PROOF-OF-CONCEPT FOR AN EASY INSTALLATION SENSING SYSTEM INTO THE PAVEMENT TO TRACK ASPHALT AGING

FINAL PROJECT REPORT

by

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16. Abstract

Oxidation aging of asphalt has always been a crucial factor in both short term and long term performance of asphalt pavements. Aging is one of the most important factors that should be considered while predicting the life of the pavement since it is related to the adhesive peculiarity of binders with different aggregate particles. Therefore, a greater understanding of the nature of oxidative aging in the asphalt pavement can possibly establish a better estimation and observation of a pavement performance before and after it is constructed.

This study includes two experimental parts on the aging of asphalt and proofing the concept of adding organic dyes into road marking paints to calibrate the relationship between the aging of asphalt binder and the degradation of organic dyes. The first phase addresses the aging in asphalt with organic dyes and their original bases. The binders are subjected to short-term aging conditions and tested for viscosity. The change in viscosity was analyzed and it was found that the viscosity of all the samples would decrease while the temperature increase. However, due to the darkness of asphalt binder, the experimental study could not proceed to the next phase of detecting the intensity changes of the organic dye with the fluorescent spectrometer. With this predicament, the solution of changing the host for the organic dye has developed, which was switching the host from asphalt binder to water-based road marking paint. The second phase focuses on combining the organic dye with the road marking paint and measuring the degradation of dye due to oxidation aging. In this phase of the project, the fluorescent spectroscopy measurement technique is used to observe the change of fluorescent intensity throughout the short-term aging period (1-3 years). With the preliminary calibrated results of change in viscosity and fluorescent intensity of asphalt binder and engineered road marking paint respectively, it shows that the fluorescent intensity of the additives.

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Asphalt Aging, Remote Sensing, fluorescent spectroscopy

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Chapter 1 Introduction

1.1 Research Background

Nowadays, more than 90% of the paved roads in the United States are covered by asphalt. Asphalt has been a very popular choice for airport runways, parking lots, highways, driveways and other applications where a durable and smooth driving surface is required. Over the past 30 years, the adaptability of asphalt has led to its increased use in other applications. Hot mix asphalt (HMA) airport runways have increased acceptance in the United States since they provide more comfortable takeoffs and landings for passengers with an adequate increase on runway maintenance and much faster construction time. HMA has been increasingly used for different heavy static loads roads, which also causes the issue of accelerating the aging of asphalt and pavement maintenance cost. Since pavement maintenance can enhance pavement performance and retard future deterioration by addressing minor distress and improving functional conditions (O'Brien 1989), it is imperative to understand the chemical properties of asphalt and the background of the asphalt aging so as to enhance the pavement maintenance development.

In this experimental study, photoluminescence spectroscopy has been introduced to help determining the aging of asphalt in the field by installing photoluminescence probes into the asphalt pavement. In these past 20 years, photoluminescence spectroscopy has been continuously growing and developing. While its initial function is an analytical tool for determining the presence of specific molecules in the solutions, photoluminescence is now routinely used in biochemistry and biophysics for studying molecular interactions and dynamics, both in solution and in cells, also other applications on identifying and characterizing the material science of a new material (Chapman and Zwillich 1994). This technology would be applied throughout the investigation to evaluate the aging of asphalt and related materials.

1.2 Research Background and Plan

This research aims to proof the concept of installing a sensing system with a potential fluorescence dye into the pavement as a signal probes for photoluminescence spectroscopy to track the aging of asphalt during the aging process. The objectives of this proposed research are as follows:

1. To understand the chemistry background of asphalt and the evaluation of asphalt throughout the aging process (oxidation).
2. To determine the potential fluorescence dye(s) that could be added into the system for photoluminescence spectroscopy.
3. To find out the relationship between the laboratory aging results of asphalt and the results of photoluminescence spectroscopy.

The main task of this research is to find out the relationship between the aging of asphalt and the degradation of fluorescence dye throughout the aging process. The following is a detailed discussion of each part, including measurements of asphalt properties, fluorescence dyes identification, influencing factors and analysis method.

Part I: Understanding the chemistry of asphalt's aging process and finding the potential fluorescence dyes.

Part II: Testing and analyzing the asphalt before and after short term aging.

Part III: Testing the photoluminescence spectrum with the dye added into the host (asphalt binder and water-based paint).

Part IV: Analyze the results from aging and photoluminescence spectroscopy.

Chapter 2 Literature Review

2.1 Asphalt Oxidation

Throughout the past years, millions of dollars were spent to fix the roads all around the country and most of the roads were built with asphalt. It is very important to understand the aging procedure of asphalt and other main materials because this would be ideal to save time and money for future preservation. Oxidation aging can affect the performance of the asphalt pavement and is mainly caused by intrinsic and extrinsic variables. Intrinsic variable includes asphalt and aggregate properties, a mixture's asphalt content, binder film thickness and air void content; extrinsic variables are associated with production (short term aging) and exposure to environmental field conditions (long term aging) (Gómez, Quintana, and Lizcano 2013). Throughout the aging process, the phase angle decreases and the complex modulus increases. Besides, the asphalt binder will become stiffer while reducing the fatigue life.

The oxidation of asphalt is a major cause of pavement failure. At a given temperature and pressure, the asphalt oxidizes in two stages: (1) a rapid-rate period followed by (2) a long period with constant oxidation rate (Domke, Davison, and Glover 2000). Oxidation of the asphalt pavement has always been a complicated relationship between the interactions and reactions. The aging of pavement has always been a tremendous concern since it is difficult to keep track of various kinds of aging. Once the physical cracking starts, the repair process will be lengthy and expensive. Oxidation can be caused by exposure to ultraviolet light, weathering, heating, etc., and the reaction occurs between the asphalt's organic components, atmospheric oxygen and UV radiation. During the two stages of aging, the carbonyl and sulfoxide groups are formed. The hardening of asphalt at room temperature, which is known as the steric hardening also happened, this process also involves the molecular reorganization of asphalt and affecting the asphaltene amount. As mentioned, there are two stages of aging, the short-term and long-term aging. For short-term aging, it takes place during mixing in a plant, production, process of storage, transport and laying of an asphalt mixture. As for long-term aging, it occurs throughout the asphalt's service life and results from the oxidation due to UV radiation, humidity and rain. To stimulate both short- and long-term aging in the laboratory environment, Rolling Thin Film Oven Test (RTFOT) and the Pressure Aging Vessel (PAV) are commonly used in laboratory for short-term aging and long-term aging, respectively (Yildirim, Solaimanian, and Kennedy 2000).

Oxidation is characterized by oxygen uptake and causes an increase in the dynamic viscosity of asphalt. The formation of different functional groups in asphalt causes the decrease in aromatic functions, resin and increase in asphaltene fractions(Fernández-Gómez 2013). There are six functional groups in the asphalt binder which contains the carbonyl group, they are: amides, aldehydes, anhydrides, carboxylic acids, esters and ketones. The structure of the functional groups is shown in Figure 2.1.

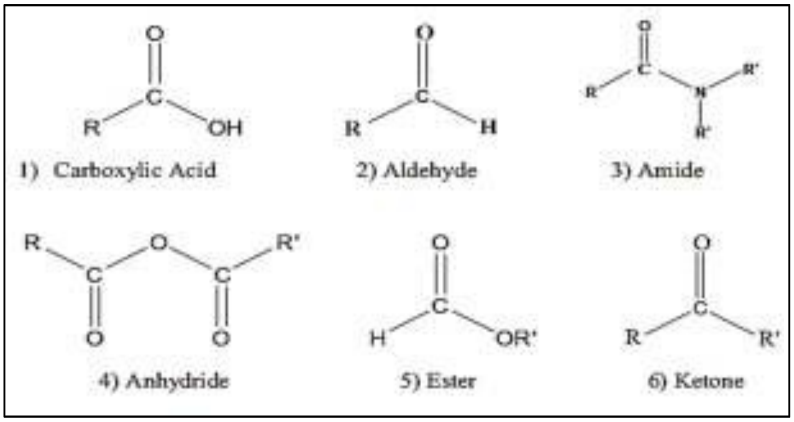


Figure 2.1-Functonal Groups in Asphalt Binder

Oxidation does not only affect the chemical properties of the asphalt binder but also its physical properties. Throughout the oxidation process, there is a conspicuous increase in the stiffness of asphalt, which causes the pavement to become brittle and hard, ultimately causing cracks with the consecutive loads applied on the road. With several of aging occurrences, the viscosity of asphalt binder would increase.

2.2 Photoluminescence Spectroscopy Theory

Photoluminescence spectroscopy is a process in which the species is excited by absorbing a photon from its ground state to one of the various vibrational states in the excited electronic state with a higher energy. Within each of the states, which are excitation, internal conversion and emission, the vibrational states are different from each other. Having absorbed energy and reached one of the higher vibrational levels of an excited state, the molecule rapidly loses its excess of vibrational energy by collision and falls to the lowest vibrational level of excited state (Sharma and Schulman 1999). Spectrofluorometry is a type of spectrophometry arrangement with photoluminescence, the phenomenon in which the light incident with the fluorescent dyes in a reference sample with a given wavelength, mostly in the range of visible spectral ranges. The spectrofluorometer consists of a light source, an excitation monochromator, a sample holder, an emission monochromator and a detector. Spectrofluorometry is one of the most sensitive techniques currently available to the analyst and is therefore of increasing general interest, as attested by several studies showing the numerous applications of this technique (Mzoughi, Dachraoui, and Villeneuve 2005). This technique has an exquisite sensitivity in determining different photoluminescence compounds, especially aromatic hydrocarbons that exhibit intense photoluminescence. Spectrofluorometry is based on the hypothesis that the photoluminescence intensity in the sample is quantitatively related to the amount of aging that the samples have went through (Figure 2.2).

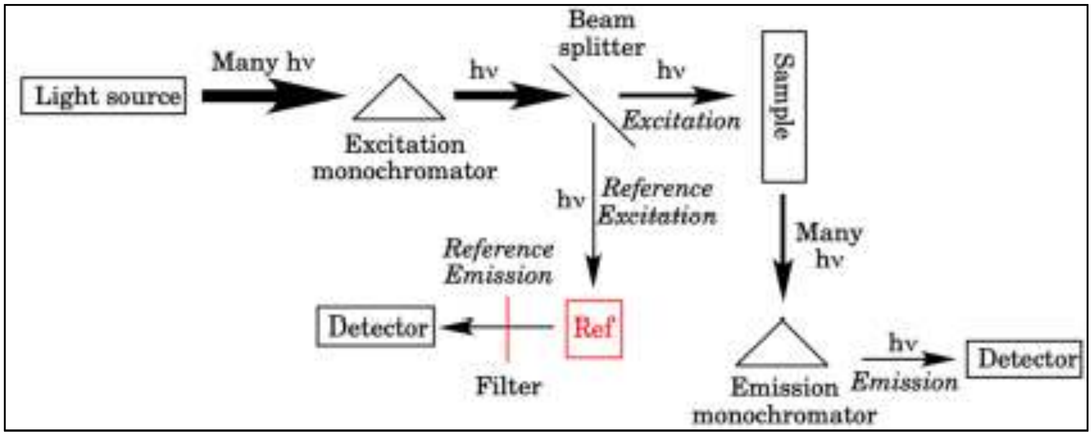


Figure 2.2-Photoluminescence Spectroscopy Schematic Diagram

There are several parameters influencing the intensity and shape of the spectra. When recoding an emission spectrum, the intensity is dependent on the excitation wavelength, concentration of the analyte solvent, path length of the cuvette and the self-absorption of the sample. While reporting the results of the spectroscopy, an absorption spectrum is used which reports the emission or photoluminescence spectrum, we can see which of the wavelengths are emitted after absorbing the incoming light. The x-axis shows the wavelength and the y-axis shows the intensity of the emission Figure 2.3.

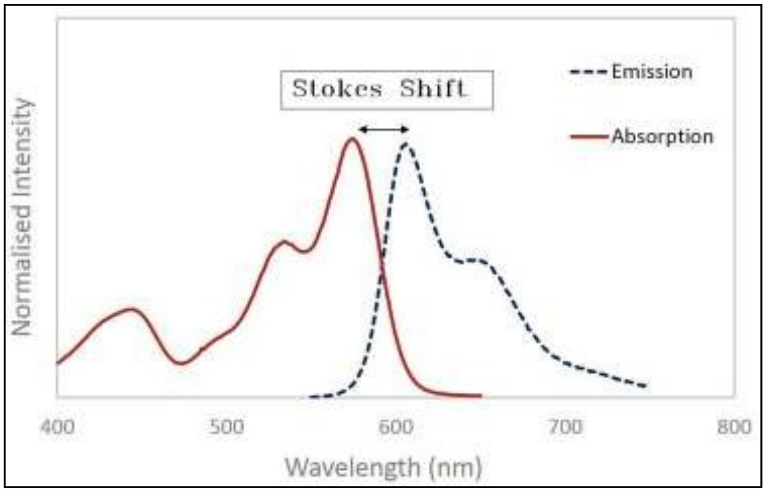


Figure 2.3-Photoluminescence Intensity Graph

2.3 Fluorescence of SARA fractions of Asphalt

Asphalt consists of two chemical classes which are, asphaltenes and maltenes. Maltenes are further divided into saturates, aromatics and resins. The composition of asphalt in terms of SARA (saturates, aromatics, resins and asphaltenes) is shown in Figure 2.4.

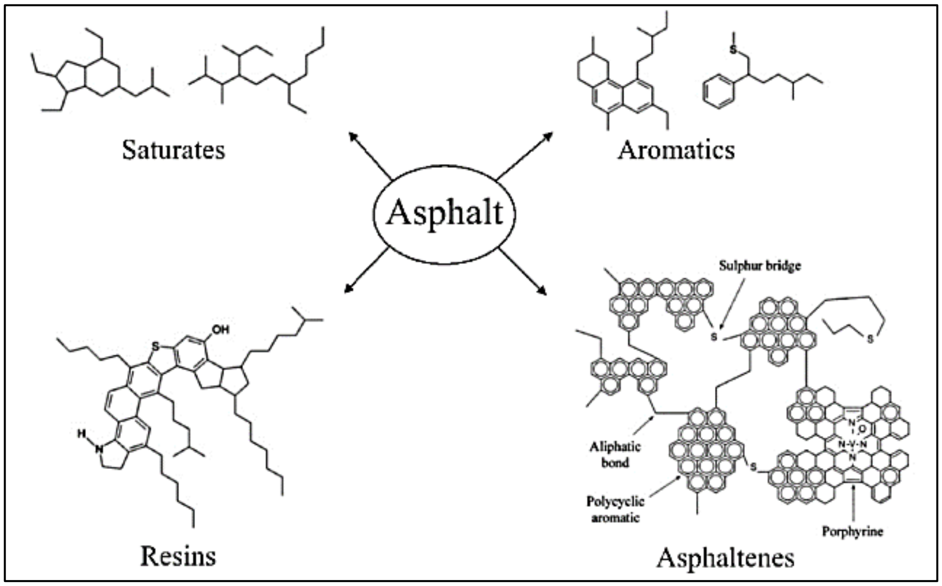


Figure 2.4 - Composition of asphalt (Fernandes et al., 2009)

The study of the fractions of asphalt under a microscope by previous researches has shown that asphaltenes show almost no fluorescence in the visible spectral range (Grossegger, Grothe, Hofko, & Hospodka, 2017; Handle et al., 2016). Similar results were seen in saturates. However, the aromatic fraction exhibits a significant amount of fluorescence. The resins also show considerable fluorescence but less as compared to the aromatic fraction.

Upon aging, aromatics change to resins, which in turn change to asphaltenes (Fernández-Gómez, 2013; Lu & Isacsson, 2002; Petersen, 1984, 2009; Qin, Schabron, Boysen, & Farrar, 2014). The comparison of fluorescence of unaged, short-term aged and long-term aged binder shows a decrease in intensity from unaged to long-term aged. This decrease in intensity can be related to the decrease in aromatics and increase in asphaltenes (Grossegger et al., 2017).

2.4 Fluorescent Organic Dye and Solvent

Photoluminescence usually occurs from aromatic molecules. Quinine, which is present in tonic water, was the first known fluorophore. When exposed to sunlight, a faint blue glow on the surface of tonic water can be seen. This observation was first made by Sir John Frederick William Herschel in 1845(Nelson and Guyer 2012). There are two types of fluorophores – intrinsic and extrinsic. Intrinsic fluorophores are those that occur naturally, and extrinsic fluorophores are those that are added to a sample that does not have any spectral properties (Lakowicz 2006).

When For the experiments described, the dyes Lumogen F RED 305 (Lumogen RED) and 6-Propionyl-2-(dimethylamino)-naphthalene (PRODAN) were used as the control and dependent variable in this experiment respectively. Lumogen RED 305 was chosen for this experiment because it has a relatively high stability and luminescence efficiency, which shows remarkable brightness and photochemical stability (Berezin et al. 2014). Lumogen F RED 305 exhibits a high photoluminescence quantum yield and relative photochemical stability in air. It also obtains a significant emission spectrum range between 580-615nm, which was easily detected under the fluorescent spectrometer before and after aging. The emission spectra and structure of Lumogen F RED 305 is shown in Figure 2.5 and 2.6 respectively.

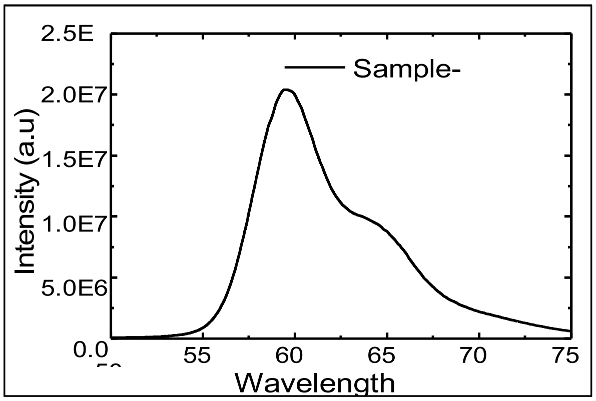


Figure 2.5-Lumogen F RED 305 Intensity

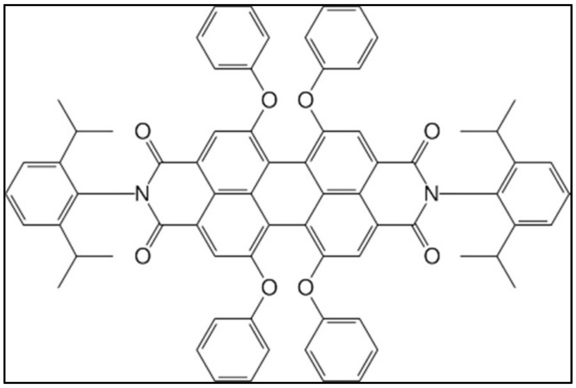


Figure 2.6-Lumogen F RED 305 Chemical Structure

Prodan is a highly fluorescent and hydrophobic molecule, it is a push pull, charge transfer chromophore which produces a substantial change in its excited-state dipole moment upon photoexcitation owing to the presence of an electron-donating dimethylamino group and electron-withdrawing propionyl group connected to the aromatic spacer by a single bond (Adhikary 2010). Prodan has an emission spectrum with a wide range from 401nm in cyclohexane, which cyclohexane is the alicyclic hydrocarbon and toluene is the liquid hydrocarbon. Besides, prodan can partition, is soluble in an extensive range of media, and it was demonstrated that it partitions from aqueous solution into more hydrophobic environments, and from nonaqueous solution into more hydrophilic environments. Because of this characteristic, Prodan can partition simultaneously into all regions of an asphaltene solution (Gabriella-Maria Pietraru, 2001). This fluorescent probe also has a broad emission spectrum from 401-531nm, and with the complex excited state kinetics, the origins of its solvatochromatic nature has always been debated. The emission spectra and structure of Prodan is shown in Figure 2.7 and 2.8 respectively.

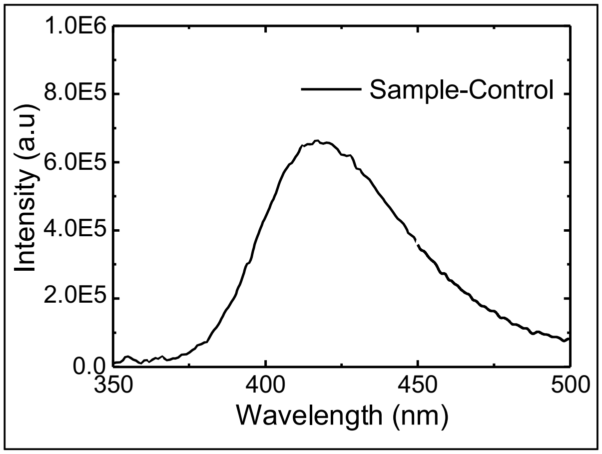


Figure 2.7-Prodan Intensity

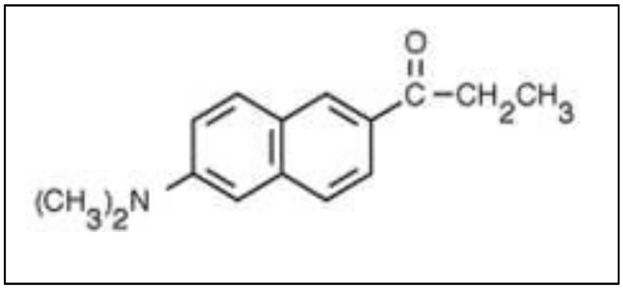


Figure 2.8-Prodan Chemical Structure

To dissolve both of the organic dyes into the water-based road marking paint, toluene was chosen as the solvent to blend the host and dyes together. Toluene, also known as methylbenzene, which is also an organic chemical compound. It is a colorless liquid, insoluble in water but soluble in organic solvent. It is also considered as an aromatic compound due to the benzene ring that is presented in its chemical structure. A benzene ring is presented when there are 6 carbon atoms connect to another alternating double bonds, creating a hexagonal ring. A fusion of a benzene ring to a heterocyclic structure results in an increase in color absorptivity of the absorption band, It's substitution causes a shift in the absorption maxima of the wavelength and changes in photoluminescence emission (Joens 2015). The structure of toluene is shown in Figure 2.9.

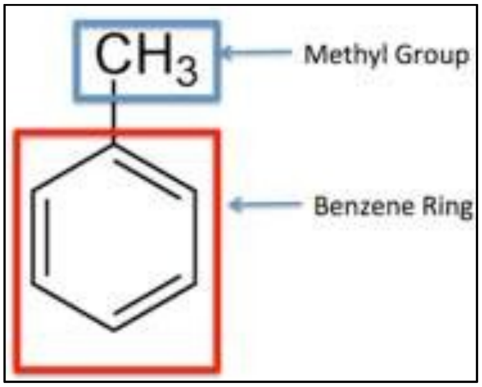


Figure 2.9-Chemical Structure of Toluene

2.5 Water Based Road Marking Paint

Road surface marking has always been the material to inform the important regulations and rules to the vehicle drivers and pedestrians. One of the important features of road marking paints is the speed at which it dries after application, since this dictates the level of disruption required to road traffic in order to be able to apply them (Savage 1985b). It is always applied on the pavement once all the pavement layers are laid and compacted on the field. Besides, they are commonly applied by road marking equipment or other facilities used by vehicles. A traffic paint of non-aqueous dispersion type has the advantages that it is low in viscosity and high in solid content and can be quickly dried, and that a hydrocarbon solvent which is photochemically inert, is usable. However, the paint has the drawback that if it is thickly coated, a film is formed on the surface area due to quick drying and a solvent is hard to evaporate from the inside (Savage 1985a). This type of paint contains a high level of prime pigments and is one of the acrylic latex binders that has been approved by the federal specification. It has an exceptional durability and bright reflection performance. Recently, water-based road marking paint has been used since it is more environmental and user-friendly compare to solvent-based paint. There are couple advantages that water-based paint is chosen, which includes: having a lower odor and volatile organic content, which resulting in less impact on the environment, also obtains an excellent durability with no risk of fire from handling flammable solvents. The water-based road marking paint is shown in Figure 2.10.

Figure 2.10-Water-Based Road Marking Paint

Chapter 3 Experimental Methods

3.1 Materials

A PG 58-28 asphalt binder was provided from Michigan Paving and Materials Co. in this research. Organic fluorescent probes Lumogen F RED 305 from WorldAccount BASF and 6-Propionyl-2-(dimethylamino)-naphthalene Prodan purchased from Thermo Fisher, were selected as the additive and toluene (>99.5% pure), purchased from the Chemistry Department of Michigan State University, was used as a solvent for both fluorescent probes. Water Based Road Marking Paint (White) from RAE Pro Stores was selected as the host of the experimental study. Solid and liquid status of Lumogen were shown in Figure 3.1 and 3.2.

Figure 3.1-Lumogen F RED

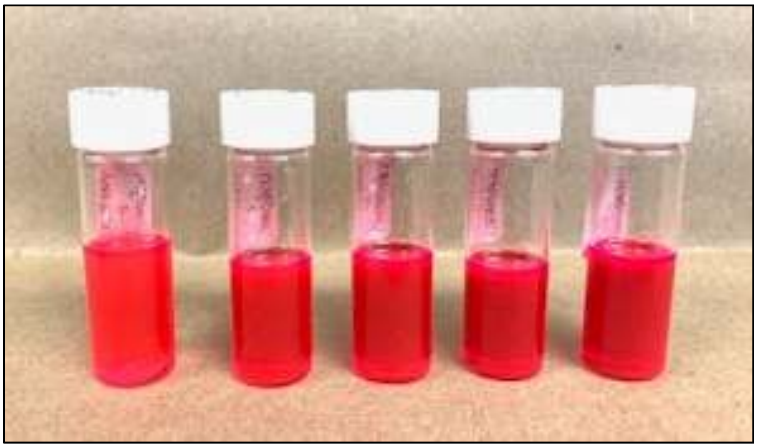


Figure 3.2-Samples of Lumogen F RED Solution

3.2 Preparation of Lumogen F RED, Prodan and Road Marking Paint Mixture

A solution of Lumogen F RED, Prodan and toluene was first prepared with toluene, and toluene was used as a dissolving medium for the two organic dyes for the pure organic dye samples and also in the water-based road-marking paint. The solutions of the two organic dyes were then added to the paint while stirring until all the solution is dissolved into the paint uniformly. The concentration of Lumogen F RED, Prodan and toluene in the 50 grams of paint is shown in Table 3.1.

Table 3.1-Concentration of Lumogen and Prodan Solution

Dyes	Sample 1	Sample 2
Lumogen F RED	2mg	-
Prodan	-	4mg
Toluene	4mL	4mL

3.3 Laboratory Testing for Asphalt Binder, Lumogen and Prodan

At the beginning of the experimental study, the PG 58-28 asphalt binder was chosen as the host for both the organic photoluminescence probes. However, the binder has such a dark background that during the photoluminescence spectroscopy measurement, none of the signals from both of the fluorescence dyes could be detected. With all the energy being absorbed by the asphalt binder background, none of the photoluminescence probes were able to have an emission spectrum, no matter how thin the asphalt binder was laid on the microscopic slide. A transmission test was performed on the asphalt binder sample as well to determine how long of a laser wavelength and excitation of photoluminescence probes should be used for asphalt binder and the acceptable wavelength was 1100-1600nm wavelength, which falls near infra-red or infra-red range. Asphalt binder sample and its transmission range is shown in Figure 3.3 and Figure 3.4.

Figure 3.3-Original Asphalt Binder Sample

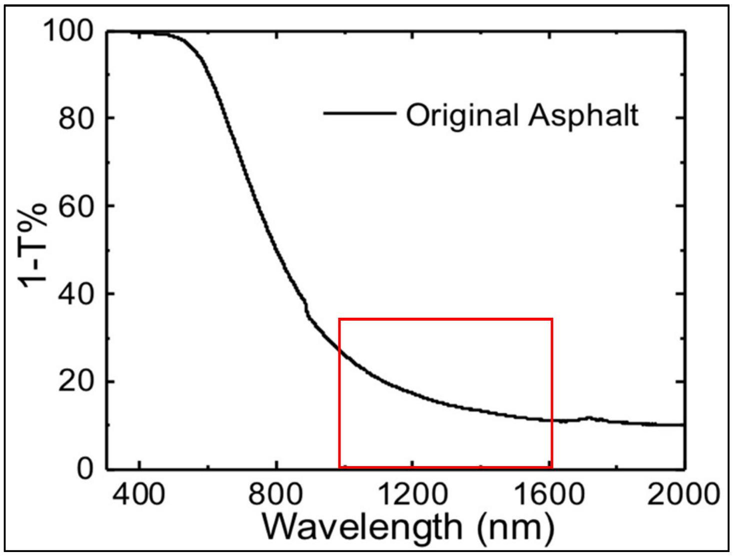
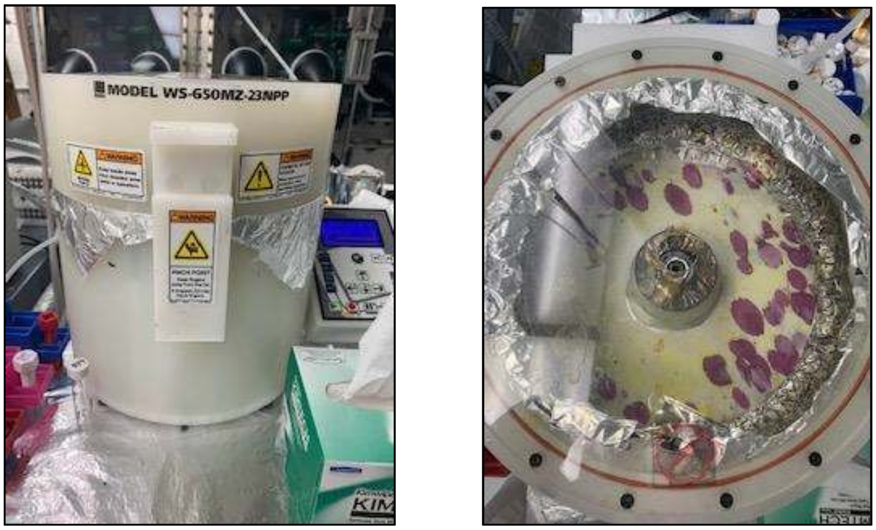


Figure 3.4-Asphalt Binder Transmission Range

As mentioned above, Lumogen F RED 305 and Prodan were chosen as the photoluminescence probes and due to the challenges mentioned above, the pure Lumogen and Prodan were tested under the photoluminescence spectroscopy before adding into the water-based paint. The fluorescent probes, Lumogen F RED and Prodan were mixed with toluene with a concentration of 0.5mg/mL and 1mg/mL respectively, then coated on microscope slides by using the spin coater (WS-650 ma-23npp) from Laurell Technologies. The spin coating is a common technique for applying thin films to substrates, with the high-speed rotation (1000rpm) throughout the process of applying the liquid organic dye onto the microscope slide, all the excessive fluid spins off the edges of the substrate and the desired thickness of the film (10nm) is achieved in 30 to 60 seconds. The images of the spin coater and a set of samples are shown in Figure 3.5(a), (b) and 3.6.



(a) (b)

Figure 3.5-Spin Coater. (a) Side view (b) Top View

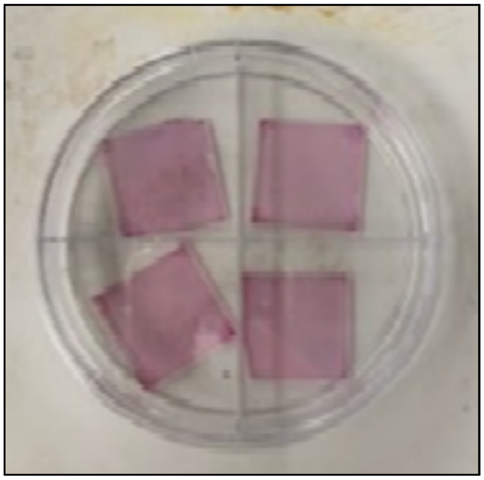


Figure 3.6-Pure Lumogen Samples

With the pure organic dye samples tested, the original and aged photoluminescence intensity of the dyes are known and could help to control the later experiments when they are mixed with the water-based paint. After testing the pure organic dyes, each organic fluorescent dye solution was mixed with the water-based paint together evenly, they were spread on the microscopic slide with the doctor plate in order to form a uniform and thin layer for the photoluminescence spectroscopy. A doctor plate and a set of samples are shown in Figure 3.7 and Figure 3.8 for a better visual to understand.

Figure 3.7-Doctor Plate

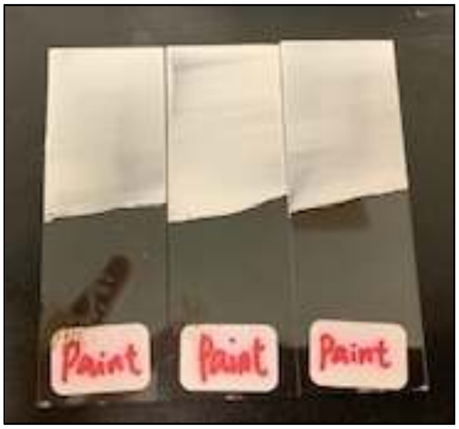


Figure 3.8-Paint Samples for Spectrum Test

3.4 Laboratory Aging Procedures

As mentioned above, the RTFO test is used to stimulate the short-term aging that occurs during the missing and construction in the laboratory. As mentioned above, different sets of samples were prepared to run through aging and tested for photoluminescence intensity. Each of the pure organic dye and mixtures of road-marking paint with the organic dyes were painted on the microscopic slides and aged using the RTFO for 45 minutes at 163˚C. The reason of doing 45 minutes of RTFO instead of the original 85 minutes is because one of the dyes, Prodan had completely broken down throughout the aging progress, so a shorter aging time period was chosen to see if the dye would be able to withstand the high temperature and pressure. Throughout the aging procedure, each sample sets are separated into different groups for different time periods of aging. Since this experimental study is to proof that the photoluminescence probes are capable to install to the pavement as a sensor to track the aging of the pavement, it is important to know if how much of the photoluminescence probes would degrade throughout the oxidation aging progress. For the Lumogen F RED photoluminescence probe, the samples are separated into 5 different sets for 5 various time slots, which are 5, 10, 20, 30 and 45 minutes. As for the Prodan photoluminescence probe, the samples are divided into 11 different time period, which includes: 2, 4, 6, 9, 12, 15, 20, 25, 30, 37 and 45 minutes. The images of the RTFO equipment are shown in Figure 3.9 and 3.10.

Figure 3.9-Rolling Thin Film Oven

Figure 3.10-RTFO Bottles for Samples

3.5 Fluorescent Spectroscopy Measurement

The fluorescent spectroscopy was measured using the PTI QuantaMaster 40 Photoluminescence Spectrometer that was available in the Chemical Engineering Department at Michigan State University. The spectrometer has the ultra-fast acquisition phosphorescence system with the microsecond resolution; it is available to utilize a pulsed microsecond xenon lamp as an excitation source. The lamp features a build-in ellipsoidal reflector with high light collection efficiency, which allows a tight focus at the excitation monochromator slit. The instrument also offers a large sample component which has a 10x10nm thermostated cuvette holder, a variable speed stirrer, high efficiency quartz optics, filter holders, real time excitation correction, lid activated emission shutter and one quartz cuvette. A better visual of the sample component and how the laser light reflects is shown in Figure 3.11

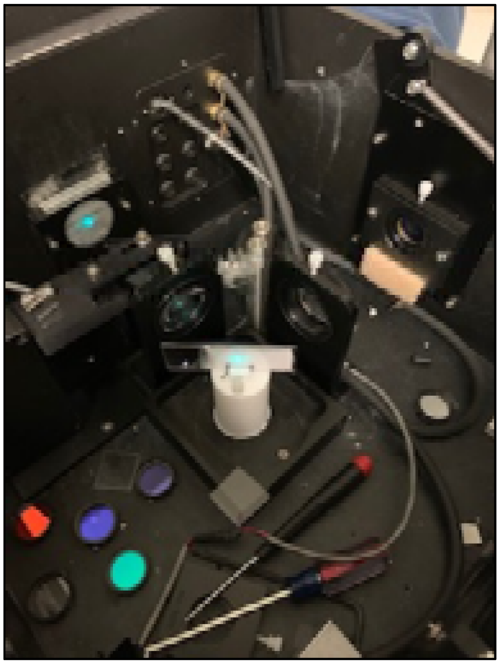


Figure 3.11- Photoluminescence Spectrometer Sample Component

This instrument also excels in very rapid measurement of phosphorescence decays while using the single shot transient digitizer (SSTD) technique. For measurements, 475nm blue laser was chosen as the excitation wavelength with a slit length of every 5 nm. The emissions were recorded in the range of 500-750nm using a slit length of every 5nm. Besides, the wavelength of laser that passed through each filter could be controlled by setting size of the condenser. For this experimental study, the condenser was all set with a 600nm width, which allows any laser light that has a wavelength lower than 600nm to pass through the condenser and focus on the sample for the emission spectrum. Throughout the measurements, the background acquirement was measured every 5 seconds and performance of the samples was measured with a 1nm step size and 0.2 seconds of integration. Fifty (50) result points were selected for each of the sample. Therefore, the spectrum obtained consisted of 50 values of the overall intensity and the trend was plotted against the wavelength in nanometers. The whole QuantaMaster 40 Photoluminescence Spectrometer and the controller for the condenser are shown in Figure 3.12 and 3.13.

Figure 3.12-QuantaMaster 40 Photoluminescence Spectrometer

Figure 3.13-Condenser Controller

A thin layer of water-based paint, which was mixed with different organic dye at room temperature, is laid on the microscope slides. Then, part of the samples is placed into the rolling thin-film oven at 163˚C for aging to stimulate the aging for 1-3 years on the field. The slide samples were allowed to cool and then taken for photoluminescence measurement. For each time slots, two slides of samples were prepared in order to have an accurate measurement. Besides, throughout the experiments each of the slides were measured both front and back to observe how much of a difference it would make by detecting the photoluminescence with and without the microscopic glass. To provide a better visual of the slide samples, a set of samples is shown below in Figure 3.14.

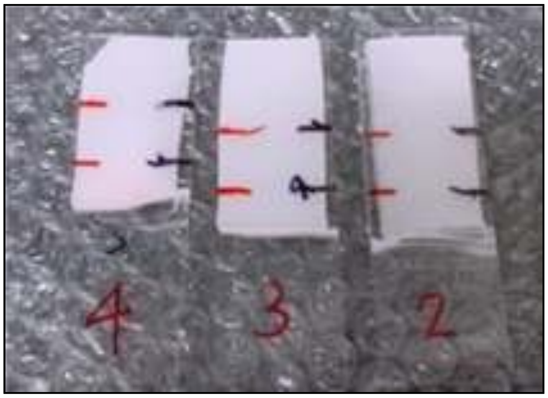


Figure 3.14-Marked Slides for Photoluminescence Spectroscopy

3.6 Viscosity Measurement of Asphalt Binder

A Rotational Viscometer shown in Figure 3.15 was used to determine the viscosity of the short-term aged asphalt binders, viscosity is the ratio between the applied shear stress and the rate of shear, which is also known as the coefficient of viscosity. Throughout the test, the viscosity readings in the unit of centipoise (cP) were taken at 135 ˚C, 145 ˚C, 155 ˚C and 165 ˚C while the speed of the spindle was set at 20 rpm. The binder and chamber were heated until it reached the liquid state at 140 degree Celsius, then 8 grams of the aged binder was poured into the preheated chamber (140˚C) and the SC 21 spindle was used for the tests. The results collected from this test is a coefficient of the resistance of the asphalt binder to flow. The viscosity was measured following the AASHTO T316 and ASTM D 4402 Standard.

Figure 3.15-Rotational Viscometer

To understand the properties of each kind of asphalt binders, 3 different samples were prepared. In order to have a better result of each sample, 2 replicates of each sample were set up and the average of both results were taken and recorded.

Table 3.2-Number of Samples for RTFO

Type of Test	Original Binder	Aged Binder	Organic dye Binder
Rotational Viscosity	2	2	2

Chapter 4 Results and Discussion

4.1 Viscosity Measurement Results

The viscosity of unaged and RTFO aged binder were measured to check what extent was short-term aging affecting the viscosity of the mixture. The results of the viscosity measurements are shown in Table 4.1. The values are an average of the measurement of the two replicates of each binder were tested. The results clearly show that the RTFO for both the original asphalt binder and Lumogen additive binder has a higher viscosity than the unaged binders. As mentioned earlier, asphalt consist of resins, aromatics and saturated oil after the manufacture process, the asphaltenes diffusion is controlled by these elements in asphalt. With the higher viscosity that the aged samples had, it means there was an increase in asphaltenes quantity because the asphaltenes have an aggregation tendency. Besides, since the key component of RTFO is the loss of volatiles throughout the process; with the loss of smaller molecules form the asphalt binder, the viscosity would increase Results of unaged and RTFO aged samples were shown in Figure 4.1.

Table 4.1-Viscosity Test Readings

Average Viscometer Readings (cP)				
Temp. (˚C)	**135**	**145**	**155**	**165**
Original	269.25	171.25	116.25	81.75
Original RTFO	376.5	239	158.5	111
Lumogen Original	244.5	155.5	92	55
Lumogen RTFO	405.15	254.5	172.75	122

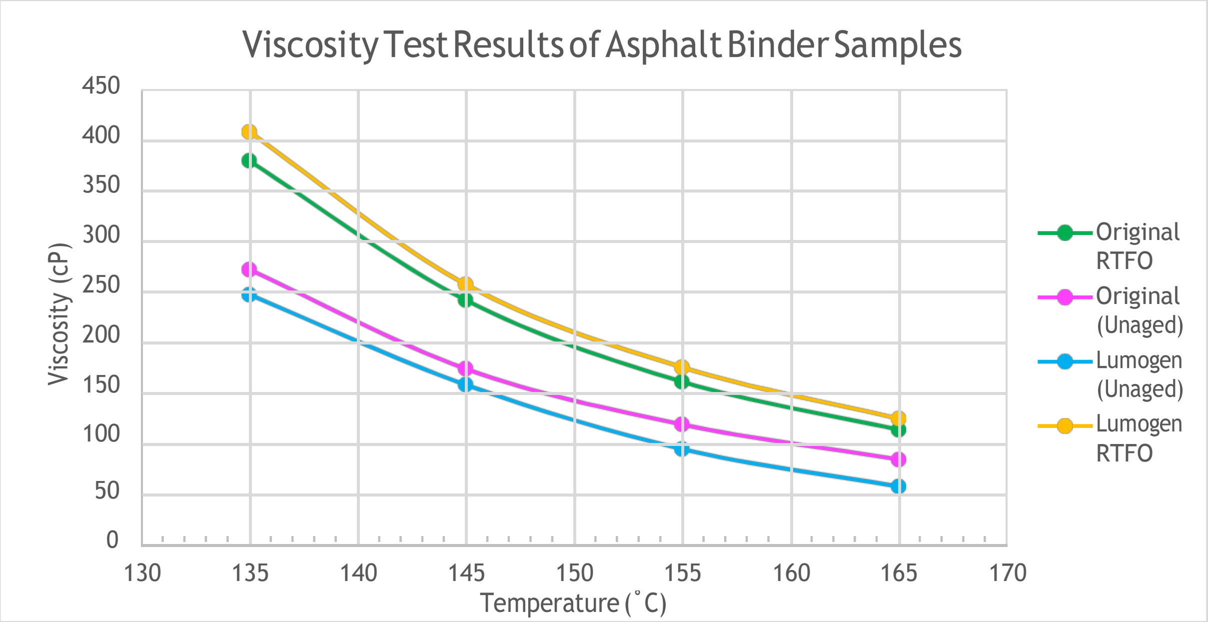


Figure 4.4 -Viscosity Test Results for Asphalt Binder

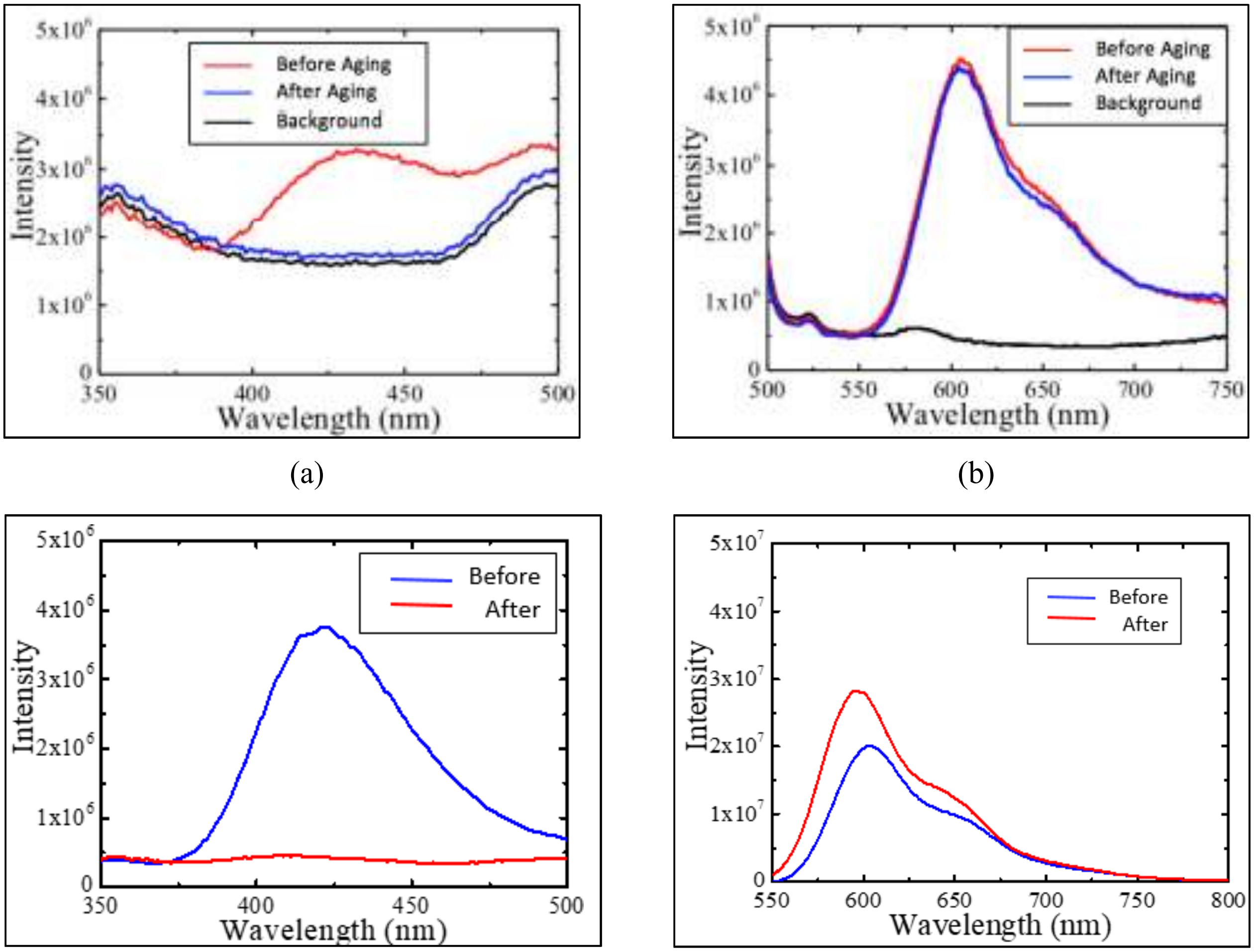
4.3 Fluorescent Spectroscopy Measurement Results

As mentioned above, the unaged and RTFO aged samples (pure fluorescence dye, mixture of each fluorescence dye with water-based road marking paint) were analyzed using the photoluminescence spectrometer. The fluorescent intensity obtained from the measurement was plotted with the overall intensity against the wavelength in nanometers. In each of the wavelength, the reflected intensity would be detected and reported. For the pure organic dyes, they have the following performances. The pure Lumogen F RED has a decrease of intensity from 4.5x10^6 to 2x 10^6 after 85 minutes of RTFO aging and for pure Prodan, it has an intensity of 3.5 x 10^6 before aging; however, after the RTFO aging, Prodan had totally broken down and it no longer had any signals detected by the photoluminescence spectrometer. Besides, to see how well the organic dyes performed when added into the water-based paint, the unaged sample of organic dyes mixed with paint were also tested under the spectrometer. It turned out that when Lumogen F RED was added to the paint, it had a better performance since the white background did not require a large amount of energy to get through which the photoluminescence probes could easily get excited by the laser projected on the sample. On the other hand, Prodan has the same performance when compared to the pure Prodan sample. From this we can proof that paint would be a good host to have the photoluminescence probes added in as a sensor signal in the field.

With the tests done on both pure and mixed paint, couple in depth tests were done in different time slots in order to observe the performance of the dyes throughout the RTFO aging progress. In general, the performance of Lumogen is stable for the control purpose, although the photoluminescence intensity actually increased as the degradation process moved forward, it is because the concentration of the Lumogen F RED added into the paint was too high which quenched the photoluminescence intensity due to the reabsorption of energy. As the degradation went on, some of the Lumogen F RED molecules broke down so the reabsorption loss was less, and the photoluminescence intensity increases, and the peak is blue shifted, meaning the wavelength had decreased with a corresponding increase in intensity.

Unfortunately, Prodan molecules did not have the expected performance during the aging progress, the molecules were not able to withstand the high pressure and temperature which caused the disability to detect any signals for any of the aging samples, even for the 2 minutes aged sample. Although Prodan probes were able to be detected in the unaged samples, it is still not an appropriate probe for this application since it is not detectable after the short-term aging.

Besides, from the figures below, it can be observed that each of the sample has a slightly different intensity peak. It is because the thickness of film on the microscope slides were different. By preparing the slides with the Doctor Blade manually, it was hard to guarantee that each of the sample is laid out uniformly and equally. This step should be improved in the fuure experiments. The photoluminescence intensity performance curves of each dye and dye additive paint are shown in Figure 4.2(a), (b), (c) and (d). For the detailed graphs of the intensity curves of unaged and RTFO aged are shown in the appendix.



(a) (b)

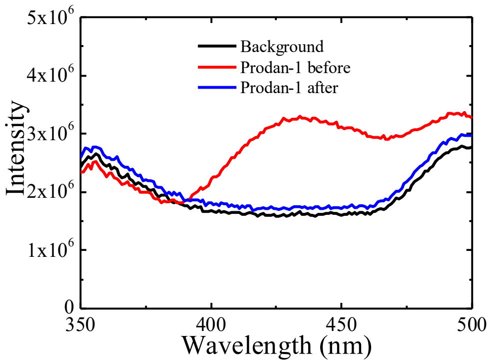
(c) (d)

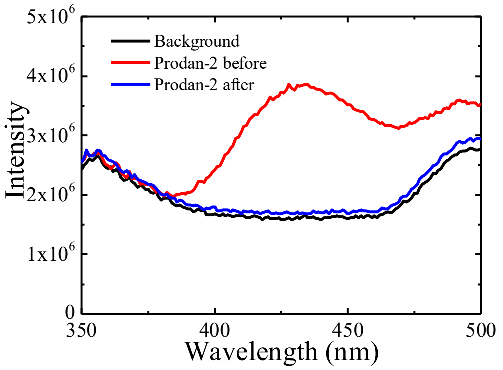
Figure 4.2-Photoluminescence Intensity Performance

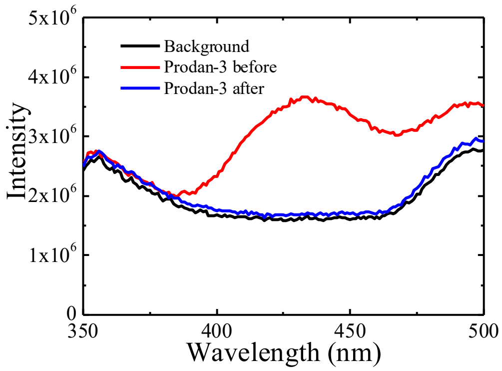
(a)Prodan+Paint (b) Lumogen+Paint (c)Pure Prodan (d)Pure Lumogen

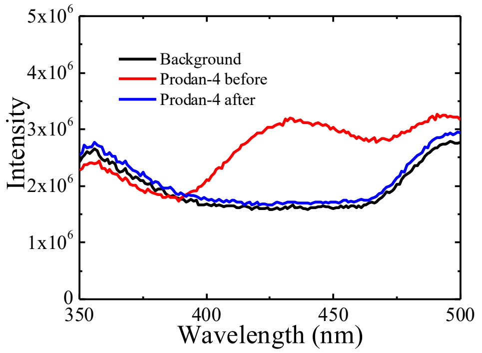
The following graphs of the average intensity vs the wavelength for each of the mixtures are shown below. The values of average intensity are an average of the two replicates.

Pure Prodan (85 Minutes)

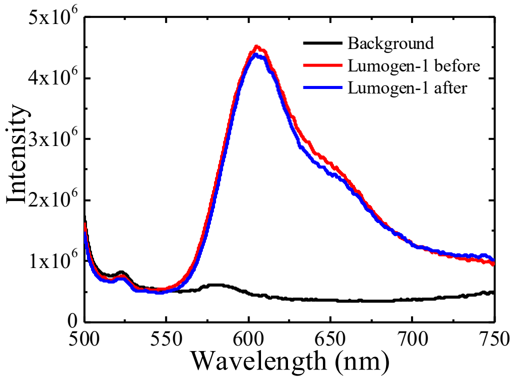


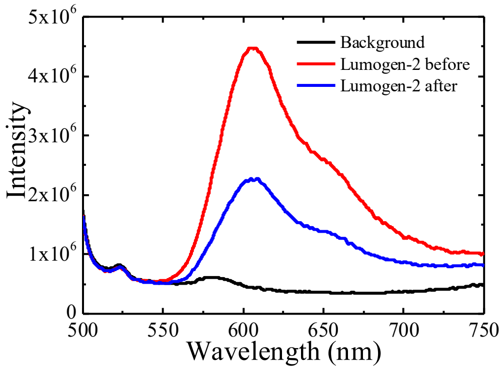


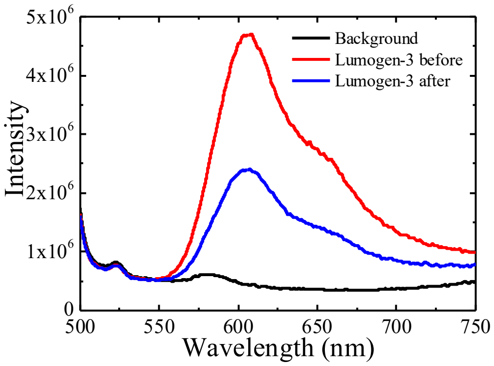


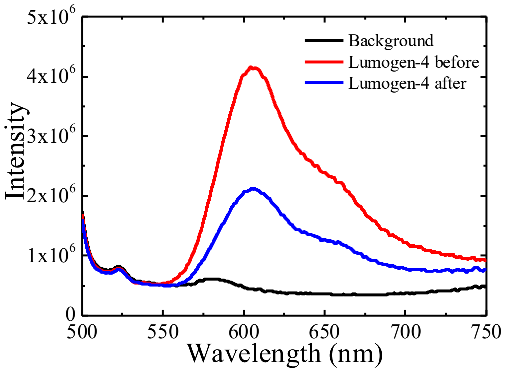


Pure Lumogen (85 Minutes)



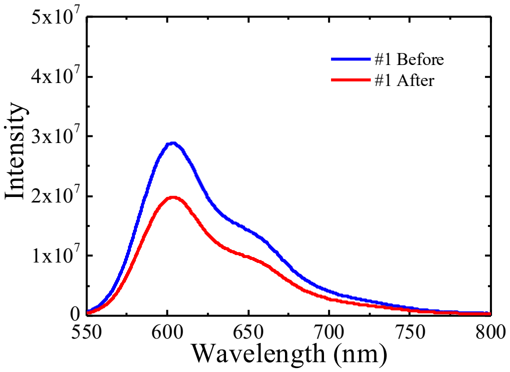


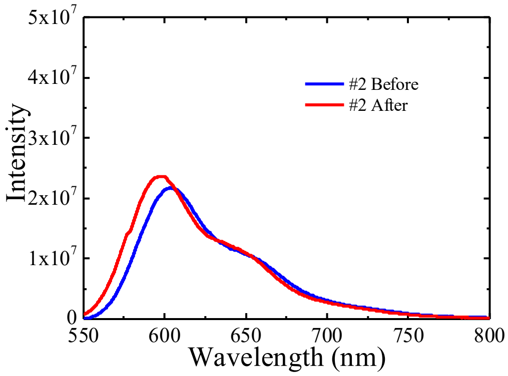




Pure Lumogen (Time Slots)

(5 Minutes)





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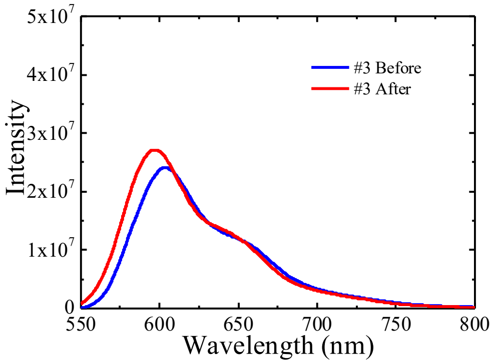

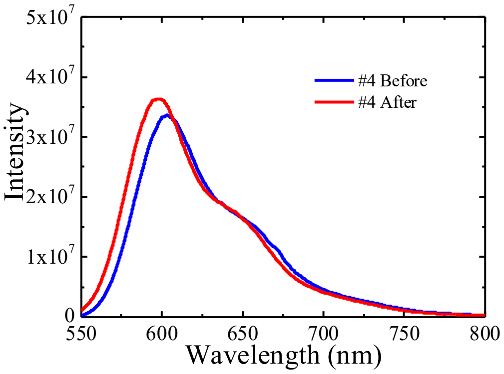

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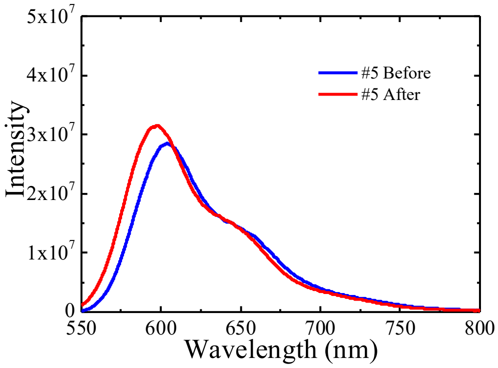

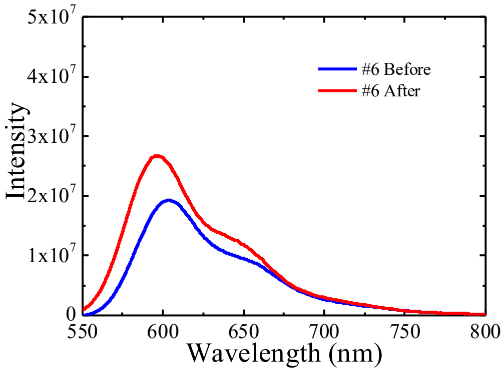

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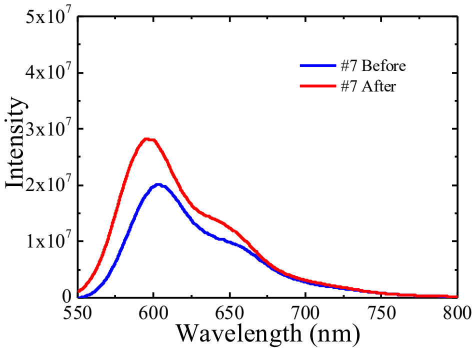

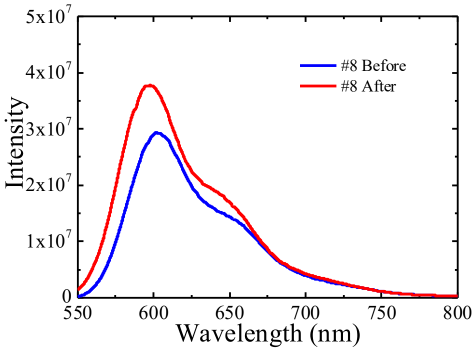

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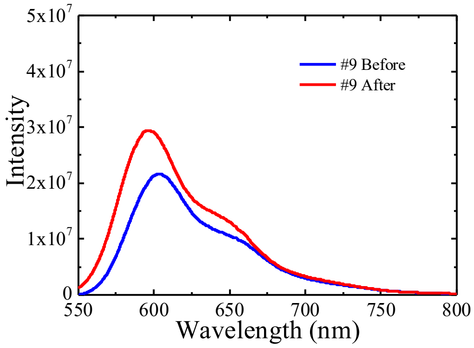
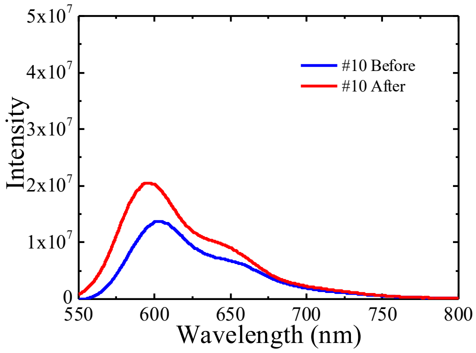
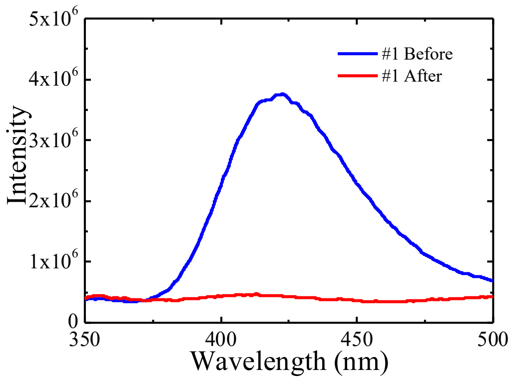




Pure Prodan (Time Slots)

(2 Minutes)



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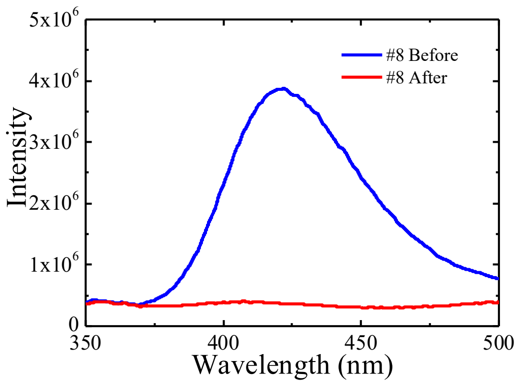

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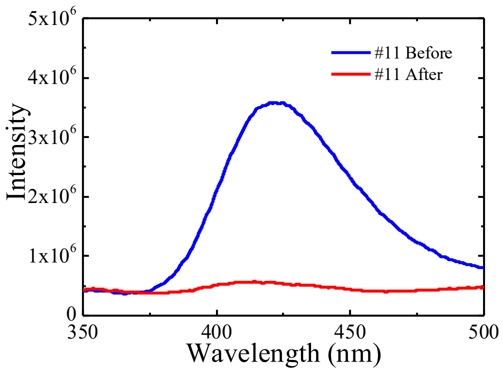

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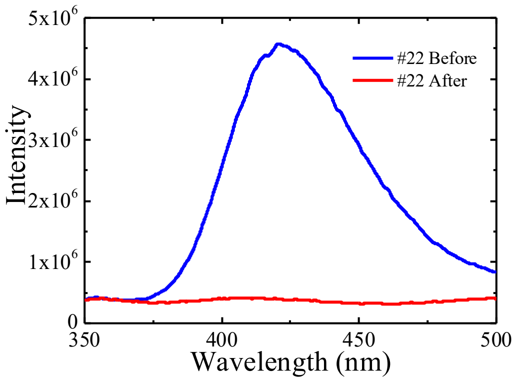

Chapter 5 Conclusion and Recommendation

In this study, it was proven that there is a high potential that an easy installation sensing system with fluorescence dye can be embedded into the asphalt pavement system. In this project, it was shown that when the aging process of RTFO is applied to the paint, the signals of the Lumogen F RED were able to be detected. This shows that it is a successful installation and thus this dye does not have any degradation throughout the oxidation aging process. Therefore, the Lumogen F RED could be considered as the control probes in the future work. This is because it has a strong chemical structure that allows it not to breakdown after the RTOF aging progress. However, Prodan could no longer be used as an observation probe since it does not have the capability to withstand the short-term aging process, not even the first two minutes of the test. With the weaker structure that Prodan has comparing to Lumogen F RED, it would have a weaker performance under high pressure and temperature.

For future work, both Lumogen and Prodan should be engineered to persist in the whole RTFO aging period. Also, the use of other environmentally sensitive fluorescent probes, such as Bodipy and Coumerin, can be considered for both control and dependent dye respectively. It would also be advisable to know if there is any reaction between the road marking paint and asphalt binder during oxidation and other aging approach. For a more accurate replication of samples, experimental conditions like extent of spin coating, fabricating the organic dye solution, stirring, duration of time to warm up the binder in the oven, surrounding temperature and humidityshould be noted.

For testing the samples in the field, a portable photoluminescence spectrometer would be needed in order to detect the spontaneous emission of the organic dye conveniently. A suggested portable photoluminescence spectrometer detector would be the handheld x-ray photoluminescence spectrometer that Thermo Fisher, Olympus and several other science and technology leaders in the global market are developing (Castro, Ann).

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