.675	0.6664	0.670	0.7290	0.737		
20.888	acenaphthene	272	26	023	34	969	0.695745	4.14E-05
		0.999	0.9170	0.985	1.1976	1.027		
22.257	fluorene	381	28	645	2	4	1.025415	5.25E-05
		1.834	2.1396	1.860	1.8568			
24.747	phenanthrene	69	9	17	4	2.232	1.984678	0.00021597
		5.526	8.3979	6.392	6.9419	7.830		
25.147	anthracene	85	8	01	3	18	7.01779	0.00032409
		16.23	20.376	19.42	19.471	20.75		
28.777	fluoranthene	03	7	78	2	18	19.25156	0.00108276
		14.19	18.107	17.20	17.541	18.04		
29.698	pyrene	36	3	25	6	86	17.01872	0.00134962
	benz{a]anthracene &	18.42	20.844	21.59	21.691	22.22		
33.45	chrysene	01	3	24	3	16	20.95394	0.00082506
		16.47			20.805	20.93		
36.401	benzo[b]fluoranthene	83	20.243	45	2	09	20.01238	0.00058758
		8.008	8.5652	8.582	8.0448	8.908		
39.315	benzo[a]pyrene	88	4	32	3	28	8.42191	0.00060041
	indeno [1,2,3-							
	cd]pyrene &	68.32	48.184			50.12		
39.966	dibenz[a,h]anthracene	88	3		51.263	35	54.6353	0.00087701
		5.007		4.557	4.8826	4.756		
40.604	benzo[ghi]perylene	77	6	94	4	17	5.020696	0.0004169

									avg con. Grams
							Peak	Concentrati	PAH/ grams
	Control	6	7	8	9	10	Avg	on Avg g/L	Dust
		2.95	3.756	2.43	2.181	2.18	2.70187		
14.914	naphthalene	886	4	001	6	251	6	0.00013864	1.23E-04
	2-			0.79					
	methylnaphthalen	0.55	0.753	730	0.776	0.98	0.77497		
17.251	e	9346	32	6	976	793	6	4.28E-05	3.79E-05
				0.19					
		0.15	0.163	898	0.201	0.04	0.15256		
20.017	acenaphthylene	1483	749	1	702	6919	7	5.19E-05	4.60E-05
				0.49					
		0.36	0.430	898	0.467	0.33	0.42001		
20.888	acenaphthene	82	546	4	732	4614	5	2.50E-05	2.22E-05
				0.31					
		0.14	0.207	563	0.348	0.43	0.29067		
22.257	fluorene	7262	041	4	285	5141	3	1.49E-05	1.32E-05
		1.39	1.505	1.86	1.765	1.09	1.52431		
24.747	phenanthrene	281	4	068	01	767	4	0.00016587	1.47E-04
				0.59					
		0.87	0.676	537	1.467	2.66	1.25585		
25.147	anthracene	6341	542	9	35	366	4	5.80E-05	5.13E-05
		2.33	1.813	1.16	1.308	1.99	1.72495		
28.777	fluoranthene	993	71	973	25	316	6	9.70E-05	8.59E-05
		0.92	0.996	1.01	1.498	1.97	1.28320		
29.698	pyrene	8168	579	711	22	596	7	0.00010176	9.01E-05
	benz{a]anthracen								
33.45	e & chrysene	0	0	0	0	0	0	0	0
	benzo[b]fluoranthe	5.58	6.570	7.00	6.973	7.67	6.75955		
36.401		124	93	018	45	196	2	0.00019847	1.76E-04
				0.87					
		0.76	0.467	221	1.124	2.14	1.07393		
39.315	benzo[a]pyrene	2814	633	8	22	277	1	7.66E-05	6.78E-05
	indeno [1,2,3-								
	cd]pyrene &								
	dibenz[a,h]anthra	46.3	37.32	40.7	39.85	36.3	40.1244		
39.966	cene	665	72	316	63	407	6	0.00064408	0.000570238
	benzo[ghi]perylen	1.21	1.238	1.29	1.318	0.21	1.05732		
40.604		268	08	819	89	8771	2	8.78E-05	7.77E-05

								Concentration
	Asphalt-based	6	7	8	9	10	Peak Avg	Avg g/L
		2.671	2.1291	2.004	2.0928	1.714		
14.914	naphthalene	65	4	44	2	09	2.122428	0.00010891
		0.726	0.2893	0.663	0.2914	1.044		
17.251	2-methylnaphthalene	223	69	79	54	71	0.603109	3.33E-05
		0.080	0.2428	0.372	0.1132	0.383		
20.017	acenaphthylene	901	82	776	03	478	0.238648	8.12E-05
		0.328	0.6611	0.807	0.6468	0.578		
20.888	acenaphthene	951	12	958	99	12	0.604608	3.60E-05
		0.430	0.4376	0.479	0.3491	0.431		
22.257	fluorene	734	23	937	99	184	0.425735	2.18E-05
		1.950	1.3773	1.908	1.8255	1.671		
24.747	phenanthrene	81	1	31	4	15	1.746624	0.00019006
		1.290	0.4455	0.299	0.8908	0.230		
25.147	anthracene	25	29	767	6	968	0.631475	2.92E-05
		0.983		0.516	0.9284	0.455		
28.777	fluoranthene	777	84	326	51	373	0.710622	4.00E-05
		1.314	1.0983	0.738	1.2126	0.717		
29.698	pyrene	62	2	974	4	893	1.016489	8.06E-05
	benz{a]anthracene &	0.826	0.7145		0.2239	0.257		
33.45	chrysene	393	31	68	55	046	0.438521	1.73E-05
		2.235	2.2960		2.8165	2.466		
36.401	benzo[b]fluoranthene	67	9	07	2	1	2.41909	7.10E-05
		2.644			0.5645	0.240		
39.315	benzo[a]pyrene	28	39	489	45	903	0.941971	6.72E-05
	indeno [1,2,3-							
	cd]pyrene &	37.08				38.88		
39.966	dibenz[a,h]anthracene	76	4	78	40.64	28	38.58252	0.00061933
		1.846	1.1641			1.185		
40.604	benzo[ghi]perylene	32	2	48	1.2694	17	1.423498	0.0001182

								Concentration
	Coal-tar-based	6	7	8	9	10	Peak Avg	Avg g/L
		2.090		1.799	2.0536	2.038		
14.914	naphthalene	8	2.2176	81	8	35	2.040048	0.00010468
		1.060	1.1858	0.918	1.2631	1.216		
17.251	2-methylnaphthalene	08	1	438	9	96	1.128896	6.23E-05
		0.783	3.1424	1.625	1.9103	3.567		
20.017	acenaphthylene	848	8	43	7	41	2.205908	0.00075046
		0.793	1.0994	0.717	0.8716			
20.888	acenaphthene	115	8	021	71	1.702	1.036657	6.18E-05
		0.641	0.8925	0.325	0.8302	0.808		
22.257	fluorene	578	69	946	4	779	0.699822	3.58E-05
		1.837		2.635	3.3604	4.293		
24.747	phenanthrene	42	4.0277	24	9	7	3.23091	0.00035158
		8.691	17.595	11.87	16.641	17.33		
25.147	anthracene	61	3	63	1	59	14.42804	0.0006663
		7.086	10.572	7.554	10.568	11.16		
28.777	fluoranthene	8	8	73	6	06	9.388706	0.00052805
		0.898		1.305	1.5972	4.238		
29.698	pyrene	874	8	46	1	80	1.876361	0.0001488
	benz{a]anthracene &	3.574	5.5611	4.605	5.0839	4.230		
33.45	chrysene	81	7	68	3	07	4.611132	0.00018156
		4.489	7.3821	5.899	6.9791	8.215		
36.401	benzo[b]fluoranthene	14	7	43	2	95	6.593162	0.00019358
		0.582	1.1120		1.0414	1.842		
39.315	benzo[a]pyrene	834	4	054	9	21	1.055926	7.53E-05
	indeno [1,2,3-							
	cd]pyrene &	51.95			45.486	50.81		
39.966	dibenz[a,h]anthracene	73	2	43	8	06	49.12544	0.00078857
		1.330			2.9942	2.308		
40.604	benzo[ghi]perylene	25	9	4	4	33	3.410002	0.00028315

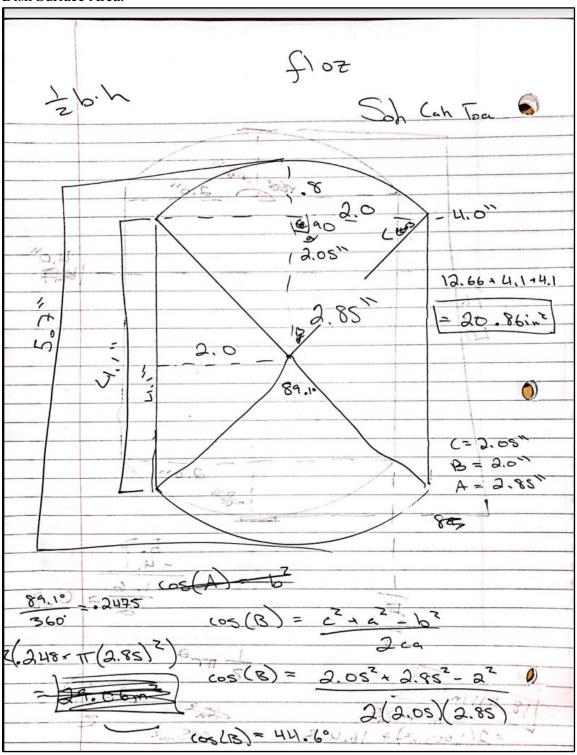
								Concentration
36.401	Bio-based	6	7	8	9	10	Peak Avg	Avg g/L
		1.888	1.6024	1.664	1.3908	1.887		
14.914	naphthalene	65	8	3	5	23	1.686702	8.66E-05
		0.758	0.2595	0.199	0.2594	0.382		
17.251	2-methylnaphthalene	271	22	441	01	898	0.371907	2.05E-05
		0.533	0.4667	0.568	0.7368	0.730		
20.017	acenaphthylene	879	94	921	31	405	0.607366	2.07E-04
		0.609	0.5349	0.512	0.7838	0.685		
20.888	acenaphthene	073	58	514	62	014	0.625084	3.72E-05
		0.201	0.0689	0.122	0.0776	0.078		
22.257	fluorene	934	56	97	17	09	0.109913	5.63E-06
		1.855	1.5325	1.404	1.7286	1.738		
24.747	phenanthrene	59	3	14	7	07	1.6518	0.00017974
		0.423	0.3293	1.520	0.2396	0.189		
25.147	anthracene	955	68	57	61	103	0.540531	2.50E-05
		0.751			0.6943	0.721		
28.777	fluoranthene	062	28	88	28	652	0.92143	5.18E-05
		0.328			0.6936	0.411		
29.698	pyrene	762	95	8	98	891	1.143889	9.07E-05
	benz{a]anthracene &	0.981	0.6511		0.8013	0.547		
33.45	chrysene	691	4	78	56	372	0.809868	3.19E-05
		3.753			4.1555	1.026		
36.401	benzo[b]fluoranthene	36		39	9	34	2.799556	8.22E-05
		0.620			0.0842	0.881		
39.315	benzo[a]pyrene	81	9	73	21	604	0.829411	5.91E-05
	indeno [1,2,3-					:		
20.055	cd]pyrene &	41.23	38.002			41.73	40 740-	0.000553.53
39.966	dibenz[a,h]anthracene	36	1	27	7	64	40.7105	0.00065349
40.604		4 207			0.7602	0.208	4 050430	0.705.05
40.604	benzo[ghi]perylene	1.207	69	53	66	53	1.059139	8.79E-05

Length of MMLS Runs/Axle Count on Machine from Run to Run

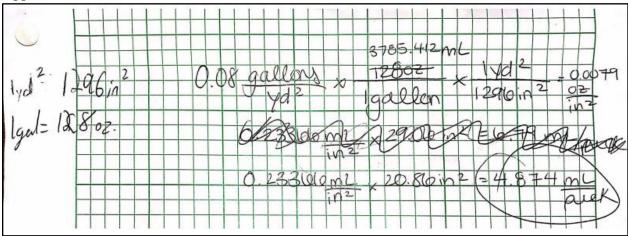
		x10 axles	x10 axles	x10 axles
				Cycle
Run's	Start date	Start cycle	End Cycle	difference
Constant 1	11/17/2017 1:26 PM	2624679	2632552	7873
Constant 2	11/29/2017 3:19 PM	2632552	2640657	8105
Asphalt-based	12/14/2017 12:49 AM	2640657	2648764	8107
Bio-based	2/3/2018 4:50 PM	2656900	2664997	8097
Coal-tar-based	1/28/2018 2:35 PM	2648765	2656900	8135

Appendix C: Experimental Calculations

Disk Surface Area:



Application Rate Calculations:

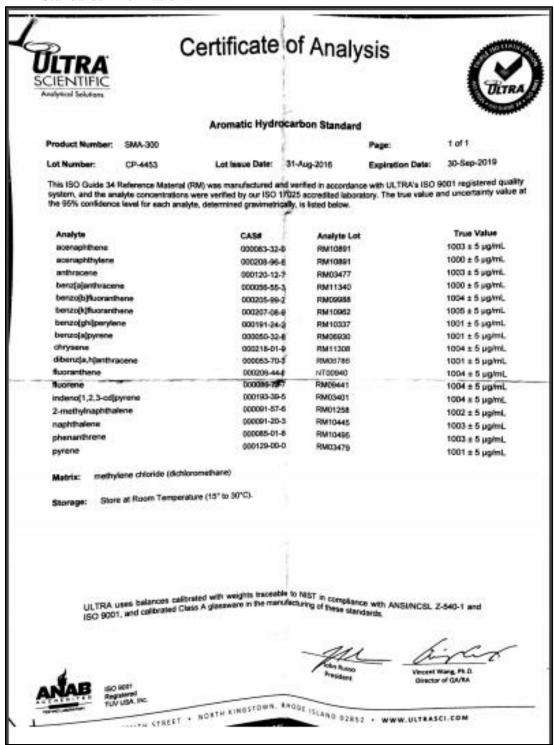


Design Calculations:

Name	Service Life (Years)	Material Cost (Per unit)	Labor Cost (per unit)	Total Cost over 10 Years (per unit)	AVG Cost per Year (per unit)
Fluorescent Thermoplastic	2	0.889	0.2	5.445	0.5445
Nonfluorescent Paint	0.5	0.0097	0.0635	1.464	0.1464

Appendix D: Supplemental Product Information

PAH Standards Information:



Appendix E: Additional Photos









