



University of  
New Haven

University of New Haven

Digital Commons @ New Haven

---

Honors Theses

Student Works

---

5-13-2020

## Photofading of Black Dyes in Cotton and Polyester Fibers Resulting from Environmental Exposure to Sunlight

Maggie E. Mahaney

Follow this and additional works at: <https://digitalcommons.newhaven.edu/honorstheses>



Part of the [Chemistry Commons](#), and the [Forensic Science and Technology Commons](#)

---


UNIVERSITY OF NEW HAVEN  
HONORS PROGRAM

**2019-2020 Honors Thesis**

**Photofading of Black Dyes in Cotton and Polyester Fibers  
Resulting from Environmental Exposure to Sunlight**

**Maggie Mahaney**

A thesis presented in partial fulfillment of the requirements of the Undergraduate Honors Program at the University of New Haven.

Student:	<u>Maggie E. Mahaney</u> (Signature)
Thesis Advisor:	<u>Virginia M. Maxwell</u> (Signature)
Department Chair:	<u>Timothy M. Palmbach</u> (Signature)
Honors Program Director:	<u></u> (Signature)

May 13, 2020

Date

## ACKNOWLEDGEMENTS

I would first like to express my sincerest gratitude to my thesis advisor, Dr. Virginia Maxwell. Without her support, guidance, and willingness to volunteer her backyard for my outdoor experiments, the completion of this thesis would have been a mere pipe dream.

Next, I would like to thank the University of New Haven's Honors Program for approving my thesis proposal and providing me with the funding to conduct my research. Finishing this thesis would—quite literally—have been impossible without their support.

I would also like to extend my appreciation to the University of New Haven's Forensic Science Department for allowing me to use their laboratory space. My thanks extends as well to their laboratory manager, Sandra Hartman-Neumann, for ordering my research supplies and ensuring that I received them in a timely manner.

## ABSTRACT

Color is one of the most important properties analyzed during forensic fiber examinations due to its discriminatory power. Differing colors in fibers are usually sufficient grounds for exclusion, but in cases where a lengthy period has passed between crime commission and evidence recovery, the high probability of environmental degradation having altered the questioned fibers' properties could lead to false exclusions. Photofading, the loss of color resulting from exposure to light, is a common form of degradation observed in fibers. Although well-known in the dyeing industry, it is not typically factored into forensic fiber examinations. Published photofading research has been limited to idealized simulations involving dye solutions rather than dyed textiles, and studies with dyed textiles have focused on cellulosic fibers and non-black dyes despite the prevalence of manufactured and black fibers.

This study investigated photofading in black cotton and polyester fibers that were exposed to sunlight in various environments over a 3.5-month period. The objective was to determine how fiber type and environmental conditions impacted the rate of photofading. Results of a control experiment indicated that photofading rates were dependent on the strength of fiber-dye interactions (which is predicated on the chemical properties of both) rather than fiber type alone. Due to the outbreak of COVID-19 during the later stages of research, results for the environmental exposure experiment were unable to be gathered. A discussion of the expected results is presented instead, along with possibilities for future photofading studies and the greater forensic implications that such work may have.

# TABLE OF CONTENTS

## INTRODUCTION

Color in Forensic Fiber Examinations .....	1
Ultraviolet-Visible Microspectrophotometry.....	2
Photofading of Textile Dyes .....	3
Limitations of Previous Photofading Studies .....	8

## EXPERIMENTAL PROCEDURE

Fabric Samples .....	11
Environment Construction and Sampling.....	11
Control Experiment.....	13
Post-Exposure Analysis .....	14

## RESULTS AND DISCUSSION

Control Experiment.....	15
Speculations on Environmental Photofading Results .....	22
Possibilities for Future Research .....	25

CONCLUSION.....	27
-----------------	----

REFERENCES .....	29
------------------	----

## INTRODUCTION

### *Color in Forensic Fiber Examinations*

Despite their small size, fibers possess a wealth of properties that are subjectable to scientific analysis. This fact is especially valuable in the forensic science field, where a primary objective is establishing linkages between evidence with questioned origins and known samples collected from suspects, victims, and witnesses. The long list of chemical, optical, and physical properties that are analyzed during forensic fiber examinations includes cross-sectional shape, birefringence, and melting point. However, a property often assessed first in these examinations is color: If a questioned and a known fiber are not of the same color, then they most likely did not originate from the same source [1].

Color is a subjective sensation perceived by the human eye resulting from the interaction of light with an object [2]. An object's perceived color is determined by the wavelength of the light that is not absorbed by the object [2]. The wavelengths perceptible to the human eye fall in the approximate range of 400 to 700 nm, otherwise known as the visible region of the electromagnetic spectrum [2]. Beginning with violet near 400 nm, the subsequent "spectral colors" observed in the visible region are blue, green, yellow, orange, and red, located near 700 nm [2]. Whereas the sensation of color is triggered by varied absorption of radiation across the visible spectrum (e.g. red results from low absorption around 700 nm and higher absorption at the other wavelengths), two additional "colors" occur from total absorption and reflection [2]. Total absorption and reflection of visible radiation are perceived as black and white, respectively [2].

Color is imparted to fibers by the application of a dye or pigment [3]. Dyes are soluble organic molecules that adhere to fibers by hydrogen bonding, ionic bonding, or entrapment amongst the fibers [3]. Another key property of dyes is that they contain two functional groups—

chromophores, which give the dye its color, and auxochromes, which increase the color's intensity [3]. Pigments, in contrast, are insoluble particles that are affixed to the surfaces of fibers via a resin [3]. Dyes are primarily used for coloring clothing, while pigments are reserved for printing graphics on pre-colored clothing [3].

### *Ultraviolet-Visible Microspectrophotometry*

As previously discussed, color is a subjective property when assessed visually. Subjectivity is to be avoided in forensic science because it feeds bias into examinations, which can lead to outcomes as severe as wrongful convictions. To circumvent this ethical concern, forensic examiners utilize an instrumental technique known as ultraviolet-visible (UV-Vis) microspectrophotometry to analyze the color of fibers. The principle of this method involves the excitation of analyte molecules' valence electrons via absorption of UV-Vis radiation, which covers the wavelength range from 240 to 700 nm [2]. The extent to which a molecule's valence electrons absorb UV-Vis radiation depends upon the type and quantity of those valence electrons [2]. Valence electrons can be placed in three categories:  $\sigma$ -electrons (participate in covalent bonds between atoms where atomic orbitals overlap end-to-end),  $\pi$ -electrons (participate in double and triple covalent bonds between atoms where atomic orbitals overlap laterally), and  $n$ -electrons (do not participate in covalent bonding) [2]. Since  $\sigma$ -electrons require greater energy than can be provided by UV-Vis radiation to be excited, only  $\pi$ - and  $n$ -electrons are excitable by this range of radiation because they require less energy to enter an excited state [2]. Dye molecules therefore contain conjugated systems—chains of alternating single and double covalent bonds—to reflect and absorb radiation in the visible range that imparts them with their perceived color [3].

A UV-Vis microspectrophotometer (MSP) functions by using a microscope to position an object and focus the radiation onto a particular area of that object to ensure reproducible results

[2]. The radiation then interacts with the object, and any unabsorbed radiation collects in the microscope's objective before entering a spectrophotometer for detection [2]. After scanning all wavelengths of the UV-Vis range, the result of the analysis is a graph of absorbance versus wavelength [2]. This provides a quantitative—and thus more objective—method of comparing color between questioned and known fibers. UV-Vis microspectrophotometry is also widely regarded as a nondestructive technique for analyzing fiber color, giving it a further edge over destructive color analysis methods such as thin layer chromatography (TLC), where elution is used to separate a dye into its components after being extracted from a fiber [2,4].

#### *Photofading of Textile Dyes*

However, it should not be immediately concluded that two fibers did not originate from the same source if their color analyses produce disagreeing results. A 2016 study by Brinsko, Sparenga, and King [5] investigated the effects of environmental exposure on properties of manufactured fibers and commented on the significant issues that can arise when questioned and known samples have been exposed to nonidentical environments. As an example, Brinsko et al. described the scenario of fibers that were collected from a body that had been submerged in saltwater being compared to fibers collected from a suspect's home: The fibers found on the body may have undergone prominent changes in their optical and physical properties due to interaction with saltwater, potentially leading to a false exclusion of the fibers gathered from the suspect [5]. This outcome can be disastrous if the exclusion plays a role in returning a “not guilty” verdict for a defendant who is actually guilty. Likewise, environmental degradation could cause two dissimilar fibers to appear identical and end up falsely including an innocent person. One form of environmental degradation that affects fibers is the photofading of their dyes, which entails a loss of color and a reduction in absorbance resulting from exposure to UV-Vis radiation, especially

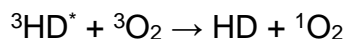


from sunlight [4,6]. Photofading is also relatively unknown in the forensic science community (according to an informal poll of trace evidence examiners that was mentioned in a 2017 photofading study by Forster, Bitter, Rosenthal, Brooks, and Watson [4]), demonstrating the need for further research on the topic to be conducted in this context.

A 2001 literature review by Oakes [6] on the photofading of textile dyes provides deeper insight into its proposed mechanisms—these still have yet to be fully understood as of 2017 [4]—and factors that impact its severity. The review begins by explaining the three relaxation modes of electrons back to their ground states after excitation by UV-Vis radiation: radiationless transitions (internal conversion and intersystem crossing), emission of radiation (fluorescence and phosphorescence), and photochemical reactions [6]. The latter is most suited to allow for reactions such as photofading because a molecule's electrons have entered a more-prolonged triplet state (where an electron's spin multiplicity has flipped during excitation), giving the reaction a longer window of opportunity to initiate [6]. However, dyes entering excited singlet states (where electrons retain the same spin multiplicity as in their ground states) may still be capable of undergoing photofading since singlet states possess greater energy to fuel the reaction, or the dye may be in close contact with reactive functional groups in the textile to which it has been applied [6].

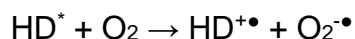
Photofading mechanisms can be divided into two categories: photo-oxidation pathways and photoreductive pathways. Photo-oxidation may occur via either singlet oxygen or a superoxide, a dioxygen anion with a charge of -1 [6]. In the singlet oxygen mechanism (Figure 1), a dye that has entered an excited triplet state transfers its excited-state energy to an oxygen molecule (which is in a triplet state in its ground state), exciting it to a singlet state in a process

known as triplet-triplet reduction [6]. The singlet oxygen then reacts with ground-state dye molecules to initiate photofading.



**Figure 1.** Scheme for photo-oxidative mechanism via singlet oxygen [6]. D is the dye molecule. The “\*” superscript indicates that the species is in an excited state. The numerical superscripts in front of the species indicate whether the species is in a singlet (1) or triplet (3) state.

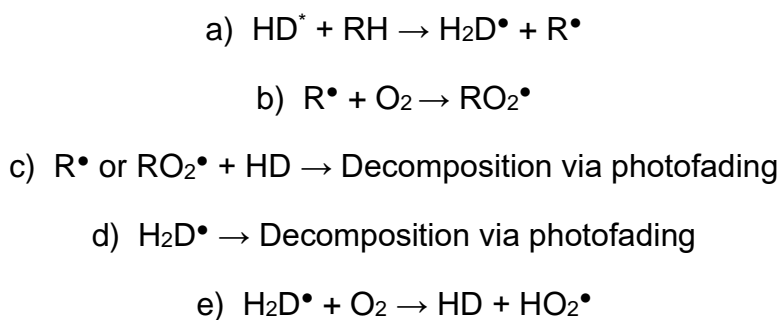
The superoxide photo-oxidation mechanism (Figure 2) occurs when a dye molecule is excited by visible radiation and then transfers an electron to an oxygen molecule, forming a dye cation radical and a superoxide that subsequently induces photofading by reacting with a ground-state dye molecule [6].



**Figure 2.** Scheme for photo-oxidative mechanism via singlet oxygen [6]. D is the dye molecule. The “\*” superscript holds the same meaning as in Figure 1. The “•” superscript indicates that the species is a radical species.

Photoreductive pathways involve the fading of a dye due to its reaction with radicals formed by reduction [6]. As such, this category of mechanisms requires higher-energy ultraviolet light to initiate them since the radicals are formed by cleavage of covalent bonds [6]. These radicals can be produced in multiple ways. One method involves hydrogen-atom abstraction from a neighboring oxidizable functional group (e.g. hydroxyl group on the textile) by an excited dye molecule (Figure 3a) [6]. The radical created from the oxidizable functional group then reacts with an oxygen molecule to form a peroxy radical (Figure 3b) that can cause photofading, or it can just react with a ground-state dye molecule to cause photofading (Figure 3c) [6]. The radical created

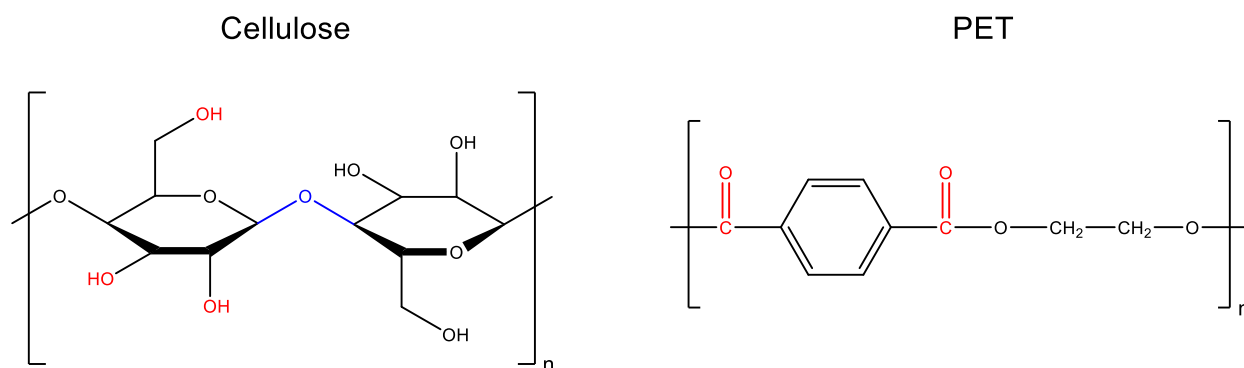
by the dye molecule accepting the abstracted hydrogen atom can also undergo degradation directly (Figure 3d) or react with oxygen to produce the starting dye molecule and a peroxy radical (Figure 3e) [6]. While the latter occurrence does not consume the dye, the buildup of peroxy radicals can eventually lead to the dye's degradation via oxidative bleaching [6]. Another method of forming radicals for photoreduction entails cleavage by ultraviolet radiation of the dye molecule itself to give radicals that can react as previously described [6].



**Figure 3.** Scheme for photoreductive mechanisms. D is the dye molecule, and R is the neighboring oxidizable functional group. The “\*” and “•” superscripts hold the same meanings as in Figures 1 and 2.

Oakes also discusses the primary factors that influence photofading. The first is the chemical structure of the dye's substrate, which can participate in the radical-forming reactions explained above [6]. This is especially true when the substrate contains carbonyl groups and hydroxyl groups that can become  $\text{R}_2\dot{\text{C}}\text{—OH}$  radicals (where R represents an organic functional group), which are good reducing agents to promote the photoreductive pathways [6]. A consequence of this is that the substrate may also undergo photo-oxidative degradation due to reaction of the formed substrate radicals with triplet oxygen to yield peroxy radicals [6]. By this logic, cotton would be expected to experience photofading at a faster rate than polyester, for example. Cotton is comprised of cellulose, a homopolysaccharide consisting of unbranched chains of glucose monomers. Each glucose molecule in a cellulose chain contains three hydroxyl groups that can become  $\text{R}_2\dot{\text{C}}\text{—OH}$  radicals [7]. In contrast, polyethylene terephthalate (PET), the most

common polyester used in clothing, contains two carbonyl groups per monomer [7]. The oxygen atom in each carbonyl group is readily excitable and can facilitate the formation of radicals that participate in photofading reactions [6]. Because PET contains one less functional group per monomer that can promote photofading, polyester should possess greater lightfastness (resistance to photofading) than cotton (Figure 4).



**Figure 4.** Diagrams of monomer units for cellulose and PET. Functional groups that can become radical species that participate in photofading are colored in red. Note that a “monomer” of cellulose is conventionally depicted as two glucose monomers linked via a  $\beta$ -glycosidic bond (blue) in order to differentiate it from amylose, another unbranched glucose homopolysaccharide whose monomers are linked via  $\alpha$ -glycosidic bonds.

Another factor that influences photofading is the wavelength distribution of the radiation to which the dye is exposed. High-energy ultraviolet radiation is key in the photoreductive pathways but is not present to a large degree in sunlight; thus, photo-oxidative pathways that are fueled by lower-energy visible radiation (e.g. superoxide mechanism) may predominate when a dye is left exposed to the elements [6]. Other factors summarized include presence of metal ions (can both promote and quench singlet oxygen photo-oxidation), dye structure (resistance to photofading is increased when a dye is covalently—rather than physically—bound to its substrate; stronger covalent bonds between dye and substrate also improve resistance), and presence of impurities [6].

A 1994 review of photofading by Allen [8] provides insight into additional influences on the process. One is an increase in humidity, which causes swelling in fibers that opens pores and facilitates penetration of oxygen from the atmosphere into the fiber [8]. This oxygen may then participate in the previously discussed photofading mechanisms. Cellulosic fibers are particularly susceptible to this effect because the radicals formed from the hydroxyl groups in cellulose participate in the photohydrolysis of dyes [8]. Like with most chemical reactions, a rise in temperature also stimulates photofading because the increase in kinetic energy of the participating molecules heightens the chance of attaining photofading's activation energy [8]. Lastly, Allen explains the impact of dye aggregation and concentration. Aggregated dyes tend to be more resistant to photofading than disperse dyes, and dyes applied to amorphous polymers are more resistant than those applied to crystalline polymers [8]. Higher dye concentrations generally reduce the severity of photofading as well [8]. Since chromophore impurities that can promote photofading are an inevitable consequence of dye manufacture, increasing the dye concentration creates a situation where pure chromophores greatly outnumber the impurities and can quench them [8].

#### *Limitations of Previous Photofading Studies*

At present, photofading knowledge is limited due to many studies on the topic using idealized conditions—namely, dye solutions that are not representative of dyes bound to textiles, a more realistic scenario [6]. Multiple studies conducted in the twenty-first century that investigated photofading in textile-bound dyes focused almost exclusively on cotton and spectral colors (i.e. non-black dyes). For example, Forster et al.'s study examined red, blue, and yellow dyes applied to cotton fibers in varying concentrations [4]. The fibers were continuously exposed to the UV-Vis radiation emitted from the xenon light source of an MSP for periods of 15 to 30

minutes [4]. All three dyes exhibited linear reductions in absorbance at their wavelengths of maximum absorbance over time, and the lower dye concentrations displayed increased color loss [4]. A 2015 National Institute of Justice report on the microspectrophotometry of fibers by C. S. Palenik, Beckert, and S. Palenik examined red, blue, and green dyes applied to wool fibers [9]. The fibers were continuously exposed to the UV-Vis radiation emitted from the tungsten and xenon light sources of an MSP for 5 minutes [9]. All fibers exhibited photofading to some extent (it was not specified whether the color loss was linear or followed another trend), and exposure to the xenon light source always caused greater photofading than exposure to the tungsten light source [9]. It is worth noting that these two photofading studies were the only ones with an explicit forensic science context that could be found.

However, two other photofading studies within this time period included the black dye CI Reactive Black 5 (RB5) amongst a group of spectrally colored dyes. The first, by Rastogi, Sen, and Gulrajani in 2001 [10], examined the photofading of five reactive dyes (those that form covalent bonds with fibers) applied to cotton and silk. After being exposed to a 500-W mercury-tungsten filament lamp for seventeen days, RB5 exhibited a nearly linear loss in color retention in both cotton and silk [10]. A hydrolyzed form of RB5 (which reduces the dye's capability to form covalent bonds with fibers) was also analyzed: The cotton and silk dyed with this form of RB5 displayed higher rates of loss in color retention [10]. The second study by Batchelor, Carr, Coleman, Fairclough, and Jarvis [11] from 2003 examined photofading in a group of sixteen reactive dyes applied to cotton. The dyes were exposed to simulated "average midday" Florida sunlight and 35% humidity for periods up to 145 hours [11]. As in Rastogi et al., RB5 exhibited linear color loss over time for both light and dark shades [11]. From this, Batchelor et al. were able to conclude that the constant rate of color loss indicated that the photofading mechanism did not

change over time nor was dependent on dye concentration [11]. They additionally observed that although the dark shade lost about twice as many dye molecules as the light shade due to its greater sunlight absorption capability, its visual color loss was less apparent than that of the light shade [11]. Batchelor et al. also investigated the effect of removing the ultraviolet portion from the simulated sunlight, which resulted in a 36% reduction in photofading for RB5 and an average 20% reduction across the seven other studied dyes in the same azo dye class (dyes that contain a C—N=N—C group) as RB5 [11]. Overall, the results of Rastogi and Batchelor's work are consistent with those of Forster.

Furthermore, no photofading studies that exposed fibers to different environmental conditions could be found. Combined with the lack of inclusion of black dyes other than RB5 in such studies, these literature findings demonstrate the significance of conducting research on the photofading of different black dyes in other types of fibers and in varying environments to determine whether outcomes are consistent with previous work. Forensic science literature further illuminates this need. A 2005 survey by Watt, Roux, and Robertson [12] that appeared in the journal *Science & Justice* studied the population of textile fibers found in washing machines in eleven Sydney, Australia households. Black fibers constituted the greatest proportion of collected fibers at 41.9%, indicating that black is a commonly worn color; black fibers can thus be expected to frequently appear as evidence [12]. A chapter by Smith and Thompson [13] in a 2017 book on forensic textile science includes a section on photodegradation, which notes that 98.8% of UVA radiation from sunlight (wavelength range of 320 to 400 nm) reaches the ground and can penetrate windows. On the other hand, only 1.1% of the higher-energy UVB radiation (wavelength range of 280 to 320 nm) that is more likely to induce photofading is capable of reaching the ground [13].

Since crime scenes can be situated outdoors as easily as they can be indoors, researching photofading from both perspectives will prove essential in improving fiber evidence interpretation.

## EXPERIMENTAL PROCEDURE

### *Fabric Samples*

Four fabric types were investigated in this study: 100% polyester fleece, 100% cotton flannel, 100% cotton smooth weave, and 65/35 polyester/cotton blend. All fabrics were purchased from JOANN Fabric and Crafts and came pre-dyed in black. The proprietary nature of the black dye formulations prevented dye identification, and time constraints did not allow for the development of a laboratory procedure to do so.

### *Environment Construction and Sampling*

Nine environments were constructed to study the photofading of black fabric dyes, and these are summarized in Table 1.

<b>Table 1. Environments Used to Study Photofading</b>		
Environment Type	Environment Location	Construction Method
Control (no sunlight exposure)	West Haven, Connecticut	Fabric samples were placed in closed laboratory closet that was only opened to remove samples for weekly fiber sampling.
Direct sunlight exposure (indoors)	West Haven, Connecticut	Fabric samples were taped to window that received sunlight exposure for majority of daylight hours.
Direct sunlight exposure (outdoors)	Hebron, Connecticut	Fabric samples were affixed to fence around pool in backyard that received sunlight exposure for majority of daylight hours.
Directional exposure (north, south, east, west)	Hebron, Connecticut	Fabric samples were affixed to exterior walls of an outdoor shed. Each wall faced in one of the four cardinal directions. Each direction was treated as a separate environment.

(continued)



Environment Type	Environment Location	Construction Method
Shaded exposure	Hebron, Connecticut	Fabric samples were affixed to tree trunks (approximately 2 feet above ground) in forested area that was shaded from sunlight during daylight hours.
Freshwater	West Haven, Connecticut	Fabric samples were submerged in 5-gallon bucket filled with tap water. Bucket top was left open to receive light exposure. Aqua Culture 5–15 Gallon Aquarium Air Pump was used in bucket to prevent water stagnation.

**Table 1.** Descriptions of the nine environments examined in this study. The first and second columns indicate the environment type and the environments' geographic locations, respectively. The third column explains how each environment was constructed.

One 4 in. by 4 in. square of each fabric type was placed in each environment. The fabric squares were deployed in the environments during the week of November 24, 2019 and remained there until the week of March 8, 2020.

Fibers were sampled from the fabric squares on a weekly basis as was feasible by pulling them from random locations with a pair of tweezers. The sampled fibers were then placed in separate coin envelopes and sealed to prevent extraneous light exposure during storage until the samples were ready to be analyzed. During the sampling period, the daily UV index for Hebron, Connecticut was recorded to serve as an approximate gauge for the amount of sunlight being received by the environments there. Sunlight exposure for the West Haven, Connecticut environments was planned to be measured with an ultraviolet light meter, but one was not able to be procured.

### *Control Experiment*

A control experiment based on the work of Forster et al. [4] was conducted prior to analyzing the fibers that underwent environmental exposure. Its purpose was to establish a baseline for the rates of photofading experienced by the black dyes with respect to fabric type.

A CRAIC FLEX<sup>TM</sup> UV-Vis MSP was used to both induce and measure photofading in the fibers. The MSP was used with a xenon light source and a 15X microscope objective in transmittance mode. Prior to each use, the MSP was calibrated for transmittance mode by running a wavelength check and photometric check with National Institute of Standards and Technology (NIST)-traceable standards. The wavelength check tested the MSP's wavelength accuracies at 360.6 nm, 417.8 nm, 445.5 nm, 535.9 nm, and 637.4 nm; each had to fall within a tolerance level of  $\pm 3.0$  nm. The photometric check tested the MSP's photometric accuracies at 280 nm (0.477), 400 nm (0.497), 500 nm (0.504), and 635 nm (0.492); each had to fall within a tolerance level of  $\pm 0.047$ . Once calibrated, the instrument parameters for the MSP were set as follows:

- Absorbance spectrum sampling range: 200–800 nm
- Number of scans: 50
- Resolution factor: 4
- Integration time: set for each sample with the MSP's optimization function
- Sampling aperture size: 15  $\mu\text{m}$  by 15  $\mu\text{m}$

Samples for the control experiment were prepared by extracting fibers from leftover fabric squares that did not need to be deployed in the environments. For each sample, one fiber was mounted horizontally in glycerol on a quartz microscope slide and covered with a quartz cover slip; five replicate samples were prepared for each fabric type. The fiber was then brought into focus under the MSP's microscope, and a background scan and reference scan were taken before

beginning the analysis. The sampling aperture was positioned at the center of the fiber's width in an area where the fiber ran horizontally across the microscope's field of view. The position of the sampling aperture remained constant throughout the analysis period.

The spectral analysis of the fiber was conducted immediately after the sampling aperture was positioned to minimize preliminary photofading from the MSP's light source. The analysis period began when the first absorbance spectrum for the fiber was collected. Completion of this measurement signaled the 0-minute mark, and a stopwatch was started at this time. Absorbance spectrum scans were taken every minute for 15 minutes thereafter, with the 1-minute interval between consecutive scans beginning upon completion of a scan.

Once all of the absorbance spectra had been collected, they were analyzed with the CRAIC MINERVA<sup>TM</sup> computer software. The program was used to average together the five replicate absorbance spectra for each fabric type at a given time interval (e.g. 0 minutes, 1 minutes, 2 minutes, etc.). The wavelength of maximum absorbance ( $\lambda_{\max}$ ) was determined for each fabric type from the averaged spectra, and the corresponding absorbances were noted. These were plotted against time in Microsoft Excel to find the average rates of photofading (i.e. loss in absorbance) for the black dyes from the slopes of the generated trendlines.

### *Post-Exposure Analysis*

Spectral analysis of the fabric squares that were placed in the environments was conducted after the control experiment had been completed. Three fibers were selected at random from each weekly environment sample. These were mounted horizontally in glycerol on a quartz microscope slide and covered with a quartz cover slip. The fibers were examined with the MSP using the same instrument parameters as the control experiment; however, each fiber within a sample was scanned once in three different locations along its length to account for intra-fiber variability. This resulted

in a total of nine absorbance spectra being collected per sample. The nine spectra were averaged together to produce a representative spectrum for a fabric type on a given date in a particular environment.

Analysis of the deployed fabric squares was not able to be completed due to the outbreak of COVID-19. About ten samples had been run prior to laboratory access being closed, so not enough data was collected to conduct any meaningful analysis. It was intended for the environmental rates of photofading to be assessed in the same fashion as used in the control experiment should the values of  $\lambda_{\max}$  not have varied greatly across weekly samples for a fabric type. The average photofading rates would then have been compared using analysis of variance (ANOVA) statistical tests to determine whether any differences among them were significant. Planned environment comparisons included the following:

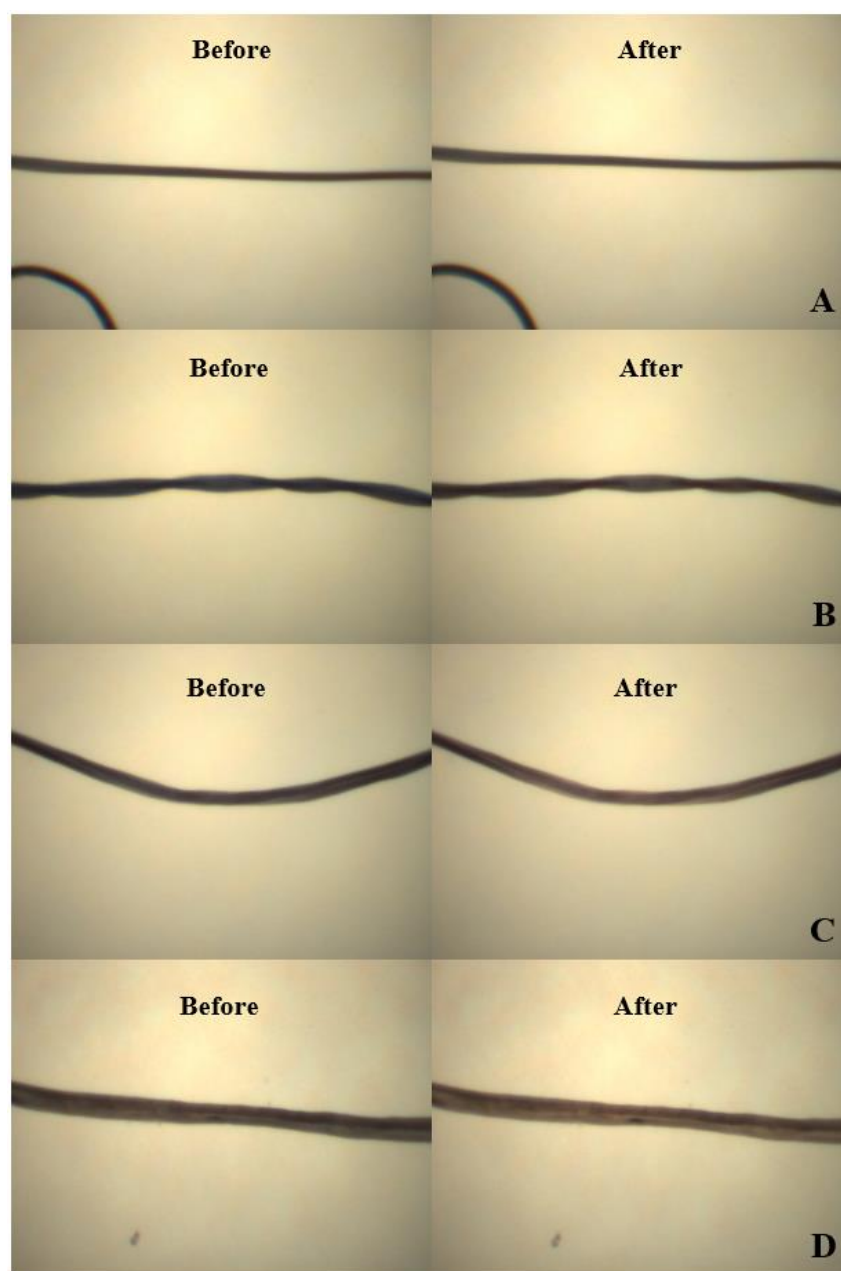
- Direct sunlight exposure (indoors) versus direct sunlight exposure (outdoors): Does window glass block enough UV radiation to reduce photofading rates?
- Direct sunlight exposure (outdoors) versus minimized exposure: Does shade provided by wooded areas reduce photofading rates?
- Directional exposure (north, south, east, west): Does direction of face impact photofading rates?

## RESULTS AND DISCUSSION

### *Control Experiment*

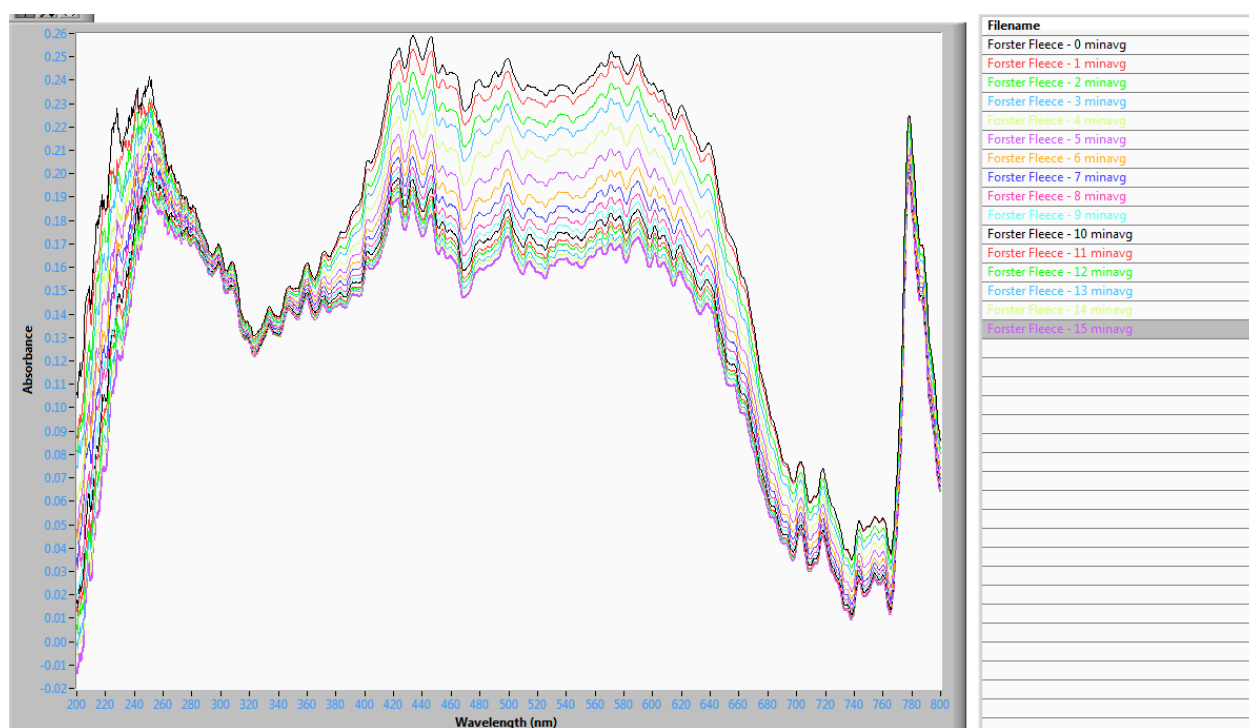
Overall, the results of the control experiment were consistent with those of Forster et al. [4]. 15 minutes of continuous exposure to the MSP's xenon light source was enough to induce noticeable photofading of the black dyes in all four fabric types, as demonstrated by the photomicrographs in Figure 5. The smooth weave and blend fibers exhibited the most visible color

loss, an observation that could be explainable in part by the smooth weave and blend fabrics having been colored with a lower concentration of dye (although this was not known). This relationship between acceleration of photofading and lower dye concentration was previously observed by Forster and Batchelor [4, 11].

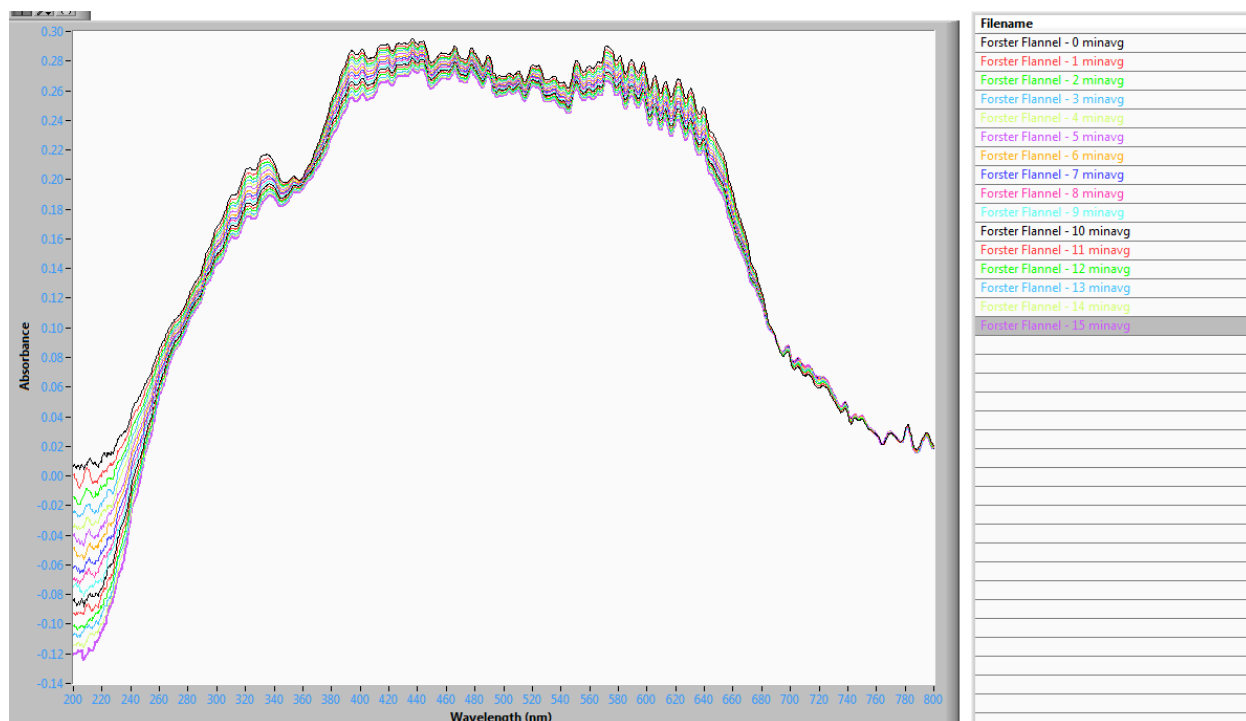


**Figure 5.** Photomicrographs (captured using 15X objective) of fibers subjected to the control experiment before and after the 15-minute analysis period. A) 100% polyester fleece, B) 100% cotton flannel, C) 100% cotton smooth weave, and D) 65/35 polyester/cotton blend.

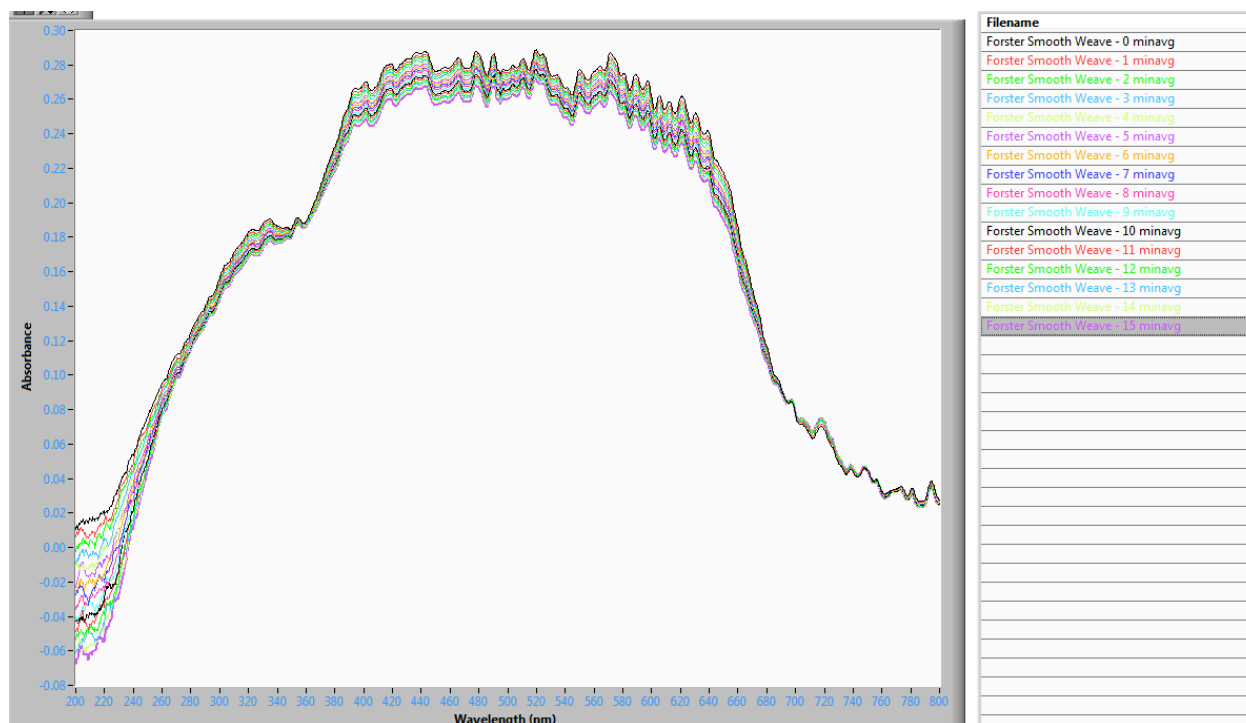
Although the smooth weave and blend fibers appeared to undergo photofading the fastest, the spectral data indicated that the fleece fibers lost their color most rapidly. Figures 6 through 9 depict the sixteen average absorbance spectra collected for each fabric type. The spectra for all four fabric types displayed the expected downward shift over time as the decomposition of dye molecules by the MSP's xenon light source reduced the dyes' absorption capabilities; however, the downward shifts between consecutive spectra were greatest for the fleece fibers.



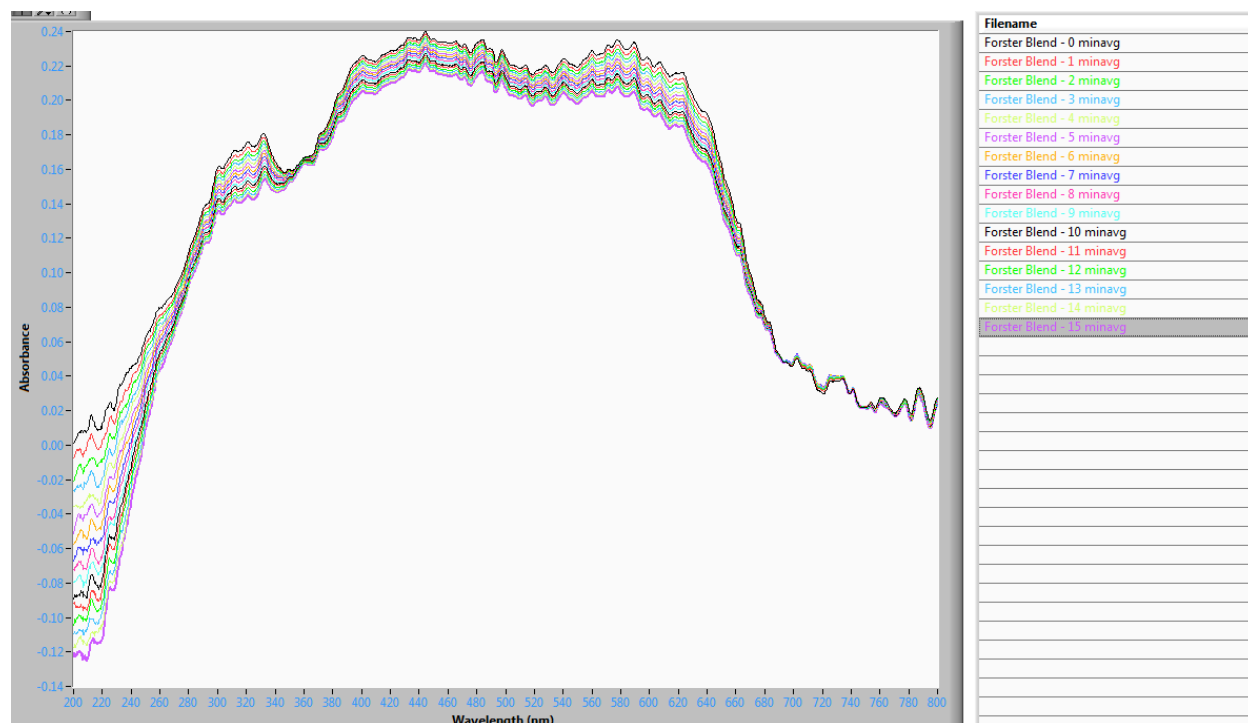
**Figure 6.** Average absorbance spectra for the 100% polyester fleece fibers at each minute during the 15-minute analysis period. The fleece fibers'  $\lambda_{\text{max}}$  occurred at 433.230 nm.



**Figure 7.** Average absorbance spectra for the 100% cotton flannel fibers at each minute during the 15-minute analysis period. The flannel fibers'  $\lambda_{\max}$  occurred at 435.850 nm.



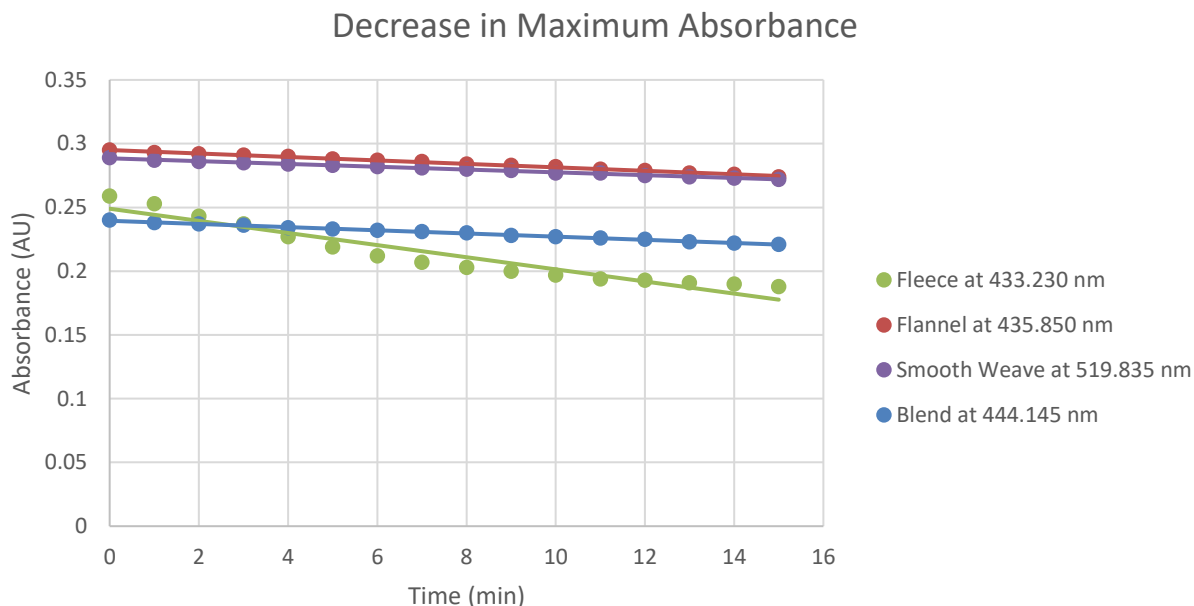
**Figure 8.** Average absorbance spectra for the 100% cotton smooth weave fibers at each minute during the 15-minute analysis period. The smooth weave fibers'  $\lambda_{\max}$  occurred at 519.835 nm.



**Figure 9.** Average absorbance spectra for the 65/35 polyester/cotton blend fibers at each minute during the 15-minute analysis period. The blend fibers'  $\lambda_{\max}$  occurred at 444.145 nm.

Over the 15-minute duration, the fleece fibers' absorbance at 433.230 nm decreased from 0.259 to 0.188 AU (absorbance units), a loss of about 27.4%. The flannel fibers' absorbance at 435.850 nm decreased from 0.295 to 0.274 AU, a loss of about 7.1%. The smooth weave fibers' absorbance at 519.835 nm decreased from  $\lambda_{\max}$  0.289 to 0.272 AU (5.9% loss), and the blend fibers' absorbance at 444.145 nm decreased from 0.240 to 0.221 AU (7.9% loss). Plotting absorbance at  $\lambda_{\max}$  versus time (Figure 10) revealed that the rate of photofading was mostly linear in all of the fibers, which is consistent with Forster et al.'s findings [4]. The black dye on the fleece fibers lost absorbance at a rate of 0.0048 AU per minute. This rate is about 4.4 times faster than that for the smooth weave fibers, whose black dye's absorbance decreased by 0.0011 AU per minute. The black dyes in the blend and flannel fibers lost absorbance at similar rates of 0.0012 AU per minute and 0.0014 AU per minute, respectively.





**Figure 10.** Plots of absorbance at  $\lambda_{\max}$  versus time for each fabric type with their respective trendlines. The trendlines for the flannel, smooth weave, and blend exhibited the best fits; their R-squared values were 0.9961 and above. The linear fit for the fleece fibers had a noticeably lower R-squared of 0.9167.

These observations suggest that fiber type by itself is not significant enough to affect photofading rates in dyed fabrics. Achieving long-lasting coloration in textiles is an endeavor involving the selection of a dye that meshes well with the textile. The strength of this interaction between the textile and dye determines the former's colorfastness, which is heavily dependent on the chemical properties of both the textile and dye. While the black dyes used in the fabrics were not identified, their general dye class can be inferred from the literature on textiles. The organic polymeric structure of polyester renders it hydrophobic and thus prevents it from being colored by most dyes since they contain hydrophilic, ionic compounds [2,14]. As a result, one of the only dye classes capable of coloring polyester is disperse dyes. Disperse dyes are named as such because they are applied to textiles as a dispersion of three main components: the dye itself (which is hydrophobic), water, and a surfactant [2]. The aqueous dispersion is applied to textiles under heat so that the fibers may swell and improve the dye's penetration of the fibers [2]. The attraction of

hydrophobic compounds to one another causes the dye molecules to separate from the aqueous dispersion and adhere to the fiber via hydrogen bonding and van der Waals forces [2]. The hydrophobic nature of the fiber-dye interactions is thought to contribute to disperse dyes' lightfastness because there is a reduced attraction to water and other polar molecules that can exacerbate photofading [15]. Despite possessing this advantage, the typical lightfastness for disperse dyes only ranks between 4 and 5 on the Blue Wool Scale (this system ranks the lightfastness of dyes on a scale from 1 to 8, with 1 being very poor and 8 being excellent), meaning fair lightfastness [15].

Cotton, in contrast, can be colored by various types of dyes because the several hydroxyl groups present in its polymeric structure make it hydrophilic. Two types that are commonly used are reactive dyes and sulfur dyes. Reactive dyes adhere to fibers by forming covalent bonds via nucleophilic substitution or addition between the dye molecules and appropriate functional groups on the fibers [2,16]. These dyes, which are water-soluble, are applied to textiles by means of an aqueous solution that contains an electrolyte [2]. The electrolyte cation neutralizes the negatively charged textile surface, allowing the dye anions to approach the fibers and bond to them [2]. The electronic stability imparted by the covalent bonds between the dye molecules and fibers is believed to explain reactive dyes' higher lightfastness, which, on average, ranks at a 6 (or very good) on the Blue Wool Scale [15]. Sulfur dyes are those that contain sulfur atoms in their molecular structures [2]. As they are water-insoluble in their natural state, sulfur dyes must be reduced to their water-soluble leuco (colorless) form in order to color textiles [2]. The dye is then oxidized back to its colored form once it has penetrated the fibers [2]. Sulfur dyes rank between 5 and 6 on the Blue Wool Scale for their lightfastness—although Sulfur Black 1 is an exception that ranks as a 7, placing it in the category of excellent lightfastness [16].

Taking the previous two paragraphs into consideration, it can be inferred that the polyester fleece fabric was most likely colored with a disperse dye and the cotton flannel and smooth weave fabrics were most likely colored with reactive or sulfur dyes. These inferences are further supported by the shapes of the absorbance at  $\lambda_{\max}$  versus time plots in Figure 10. Allen explains that dyes undergo photofading in multiple ways that have been classified into five categories called Curves I through V [8]. The fleece plot follows a Curve II pattern where the loss of absorbance is fast at first before slowing to a linear progression [8]. Curve II-type photofading occurs in dyes that contain molecular and particulate dispersions, and given the nature of disperse dyes, it is logical for dyed polyester fibers to exhibit this behavior [8]. The flannel, smooth weave, and blend plots follow a Curve III pattern where the loss of absorbance occurs at a constant rate for the entire duration of light exposure [8]. Curve III-type photofading is seen in entirely particulate (i.e. non-disperse) dyes with good lightfastness [8]. These characteristics are consistent with reactive and sulfur dyes and would be reasonable to observe in 100% cotton and polyester/cotton blends. However, it must be noted that cotton/polyester blends will also contain disperse dyes to color the polyester fibers. It could be that of the random blend fibers analyzed, most or all of them were cotton; this would cause them to display photofading behavior more akin to reactive and sulfur dyes.

#### *Speculations on Environmental Photofading Results*

Given the results of the control experiment, it would be reasonable to anticipate that photofading rates in the fabrics that were exposed to sunlight in air would have exhibited a similar overall trend of fleece having faded the fastest, with the other three fabrics having faded slower at near-identical rates. In terms of the environment comparisons, predictions of photofading rates are limited to foundation on rationale from previously published studies.

The fabric squares in the outdoor direct exposure environment would have been expected to have faded more than those in the indoor direct exposure and shaded exposure environments. As previously stated in the introduction, almost all UVB radiation from sunlight is absorbed by the Earth's atmosphere, but most UVA radiation reaches the ground and thus can come into contact with windows. A 2009 study by Duarte, Rotter, Malvestiti, and Silva [17] measured the proportions of UVA radiation that penetrated various types of glass. Depending on its thickness, smooth ordinary glass—commonly used in windows—transmitted between 51.4% and 75.7% of incident UVA radiation when located 0 cm away from a radiation source with a power of 7.4 W/cm<sup>2</sup> [17]. The window to which the fabric squares were affixed likely blocked a large portion of incident sunlight when considering the great distance between the Sun and the Earth, so photofading would have been hindered in this environment. Photofading would have been similarly limited in the shaded exposure environment due to the shade provided by trees. Tree shade has been found to have a protection factor of between 2 and 20 under various conditions, meaning that it reduces the amount of UVB radiation reaching the area by 2 to 20 times [18]. With the penetration capabilities of UVB radiation further limited by tree cover, photofading would be more difficult to initiate. However, it is also possible that not much difference in photofading rates would have been observed across these three environments when considering that the exposure period occurred primarily during winter. The average UV index for Hebron, Connecticut from November 24, 2019 to March 8, 2020 was 1.4, indicating that the intensity of UV radiation reaching ground-level was rather low, so not enough light energy may have been present to induce photofading.

For the directional exposure environments, it is expected that the fabric squares facing south would have experienced the most photofading and those facing north the least. Due to the

Earth's tilt on its rotational axis, the south receives the most sunlight during the day in the Northern Hemisphere (where Hebron and West Haven are located) [19]. The east- and west-facing fabric squares would have experienced roughly equal rates of photofading because the Sun spends similar amounts of time in the east when it rises and in the west when it sets [19].

Speculation on the results for the freshwater environment is not as simple. The literature suggests that cotton would undergo photofading faster than polyester in the presence of water, so the results may have displayed a reversed trend in photofading rates when compared to the control experiment. A 2019 study by Zambrano et al. [20] that investigated the aquatic biodegradation of cotton, rayon, and polyester yarns observed results that were consistent with Allen's discussion [8] about the impact of water on photofading. After 243 days of exposure to a "natural aquatic aerobic environment," the 100% cotton yarns had disintegrated completely while the 100% polyester yarns did not change significantly [20]. In 50/50 polyester/cotton yarns, only the polyester fibers remained as all of the cotton fibers had disintegrated [20]. Although this study focused on the biodegradation (breakdown of organic matter by microorganisms) of these fabrics, the authors still commented that degradation likely occurred in part due to nonbiological factors: The highly hydrophobic structure of polyester reduces its susceptibility to hydrolysis [20]. Another facet of polyester's hydrophobicity is its low propensity to absorb moisture, meaning that polyester fibers will not swell and open pores that facilitate oxygen penetration—and consequently, photofading—as is seen in cotton [8,20].

It is also possible that the results for the freshwater environment may have followed the same trend as the control experiment if it happens that dye chemistry contributes greater weight in affecting photofading rates than fiber type. The reactive dyes that are commonly used to color cotton have exceptionally good wash fastness (resistance to fading or running during washing)

because the dye is covalently bonded to the cotton fibers; separating the dye from the fibers therefore requires more energy [21]. The sulfur dyes that are also used to color cotton and the disperse dyes that are used to color polyester both have good wash fastness attributed to their hydrophobic nature [15]. Which factor—covalent bonding between dye and fiber or hydrophobicity—would better mitigate photofading is dependent on the chemical properties of the particular dyes that were used to color the four fabrics. Without having identified them, rendering an opinion on the expected results for the freshwater environment is difficult. This is further complicated by the established relationship between fiber type and aquatic degradation, so obtaining results for the freshwater environment at a later date would be the only path towards a more definitive answer to this question.

#### *Possibilities for Future Research*

The possibilities for future research on the photofading of dyed fibers are numerous. An obvious route to take would be for another student to complete this project by either analyzing the weekly fiber samples that were collected from the environments or starting fresh. If the environmental exposures showed promising results, then the door would open to a wide range of variables that could be investigated. This study examined fabrics that were exposed during the winter months, so an easy variation would be to change the exposure season to summer to see whether the additional sunlight hours hasten photofading to an appreciable extent. Other variations could include new environments (e.g. saltwater or burial under snow) or fabric types besides cotton and polyester. Climates that are markedly different from New England could also be studied.

Another avenue of photofading research would consist of taking further steps towards more certain elucidation of photofading mechanisms. Investigations in this realm could begin with measuring the fluorescence spectra of dyed fibers in a similar fashion as to how absorbance spectra

were measured in this study; doing so would be straightforward because MSPs also come equipped with a fluorescence mode. In terms of the usefulness of fluorescence in determining photofading mechanisms, dyes with low lightfastness have been noted to fluoresce highly due to the production of free radical species that participate in photofading [8]. This phenomenon has been observed in 2-substituted anthraquinone dyes in particular, where the dye molecule's greater dipole moment in its ground state makes it more likely to interact with a polar environment—whether that be a solution or fiber [8]. These dyes consequently undergo phosphorescent emission caused by the excited triplet state of the dye removing an electron from its environment to form an anionic radical [8].

Examining the fluorescence of dyes merely provides a preliminary idea as to how they might be experiencing photofading. To get a fuller picture, investigations would need to involve extraction of the dyes from fibers to assess their chemical nature before and after photofading transpires. Dye separation is typically performed in forensic contexts with ion-pair liquid chromatography (LC) because most dyes are charged species [22]. In ion-pair LC, the mobile phase consists of an aqueous buffer with a pairing agent that is opposite in charge to the analyte, and as the analyte moves through the separation column, it binds to the pairing agent to form an ion pair [22]. The ion pair is more hydrophobic than the dye's molecular ion and so will be retained on the column longer due to ion-pair LC being a reverse-phase chromatographic method that utilizes a hydrophobic stationary phase; this is what leads to effective separation of a dye [22]. LC techniques provide a vital advantage in structural elucidation in that they can be coupled to mass spectrometers, which determine the molecular masses of the separated ions that were eluted from the liquid chromatograph. The resulting mass spectrum can be used to figure out the structures of the separated ions, and from there, it may be possible to work backwards to the structure of the

parent dye molecule. These pathways would provide some of the most concrete experimental evidence pertaining to photofading mechanisms.

The ultimate objective of pursuing further research into the photofading of dyed fibers is to expand the available knowledge in this area and promote its applicability to forensic science. As the nature of photofading becomes less of an enigma over time, forensic examiners will be more likely to consider its impact when conducting fiber examinations because testifying to the phenomenon in court will entail fewer uncertainties regarding its scientific basis. Perhaps with enough research into the environmental effects on photofading rates, the value of photofading to forensic science may grow beyond being merely a reason to explain why a questioned and a known fiber were concluded to originate from the same source despite appearing different in color: It could potentially serve as an indicator for the amount of time that has passed since fiber evidence was deposited (assuming that known reference fibers are available for comparison). This would be a great boon to the crime scene reconstruction process, which is undertaken to illustrate the links between victim, suspect, and crime scene that are used to establish proof beyond a reasonable doubt in United States criminal trials.

## CONCLUSION

This study demonstrated that the photofading of black dyes in cotton and polyester fibers occurs linearly for the most part, and these findings were consistent with those of previous photofading studies where dyes were applied to fibers. It was observed, however, that the fleece fibers faded much faster than the flannel, smooth weave, and blend fibers, suggesting that fiber type alone is not significant enough to impact photofading in dyed fabrics. Instead, photofading behavior is mainly influenced by the strength of fiber-dye interactions, which depends on the chemical properties of the fiber and dye. When considering the lightfastness of the most probable



dye classes used to color the fabrics, these results are reasonable. A similar trend among the photofading rates of the four fabrics is expected to have emerged for the samples subjected to environmental exposure, but speculating on the outcomes of this experiment is difficult without having been able to complete the spectral analyses. It is therefore recommended that this work be continued in the future so that the impact of varying environmental conditions on photofading can be properly assessed. Further studies in the area should involve extraction and structural identification of dyes from fibers before and after photofading has taken place; this could be a promising step towards eroding the uncertainty that has surrounded photofading mechanisms since the late twentieth century. As for the forensic benefits of expanding photofading research, there are multiple. Examiners will be less likely to disregard the prevalence of photofading in fiber evidence once it is better understood, and photofading could possibly serve the crime reconstruction process as a marker of time passage.

## REFERENCES

1. Saferstein, H. (2015). *Criminalistics: An introduction to forensic science* (11<sup>th</sup> ed.). Boston, MA: Pearson.
2. Biermann, T. W., & Wiggins, K. G. (2017). Colour analysis of fibres. In J. Robertson, C. Roux, & K. G. Wiggins (Eds.), *Forensic examination of fibres* (3<sup>rd</sup> ed., pp. 179-243), Boca Raton, FL: CRC Press.
3. Hatch, K. L. (1993). *Textile science*. Saint Paul, MN: West Publishing Company.
4. Forster, A. L., Bitter, J. L., Rosenthal, S., Brooks, S., & Watson, S. S. (2017). Photofading in cotton fibers using red, yellow, and blue direct dyes during examination with microspectrophotometry (MSP). *Forensic Chemistry*, 5, 72-78.
5. Brinsko, K. M., Sparenga, S., & King, M. (2016). The effects of environmental exposure on the optical, physical, and chemical properties of manufactured fibers of natural origin. *Journal of Forensic Science*, 61(5), 1215-1227. doi:10.1111/1556-4029.13140
6. Oakes, J. (2001). Photofading of textile dyes. *Review of Progress in Coloration and Related Topics*, 31(1), 21-28. doi:10.1111/j.1478-4408.2001.tb00134.x
7. MacArthur, S., & Hemmings, F. J. (2017). Fibres, yarns and fabrics: An introduction to production, structure and properties. In J. Robertson, C. Roux, & K. G. Wiggins (Eds.), *Forensic examination of fibres* (3<sup>rd</sup> ed., pp. 1-59), Boca Raton, FL: CRC Press.
8. Allen, N. S. (1994). Photofading and light stability of dyed and pigmented polymers. *Polymer Degradation and Stability*, 44(3), 357-374. doi:10.1016/0141-3910(94)90095-7
9. Palenik, C. S., Beckert, J. C., & Palenik, S. (2015). *Microspectrophotometry of fibers: Advances in analysis and interpretation*. (Report No. 2012-DN-BX-K040). Report

prepared for the National Institute of Justice, Office of Justice Programs, U.S. Department of Justice.

10. Rastogi, D., Sen, K., & Gulrajani, M. (2001). Photofading of reactive dyes on silk and cotton: Effect of dye-fibre interactions. *Coloration Technology*, *117*(4), 193-198. doi: 10.1111/j.1478-4408.2001.tb00060.x
11. Batchelor, S. N., Carr, D., Coleman, C. E., Fairclough, L., & Jarvis, A. (2003). The photofading mechanism of commercial reactive dyes on cotton. *Dyes and Pigments*, *59*(3), 269-275. doi:10.1016/S0143-7208(03)00118-9
12. Watt, R., Roux, C., & Robertson, J. (2005). The population of colored textiles in domestic washing machines. *Science & Justice*, *45*(2), 75-83. doi:10.1016/S1355-0306(05)71632-4
13. Smith, M. J., & Thompson, K. (2017). Forensic analysis of textile degradation and natural damage. In D. Carr (Ed.), *Forensic textile science* (1<sup>st</sup> ed., pp. 41-69), Duxford, England: Woodhead Publishing. doi:10.1016/B978-0-08-101872-9.00004-2
14. Chavan, R. B. (2011). Environmentally friendly dyes. In M. Clark (Ed.), *Handbook of textile and industrial dyeing* (Vol. 1, pp. 515-561). Sawston, England: Woodhead Publishing.
15. Chattopadhyay, D. P. (2011). Chemistry of dyeing. In M. Clark (Ed.), *Handbook of textile and industrial dyeing* (Vol. 1, pp. 150-183). Sawston, England: Woodhead Publishing.
16. Chakraborty, J. N. (2010). *Fundamentals and practices in colouration of textiles*. New Delhi, India: Woodhead Publishing India.
17. Duarte, I., Rotter, A., Malvestiti, A., & Silva, M. (2009). The role of glass as a barrier against the transmission of ultraviolet radiation: An experimental study. *Photodermatology, Photoimmunology & Photomedicine*, *25*(4), 181-184.

doi:10.1111/j.1600-0781.2009.00434.x

18. Parisi, A. V., & Turnbull, D. J. (2014). Shade provision for UV minimization: A review. *Photochemistry and Photobiology*, *90*(3), 479-490. doi:10.1111/php.12237
19. Diffey, B. L. (2018). Time and place as modifiers of personal UV exposure. *International Journal of Environmental Research and Public Health*, *15*(6), 1112. doi:10.3390/ijerph15061112
20. Zambrano, M. C., Pawlak, J. J., Daystar, D., Ankeny, M., Cheng, J. J., & Venditti, R. A. (2019). Microfibers generated from the laundering of cotton, rayon and polyester based fabrics and their aquatic biodegradation. *Marine Pollution Bulletin*, *142*, 394-407. doi:10.1016/j.marpolbul.2019.02.062
21. Shang, S. M. (2013). Process control in dyeing of textiles. In A. Majumdar, A. Das, R. Alagirusamy, & V. K. Kothari (Eds.), *Process control in textile manufacturing* (pp. 300-338). Cambridge, England: Woodhead Publishing Limited.
22. Tapley, K. N. (2005). Chemical analysis of colorants. In Q. Fan (Ed.), *Chemical testing of textiles* (pp. 270-315). Cambridge, England: Woodhead Publishing Limited.