

ABSTRACT

SCHOLLER, ERIC K. Color Enhancement by Atmospheric Pressure Plasma and Novel Chemical Treatments. (Under the direction of Dr. Peter Hauser.)

APJeT® Plasma Technology is currently being investigated for use in various applications, including textiles. The main objective of the following work is to determine if fabric color can be enhanced using APJeT® Plasma Technology, a chemical treatment, or by using both in combination. The key fabric finish developed as a result of this study, is applied by chemical exhaustion. Silica nanoparticles are applied to a substrate in a high temperature (~70 °C), liquid environment. At the molecular level, as the bath temperature increases, increasingly more silica nanoparticles diffuse into the surface of the fiber giving the fabric an enhanced (darkened) quality. The finish creates a 10% measureable change in color of the fabric. By performing AATCC Test Method 61-2006 on treated samples, the washfastness of the treatment was determined. The resulting data would suggest that the darkening effect imparted by the finish becomes even darker (by an additional 5%) after laundering.

APJeT® Plasma Technology was determined to be useful for color enhancement applications; however, it is not required in order to achieve a measurable color enhancing effect on wool fabrics. By utilizing APJeT® Plasma Technology, the enhancing effect can be augmented by an additional 2%, i.e. making the fabric measurably darker by 2%, as compared to the silica nanoparticle treatment alone. In this study, fused silica nanoparticles and cationic silicone softeners were used to enhance the color of a wool substrate supplied by ITG, Inc. By using a cationic silicone softener, the fabric color was measurably and significantly darker than compared to the nanoparticle treatment, yielding an enhancing effect that was 17.6% darker based on the standard (no treatment). This treatment was 2.0% darker than the best experimental treatment. In terms of ΔE^* , only the laundered cationic silicone softener treatment produced a visually noticeable change in color. All of the other treatments produced only slight changes in fabric color.

Color Enhancement by Atmospheric Pressure Plasma and
Novel Chemical Treatments

by
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TABLE OF CONTENTS

LIST OF TABLES	vii
LIST OF FIGURES	viii
1. BACKGROUND	1
2. LITERATURE REVIEW	3
2.1 Introduction.....	3
2.2 Plasma Formation	3
2.3 Atmospheric Pressure vs. Low Pressure Plasmas.....	4
2.4 APJeT ® Plasma Technology.....	5
2.5 APJeT ® Substrate Treatment and Proposed Mechanism.....	7
2.6 Colorimetry.....	8
2.7 Light.....	8
2.7.1 Blackbody Radiator	8
2.8 Standard Illuminants	11
2.8.1 Standard Illuminant A.....	11
2.8.2 Standard Illuminant D65.....	12
2.8.3 Illuminant F.....	12
2.9 Object and Observer	13
2.9.1 The Eye	13
2.9.2 Interaction of Light with Substrate	14
2.9.3 Measuring Color	14
2.9.4 Lightness (L*).....	17
2.9.5 Measuring Color Difference	18
3. COLOR ENHANCEMENT.....	19
3.1. Chemical Fabric Finishes.....	20
3.1.1 Nanoparticle Coatings Used To Achieve Color Enhancement.....	20

3.1.2	Silicone Softeners Used To Achieve For Color Enhancement.....	20
3.1.3	Silica Nanoparticle Effects and Applications	21
3.1.4	Siloxanes and Silicas for the Color Enhancement of Inks.....	22
3.1.5	Color Enhancement by the Exhaustion of Silica Nanoparticles	25
4.	MATERIALS AND EXPERIMENT.....	27
4.1	Fabric	27
4.2	Atmospheric Pressure Plasma Unit.....	28
4.3	Chemicals.....	29
4.3	Ahiba® Texomat Bench Dye Machine.....	30
4.4	Atlas Ci3000+ Xenon Weather-Ometer ®	30
4.5	Procedure	32
4.5.1	Nanoparticle Exhaustion.....	32
4.5.2	Process Steps.....	33
4.5.3	Plasma Unit Parameters (pretreatment)	33
4.5.4	Instrumental Color Evaluation Procedure.....	34
4.5.5	Weatherometer Evaluation Procedure	35
5.	RESULTS AND DISCUSSION.....	37
5.1	Silica Treatment (Aerosil®).....	37
5.2	The Effect of Silica Treatment on Colors Other Than Black	45
5.3	Cost of Applying Aerosil® Treatment	45
5.4	Silicone Softener Treatment	46
5.5	Effect of Plasma Pretreatment	46
5.6	The Chemical Treatment's Impact on Physical Properties	47
5.7	Washfastness.....	48
5.8	Lightfastness and Weatherometer Testing.....	51

5.9 Tear Strength.....	52
5.10 The Best Performers in Terms of ΔE^*_{cmc}	52
6. CONCLUSIONS & FUTURE WORK.....	54
6.1 Conclusions.....	54
6.2 Future Work	55
LIST OF REFERENCES	56
APPENDICES	60
Appendix A: Xrite® Spectrophotometer Data	61
Appendix B: Estimated Cost of Treatment.....	63
Appendix C: Instron Data	64

LIST OF TABLES

Table 1. Aerosil® 200 Silica Concentration and L* (15 minutes)	37
Table 2. Aerosil ® 380 Silica Concentration vs. L*(15 minutes)	37
Table 3. Silica Concentration vs. L* (10 minutes)	42
Table 4. Aerosil ® 200 Treatments on Colors Other Than Black	42
Table 5. Washfastness Test Results	48
Table 6. Effectiveness of Each Treatment	50
Table 7. Weatherometer Test Results in terms of L* (Aersoil ® concentration 2.00g/L)	51
Table 8. Performance of Top Treatments by ΔE^*_{cmc}	53

LIST OF FIGURES

Figure 1. The spectral energy distribution of a blackbody radiator in the visible spectrum	10
Figure 2. CIE Chromaticity Space Illustrating Color Temperature.....	11
Figure 3. Reflection of Light.....	13
Figure 4. CIELAB (L*a*b*) Color Space (Williams)	15
Figure 5. Silica chemical structure	25
Figure 6. APJeT Laboratory Plasma Unit	28
Figure 7. Alpha TexJet Unit ^[27]	29
Figure 8. Ahiba ® Texomat Bench Dyeing Machine.....	31
Figure 9. Atlas Ci3000+ Xenon Weather-Ometer ®.....	32
Figure 10. Aerosil® 200 with a dwell time of 15 minutes at 70 °C.....	40
Figure 11. Aerosil® 380 with a dwell time of 15 minutes at 70 °C.....	41
Figure 12. Aerosil® 200 dwell time comparison plot, 15 minutes (□) and 10 minutes (◇) at 70 °C. .	43
Figure 13. Aerosil® 380 dwell time comparison plot, 15 minutes (□) and 10 minutes (◇) at 70 °C. .	44
Figure 14. Treatment Comparison (excluding laundered).....	47
Figure 15. Treatment Comparison (including laundered)	49

1. Background

Plasma is one of the four states of matter and is formed by the electrical breakdown of gaseous atoms.^[19] In order to successfully and effectively strip atoms of their electrons high amounts of energy are required. Helium, oxygen or argon gas are normally used in combination to produce a gaseous atmosphere inside a chamber which is subsequently excited by electrical energy. Plasma has the unique ability to etch the surface of or deposit particles onto the surface of a wide range of substrates, including fabrics. It is this characteristic that is the main focus of recent work regarding plasmas. However, the main scope of this research deals with plasmas ability to etch fabric and affect the color of textile substrates.

Surface etching modifies the substrate in such a way that light is reflected differently than prior to treatment. In relative terms, the surface is no longer uniform after treatment. Light is consequently reflected at various angles, and the light that reached the eye before becomes scattered and the fabric appears darker, even though no additional was added to the fabric.

The main challenges for this study stem from the fact that little is known regarding plasma's effect on color. In most cases, the effect on color is only mentioned rather than the main focus of the investigation. Since plasma technologies are relatively new, this study will be supplemented with an additional study in which silica nanoparticles will be applied to the substrate by traditional wet processing methods.

The main objective of this project is to investigate color enhancing technologies. This study will include two directions of study: 1) to evaluate APJeT ® Plasma Technology as it applies to treating textile materials and enhancing the color of those materials, and 2) to evaluate the use of silica nanoparticles in order to impart a color enhancing effect to the substrate.

This study also will attempt to ascertain its secondary objective to determine if plasma treatment imparts a significant color enhancing effect. This is useful in order to determine the viability of using plasma technology in an industrial setting.

Consequently, there are three specific questions this study will entertain in order to determine if plasma treatment is necessary to enhance fabric color: What is the effect of, 1) a plasma pretreatment, 2) a plasma pretreatment and silica nanoparticle combination treatment, and 3) a silica nanoparticle treatment on the substrate's color? By answering these questions, the effect of a plasma pretreatment will be determined. The study will use a color spectrophotometer to generate supporting evidence.

- Assess whether plasma pretreatment is necessary to enhance fabric color.
- Investigate the use of a 1) chemical, 2) plasma or 3) combination treatment to enhance fabric color.
- Outline a methodology for enhancing (darkening) fabric color.
- Assess whether the resulting treatments present a noticeable change in color or whether the difference is only measurable (i.e. $\Delta E^*_{cmc} < 2.3$).
- Determine the cost of using the Aerosil® nanoparticle treatment.

2. Literature Review

2.1 Introduction

Plasma is known as the fourth state of matter, but despite its unfamiliarity among the general public, it happens to be the most abundant state of matter in the universe. Plasma can be found in the countless star systems, and plays a vital role in thermonuclear fusion, which gives the sun its ability to provide the earth with an abundance of energy. Moreover, plasma can be found on earth, too, in a variety of places such as lightning bolts, high energy particle accelerators, in the natural phenomenon of high altitude static discharge, and in instances where a corona discharge, indicating high voltage, is observed.

Plasma was first identified and observed in a discharge (or Crookes) tube by Sir William Crooke in 1879,^[40] however, the term “plasma” was first adopted by Irving Langmuir in 1928, because of the material's fluid nature.^{[39][40]}

2.2 Plasma Formation

Plasma is formed by the electrical breakdown of gaseous atoms.^[19] In order to successfully and effectively strip atoms of their electrons, high amounts of energy are required to break the intra-atomic force exerted on the electrons by protons in the nucleus.^[40] Once electrons are stripped away, a charge is induced and the subatomic particles become ionized. The resulting ionized gas is capable of conducting electricity and responding to electromagnetic fields.^[40] Ionization of a gas, whether oxygen, helium, or argon, etc., is essential when forming plasmas. To generate plasma a gas is required, thus, plasmas cannot be generated in a true vacuum. The degree of ionization of the gas is normally measured as electron density or as free electrons per unit volume.

The degree of ionization, α , is defined as,

$$\alpha = \frac{n_i}{n_i + n_a} \quad (1)$$

where n_i is the number density of ions and n_a is the number density of neutral atoms. The electron density of the ionized gas is determined using the average charge state, Z , of the ions contained in the volume such that,

$$n_e = Z n_i \quad (2)$$

where n_e is the number density of the ionized electrons.^[12]

According to quantum mechanics, calculating the n th ionization energy involves subtracting the energy of $Z - n + 1$ electrons in the system from the energy of $Z - n$ electrons thereby measuring the total ionization energy of the system. Additionally, the total ionization of the gas can be explained in other terms by the Boltzmann Distribution, where a statistical, spatial arrangement of the subatomic particles is considered.^[12] Ionizing a gas can potentially produce a large amount of reactive species. It is these reactive species that are the main mechanism of APJeT technology.

2.3 Atmospheric Pressure vs. Low Pressure Plasmas

Atmospheric pressure plasmas are generated by electric arc discharges that are intentionally created to suppress arcing and inhibit the formation of thermal plasmas. Like atmospheric pressure plasmas, low pressure plasmas may be produced by corona discharge, dielectric barrier discharge, and microwave discharge.

Low pressure plasmas, like atmospheric plasmas, may exhibit arcing between electrodes, however, in low pressure cases the electrons produce more heat, making the system less stable. Consequently, in terms of textiles, the more stable plasma is the desirable plasma, since, in the event of arcing, the fabric substrate is less prone to surface damage.

First patented in 1999 by the founders of APJeT[®], the atmospheric plasma jet is capable of producing a chemical flux 100x greater than a dielectric barrier discharge and 1000x greater than a corona discharge. The use of helium, to prevent arcing in the absence of a dielectric cover, the gap between the unit's electrodes as well as the RF frequency used to generate the glow discharge have all been patented by APJeT[®]. The main characteristic of APJeT[®] atmospheric plasma is that the plasma is generated at temperatures less than 150 °C.

2.4 APJeT[®] Plasma Technology

APJeT[®] Plasma Technology is a concept developed at the Los Alamos National Laboratory and commercialized by a group of Los Alamos employees for the surface treatment of numerous substrates. This group which has now become its own entity is known as APJeT, Incorporated. APJeT[®] (also known as Affiliated Plasma Jet Technologies) was founded and incorporated in September 2000, by the original inventor of the technology, Dr. Gary S. Selwyn.^{[35][39]}

Since its inception, APJeT[®] has executed exclusive licenses with the University of California for all fields of work involving Atmospheric Pressure Plasma Jet (APPJ[®]) technology. The initial licenses were created in cooperation with Los Alamos National Security, LLC (LANS), the current operator of Los Alamos National Laboratory, however, the current APPJ[®] technology license consists of a broad-based, platform technology

including multiple methods, procedures, and patents for generating and using low-temperature, highly reactive, plasma generated under standard pressure conditions.^[39]

APJeT ® Plasma Technology utilizes, primarily, a helium-oxygen gas mixture to generate high concentrations of reactive species. Helium is mixed with oxygen in order to stabilize the gas at atmospheric pressure. If the gas were unstable, it would be very difficult to generate sustainable atmospheric pressure plasma at all. The objective is to generate and sustain the plasma created so that it may be used to treat the substrate.

Temperature is always a concern when dealing with textile materials, and since atmospheric pressure plasma is only known to reach a maximum mean temperature of 150 °C, according to the literature,^[3] it may be used on textiles without compromising the fabric. At atmospheric pressure, the charged species produced in the chamber can be directed and accelerated toward a substrate using electromagnetic fields. According to APJeT ® the particles bombarding the substrates surface will cause “directional etching of submicron features.”^[39] This etching capability allows APJeT’s plasma technology to be very useful in making functional and/or surface treated fabrics.

The process of generating plasma is very energetic at the molecular and atomic level. Since high voltage is being used to induce a charge, the gas will emit a glow discharge. The glow discharge is seen as light caused by the excitation of electrons to higher energy states. Although the emission of light results in a loss of energy, atmospheric pressure plasmas are usually able to compensate for this loss of energy by drawing more gas into the chamber and utilizing more electrical energy; however, the plasmas inability to sustain a glow discharge indefinitely produces additional challenges when treating a substrate material for the following reasons: 1.) higher voltages promote continued gas breakdown at standard pressure eventually making the gas unstable and 2.) arcing may occur between electrodes if foreign

particles (dust, dirt, etc.) are present on the substrate's surface. Arcing will damage the substrate by burning holes in its surface. ^{[3][39]}

Arcing is a common problem observed when dealing with atmospheric pressure plasmas and sustained glow discharges. In practice, to discourage arcing, a smooth, low-profile surface is an essential characteristic of the substrate. Rough irregular surfaces should be avoided, because uneven surface characteristics increase the chance of concentrating charged particles, much like a lightning rod on a house. ^[39]

2.5 APJeT ® Substrate Treatment and Proposed Mechanism

In the textile industry, APJeT substrate treatment is not used in production since the methodology of applying treatments is largely experimental. In the laboratory, APJeT ® fabric treatment is carried out using small fabric samples, where plasma exposure time, power, and gas content can be controlled by the operator.

In the case of color enhancement and using atmospheric plasma treatment, little is known about the mechanism of how plasma darkens fabrics; however, current thoughts surmise that, in the case of wool, the scaly surface is etched, by “directional etching,” in such a way as to alter the fiber's surface and the reflected light is, conversely, diffracted away from the eye. By diffracting light away from the eye, the fabric will show a measurable, if not visible, change in color. ^[2]

To gain a clear understanding of the purpose of color enhancement, consider the following instance: In order to adjust the color of a previously dyed garment, additional dye and processing time are required. Moreover, the inconvenience of having to re-dye a garment that has already been processed is very undesirable and costly from a dyers perspective. To

combat this undesirable characteristic, then, it would be logical to study other approaches to enhancing the color of a fabric. By studying color enhancement by plasma treatment and novel chemical finishes, a fast, effective treatment may be developed to prevent additional processing or cost of dye to be incurred on the dyers behalf.

2.6 Colorimetry

Color is a subjective experience that results from the combined interaction of a light source, the surface of an object, the response of the eye and the interpretation of that response by the brain of a person with normal color vision. In order to quantify color, these three factors can be measured. Light from a source can be quantified by measuring the spectral power distribution. An object can be quantified in terms of its reflectance spectrum, which is independent of the light source. The response of the eye and the interpretation of the brain, although not fully understood, can be defined in terms of color matching properties that represent the response of the eye to the absorption of light. ^[2]

2.7 Light

The visible spectrum consists of electromagnetic radiation of wavelengths between 380 and 780 nm. The electromagnetic spectrum is composed of a very wide range of radiation, only a narrow band of which can be detected by the human eye. ^[2]

2.7.1 Blackbody Radiator

A blackbody radiator is a description of light based on quantum mechanical concepts where an object is heated until it glows, or emits light. The brightness varies depending on the

material; however, the spectral distribution of the emitted light depends only on temperature. The ideal case is called a blackbody radiator and is described by Planck's Radiation Law.^[12]

Planck's Radiation Law describing the spectral energy density of the light emitted is defined as:

$$U(\lambda, T) = \frac{8\pi hc\lambda^{-5}}{e^{\left(\frac{hc}{\lambda kT}\right)} - 1} \quad (3)$$

Where,

λ is the wavelength, in meters

T is the temperature in Kelvin

$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$ [Planck's constant]

$k = 1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$ [Boltzmann's constant]

$c = 3.0 \times 10^8 \text{ m}\cdot\text{s}^{-1}$

Color temperature depends on the resulting spectral energy density as determined by Planck's Radiation Law and is denoted in terms of Kelvin. For example, the color temperature of a new CWF light bulb is given a color temperature grading of 6500 K. This means that if an object were heated to glow with the same color, it would exhibit a temperature of 6500 K or 6227 °C.

The solar spectrum exhibits wavelengths between 200 nm to 4000 nm. Sunlight is usually given a color temperature of 6500K. Color temperature is a characteristic of visible light and is determined by comparing its chromaticity with that of an ideal black-body radiator. Sunlight is given a range of color temperatures depending on the time of day, climate,

spectral spread, and season; the spectral color temperature range occurs between 4000 and 6000 K.^[2]

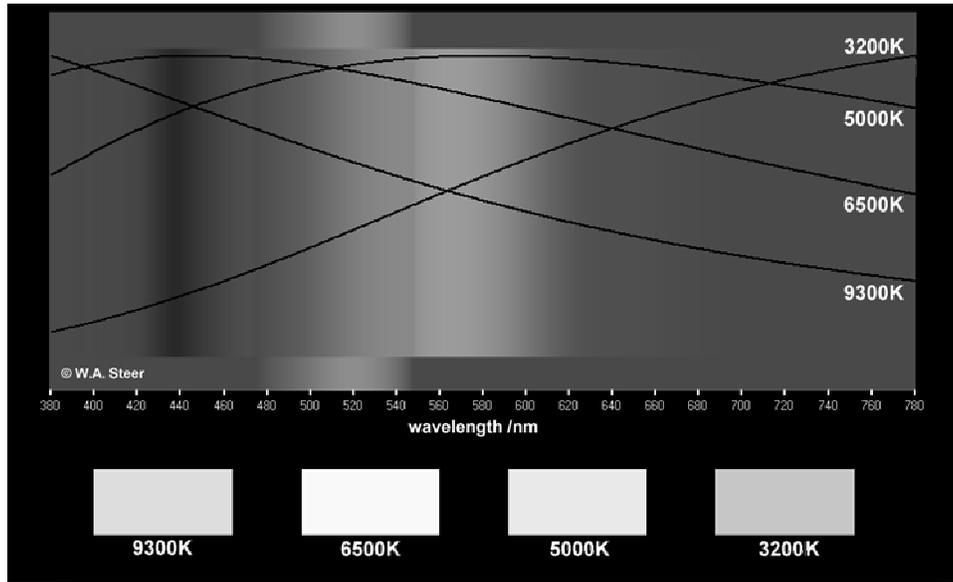


Figure 1. The spectral energy distribution of a blackbody radiator in the visible spectrum

Figure 1 illustrates the relative amounts of spectral energy at each wavelength across the visible spectrum, for a 'black body' at 3200 K, 5000 K, 6500 K, and 9300 K. To put this into perspective, a conventional incandescent light bulb emits light from a tungsten filament heated to temperature by an electric current and is represented by a blackbody radiator with a temperature below 3200 K. Figure 2 illustrates color temperature within the CIE color space.

Moreover, light from the sun, measured in space and outside of Earth's atmosphere, is represented by a black body radiator emitting light at temperatures between 5000-6500 K.

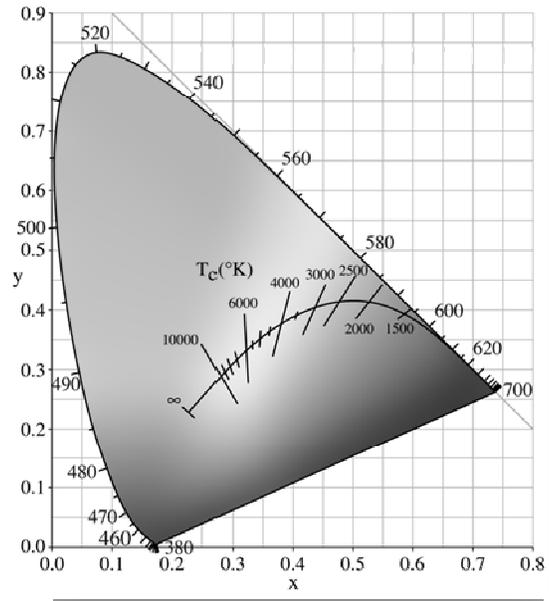


Figure 2.CIE Chromaticity Space Illustrating Color Temperature

2.8 Standard Illuminants

In the field of color science, there are several standard illuminants used for interpreting and quantifying color.

2.8.1 Standard Illuminant A

CIE standard illuminant A is intended to represent typical, domestic, tungsten-filament lighting. Its relative spectral power distribution is that of a Planckian radiator at a temperature of approximately 2856 K. CIE standard illuminant A should be used in all

applications of colorimetry involving the use of incandescent lighting, unless there are specific reasons for using a different illuminant.

2.8.2 Standard Illuminant D65

Standard Illuminant D65 is intended to represent average daylight and has a correlated color temperature of approximately 6500 K. CIE standard illuminant D65 should be used in all colorimetric calculations requiring representative daylight, unless there are specific reasons for using a different illuminant. Variations in the relative spectral power distribution of daylight are known to occur, particularly in the ultraviolet spectral region, as a function of season, time of day, and geographic location. Values for the relative spectral power distribution of CIE standard illuminants A and D65 are given in Table 1 of this International Standard ^[2], with an accuracy of six significant digits. Values are given at 1 nm intervals from 300 nm to 830 nm.

2.8.3 Illuminant F

Illuminants F1 through F6 represent various fluorescent lamps. F illuminants consist of two semi-broadband emissions of antimony and manganese activations in calcium halophosphate phosphor.

F4 is of particular interest since it was used for calibrating the CIE Color Rendering Index (CRI). F7–F9 are "broadband" fluorescent lamps with multiple phosphors, and higher CRIs. F10–F12 are narrow tri-band illuminants consisting of three narrowband emissions (caused by ternary compositions of rare-earth phosphors) in the red, green, blue regions of the visible spectrum.^[2]

2.9 Object & Observer

When measuring color, the type of material being measured is as important as the light source. Incident light measures the object's color in terms of reflectance. Reflectance refers to the fraction of incident light that is returned to the source at an interface. The light that is returned, as shown in figure 3, can be interpreted by an observer with normal color vision.

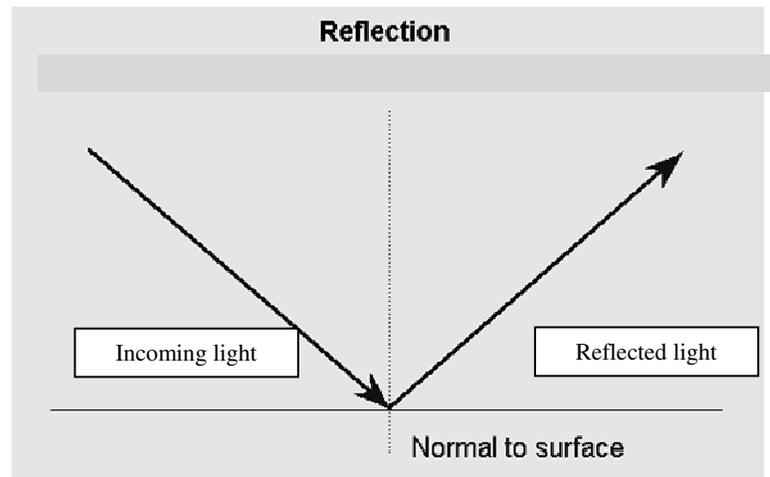


Figure 3. Reflection of Light

In some instances, light is also scattered at the interface. Light that is scattered is not measured and therefore not used to determine the object's color. Consequently, the light that is scattered cannot be interpreted as color by the observer's brain.

2.9.1 The Eye

The human eye is about 2.5 cm in length and weighs about 7 grams. Light passes through the cornea, pupil and lens before hitting the retina. The retina contains photoreceptor cells, both

rods and cones that are responsive to light. Rods are responsive to low level light, and cones are responsive to bright light and color.

After light passes through the retina, the signal impulses travel to the brain for interpretation. Human vision can only detect a narrow band the electromagnetic spectrum. The wavelengths in this portion of the spectrum measure from 380 nm to 760 nm. Variations in the ability to detect certain wavelengths of light, due to variations in photoreceptor cells, do occur and are considered to be abnormal. The interpretive information in this document is only valid for individuals with normal color vision.

2.9.2 Interaction of Light with Substrate

Any object is able to reflect light to the eye. The amount of light the eye detects determines the object's color. Any reduction in the amount of light reaching the eye will be perceived as a darkening of the object's color.

2.9.3 Measuring Color

Color can be systematically arranged into a color space. Many color spaces have been developed over the years. Since the first development of a color space, many attempts have been made to improve the perceptual uniformity of such spaces. One of the most important attempts resulted in the CIE 1984 ($L^*a^*b^*$) color space. The CIELAB color space consists of three mutually perpendicular opponent color axes denoted as L^* , a^* , b^* as shown below in Figure 4.

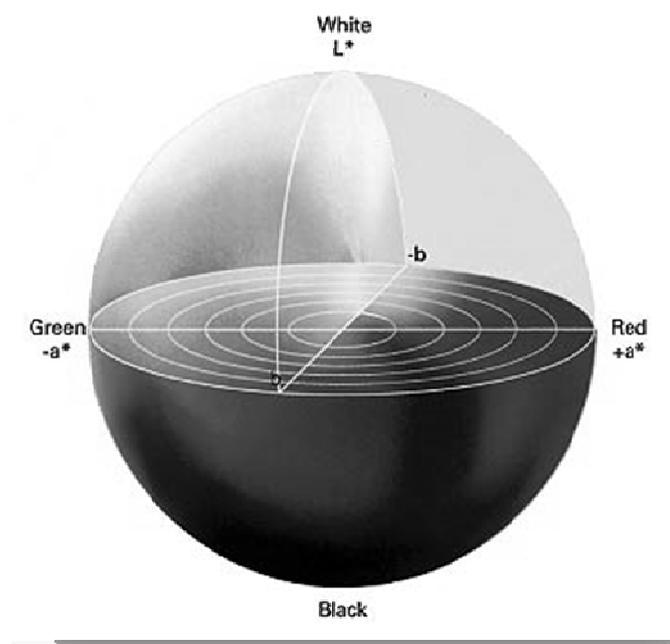


Figure 4. CIELAB ($L^*a^*b^*$) Color Space (Williams)

http://www.newsandtech.com/issues/2002/02-02/ifra/02-02_greybalance.htm

The mathematical expressions for the CIE $L^*a^*b^*$ component axes are: ^[2]

$$L^* = 116 f\left(\frac{Y}{Y_n}\right) + 16 \quad (4)$$

$$a^* = 500 \left[f\left(\frac{X}{X_n}\right) - f\left(\frac{Y}{Y_n}\right) \right] \quad (5)$$

$$b^* = 200 \left[f\left(\frac{Y}{Y_n}\right) - f\left(\frac{Z}{Z_n}\right) \right] \quad (6)$$

where,

$$f(t) = \begin{cases} t^{\frac{1}{3}} & t > \left(\frac{6}{29}\right)^3 \\ \frac{1}{3} \left(\frac{29}{6}\right)^2 t + \frac{4}{29} & \text{Otherwise} \end{cases} \quad (7)$$

X_n , Y_n , and Z_n denote the CIE XYZ tristimulus values of a reference white point. Ultimately the $f(t)$ function was divided into two domains to prevent an infinite slope at $t = 0$. The variable t was subsequently assumed to be linear below $t = t_0$ and was assumed to match the $t^{1/3}$ function at t_0 in both value and slope. In other words,

$$t_0^{\frac{1}{3}} = at_0 + b$$

$$\frac{1}{3t_0^{\frac{2}{3}}} = a$$

In these equations, b was assigned a value of 16/116. The following equations were then solved for a and t_0 :

$$a = \frac{1}{3\delta^2} = 7.787037 \quad (8)$$

$$t_0 = \delta^3 = 0.008856... \quad (9)$$

Where $\delta = 6 / 29$. The slope of the function where the two domains are joined is $b = 16 / 116 = 2\delta / 3$.

2.9.4 Lightness (L^*)

Lightness, according to the CIELAB color space, is assigned the variable L^* .

Conventionally, when L^* is discussed, it is given in terms of dL^* or the total change in L^* compared to the standard. The $L^*a^*b^*$ color system, of which L^* is a variable, is composed of three nonlinear relationships that are intended to mimic the nonlinear response of the human eye. L^* is one of these nonlinear response variables measuring lightness; the other two, a^* and b^* , model chromatic color values and make the CIELAB color space a chromatic value color space. In order to discuss a^* and b^* logically, they must be defined as lightness transformations of cone cell responses in the human eye.

Mathematically, these nonlinear transformations can be expressed in terms of the CIE XYZ tristimulus values, X_n , Y_n , and Z_n . These values, or chromaticity coordinates, mark the reference white point in the color space and depend largely on the illuminate.

The use of different illuminates can trigger different responses of the tristimulus values. This makes selecting the proper illuminate a challenge; however, selecting the proper illuminate will yield better results depending on the garment's application and the designer's preference. Conventionally, the industry standard is referred to as D65, a lamp designed to imitate daylight.

2.9.5 Measuring Color Difference

Measuring color difference in the CIELAB color space using the L* a* b* transformations requires calculating the Euclidean distance between two points in a three dimensional space. The distance metric used by the CIE for color difference is assigned the variable ΔE and is expressed as a function of dL^* da^* and db^* : Thus,

$$\Delta E_{CMC}^* = \sqrt{\left(\frac{L_2^* - L_1^*}{lS_L}\right)^2 + \left(\frac{C_2^* - C_1^*}{cS_C}\right)^2 + \left(\frac{\Delta H^*}{S_H}\right)^2} \quad (10)$$

Using the CIE interpretation of DEcmc established in 1984, a value of approximately 2.3 corresponds to “just [a] noticeable difference” in color. This ΔE^*_{cmc} value represents a threshold above which the change in color is statistically significant, meaning that the difference in color relative to the standard is enough for the observer to perceive a difference in color. This threshold will be examined later in more detail, to assess the results of this work's treatment. ^{[42][43]}

3. Color Enhancement

Color enhancement, in terms of this study, is defined as darkening the substrate's color enough to create a measurable change in lightness. Color enhancement may be described as deepening, darkening or intensifying the fabric's color to a degree that the difference is noticed by a spectrophotometer or an observer. This color difference may be perceived, but seeing a visual change in color is not currently a rigid requirement in achieving color enhancement. In order to accomplish this measurable color difference, the lightness axis of the CIELAB color space must be defined.

Consequently, color enhancement is intended to describe this darkening effect imparted to the fabric by the treatment. In quantitative terms, color enhancement can be thought of as movement along the L^* axis as defined by the CIELab Color Space.

Moving along the L^* axis has the implications of changing the lightness of the fabric's color. Increasing L^* corresponds to an increase in the color's lightness, and decreasing L^* corresponds to a decrease in the color's lightness, i.e. the color becomes darker. Changing the lightness of any fabric color is quite desirable to the dyeing industry. In many cases, fabrics are returned to the dyer to be darkened or re-dyed because of fading due to laundering or over exposure to sunlight, etc. The dyer must add more dye to the fabric, costing extra time and money.

3.1. Chemical Fabric Finishes

Chemical fabric finishes have shown promise in the area of color enhancement. There are a variety of chemical treatments, such as silicon dioxide, titanium dioxide, zinc oxide, and silicone softeners that have been successfully used to enhance fabric color.

3.1.1 Nanoparticle Coatings Used To Achieve Color Enhancement

Nanoparticles have shown promise in the area of color enhancement because they have been shown to create a measurable color difference on a variety of substrates.^{[20][21][22][23][24]}

Nanoparticles that can be used for color enhancement include silicon dioxide, titanium dioxide, and zinc oxide. The supplier of nanoparticles for this study was Evonik-Degussa®.

3.1.2 Silicone Softeners Used To Achieve For Color Enhancement

Aside from nanoparticle coatings used to enhance fabric color, silicone softeners have also been shown to be effective. Most notably, silicone softeners have been used in the past to enhance indigo dyed fabrics, like jeans and other denims.^[36] Additionally, Parvinzadeh mentions in the Journal of Surfactants and Detergents that silicone softeners can be used on sulfur dyed fabrics to enhance fabric color.^[14] It was briefly mentioned in this study that measured L* values decreased after the substrate had been treated with a silicone softener. The authors noted slight changes in measured a*, b* and C values and only minimal changes in washfastness compared to untreated samples, which indicates little change in color.^[14]

Minimal changes in hue and chroma are best since a drastic change in either is very undesirable for color enhancement. Essentially, the ideal situation would show no change in hue, chroma, and only a decrease in L^* .

3.1.3 Silica Nanoparticle Effects and Applications

Silica nanoparticles are generally used as chemical auxiliaries because of their inherent ability to act as light stabilizers on treated fabrics. Silicon dioxide, silica's chemical name, because of its ability to form a networked lattice structure, is able to absorb ultraviolet light and disperse the energy in the form of molecular vibrational and translational motion. In addition to silicas acting as light stabilizers, siloxanes, which are closely related to silicas by certain structural characteristics, are known to soften the hand of fabrics much like fabric softeners. Aside from softening the fabric, the ability of silica to act as a light stabilizer introduces an interesting ability of the fabric to which it is applied. Similar to modern stealth technology, silica, when used in a coating, can absorb light refract it or scatter it, thus diminishing the amount of light returning to the source. This characteristic decreases the color's L^* value and if significant its color signature as perceived by the observer, thus appearing darker. Silicas, more recently, have been used to enhance soil removal release properties.^[22]

When silicas are applied to a substrate they have the ability to: 1.) enhance soil removal/release characteristics, 2.) improve fabric hand, and 3.) provide color enhancement effects. The following sections look at these characteristics individually and the research currently being done them.

Silicas have been used as auxiliaries to produce coatings such as those applied to solid color optical lenses (contacts/sunglasses), oil-free pharmaceutical cosmetics, and various flame retardant compositions.^{[15][16]}

Silicas are also used widely for dry cleaning and laundering fabrics. There are several laundering products on the market containing silicas which are used to enhance color.^{[23][32]} Silicon dioxides are capable of removing soils sensitive to water and can even enhance the fabric's soil removal/release during future launderings.^[22]

Silicas can be used much like softeners in order to impart a soft hand, particularly to wool substrates.^[20] In combination with laundry detergents, silicas impart both fabric softening and anti-static control to the fabrics they are applied to. Like most inorganic particulates, silicas are used frequently for the fabric softening effect they provide and not for their anti-static feature.^[20-25]

These patents all use silica nano-clay based cleaning compositions for the softening, freshening, and deodorizing of carpet textiles.

3.1.4 Siloxanes and Silicas for the Color Enhancement of Inks

Current research suggests that polysiloxanes, as shown in Figure 5, can be applied to ink printing processes and other color related applications in order to enhance the photoprotective characteristics and lightfastness of printed inks. As noted in US Patent 6,803,395^[28] the ink containing the lightfastness-enhancing siloxane agent, effectively enhances ink color.

rejuvenate faded or worn garments as well as prevent fabric color loss when laundered. The patent goes on to mention that nanoparticles have been used to treat certain “natural fibers,” i.e. wool, silk, fur, hair, cellulose, cotton, flax, linen, and hemp, for fabric color enhancement. Moreover, it discusses in detail the addition of nanoparticles to synthetic fibers by including them in the molten polymer state before extrusion.

US Patent 6,916,774^[30] which presents a method for rejuvenating color of worn or faded fabric by applying a “color care composition” of water soluble and/or water dispersible polymers, and surfactant. The mixture, however, consists primarily of polysaccharides and not silicas.

In addition to this research, others have further investigated coatings for the color enhancement of fabrics: Researchers have been using polymers with amide functional groups (having a molecular weight of 300 to 1,000 g/mol) to enhance fabric color. According to patents filed, the polymers used are insoluble at 25°C and have a refractive index of 1.20 to 1.45. Their main claim is that this kind of mixture is capable of rejuvenating faded or worn clothing in the home.^[29]

Still other groups have focused on more on using nanoparticle-based mixtures:

US Patent 7,048,771^[31] filed by the University of California in October of 2001 claims to have enhanced the dyeing of synthetic materials. Utilizing mainly metal oxides, the nanoparticles are embedded in a synthetic polymer matrix for color enhancement.

Polyethylene terephthalate (PET) and acrylics have been main focus of this research, but the inventors have not limited the use of this method to any specific fibers or have even recommended suitable fibers for this application.

Although these inventions apply to both silica nanoparticles and color enhancement, patents utilizing nanoparticles for color enhancement of wool fabrics are nonexistent.

Silicas, which are the primary focus of this research, impart three main characteristics to their substrates: 1.) improved soil removal/release, 2.) improved hand, and 3.) color enhancement, as previously discussed. Even though silicas have been mentioned in connection with color enhancement, the following methodology is unconventional relative to commonly used application methods for fabric finishes.

3.1.5 Color Enhancement by the Exhaustion of Silica Nanoparticles

According to the triboelectric effect (series), wool is primarily a positively charged material. [37][40] Silicon dioxide forms a crystalline lattice structure that generates an overall negative charge. These characteristics make an exhaustion procedure for applying silica to wool a viable method since electronic attraction between silica and wool is present. [41] Fused silica is inherently water insoluble, which increases the particles affinity for the fabric in solution. [42]

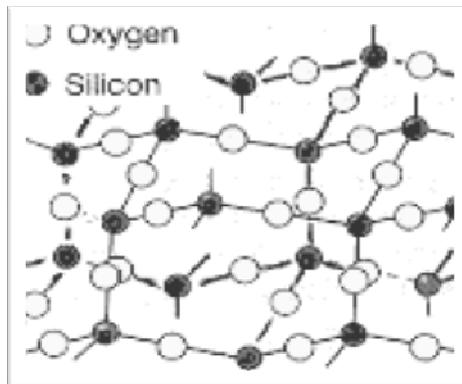


Figure 5.Silica chemical structure

Silica occurs in nature as sandstone, silica sand or quartzite. It is the starting material for the production of silicate glasses and ceramics. Silica is one of the most abundant oxide materials in the Earth's crust. It can exist in an amorphous form (vitreous silica) or in a variety of crystalline forms. The general crystalline structure for silica is illustrated in Figure 6. Often it will occur as a non-crystalline oxidation product on the surface of silicon or silicon compounds.^[42]

Fused silica, which is used in this study, is produced by carbon arc, plasma arc, or gas fired continual extrusion or carbon electrode fusion. Silica exhibits good abrasion resistance, electrical insulation, and high thermal stability.^[42] Silica is also used for its superior insulating properties. With these properties, silica is primarily used in the electronics and semiconductor industries.

4. Materials & Experiment

4.1 Fabric

The fabric for this investigation was donated by the International Textile Group (ITG). 65 yards of merino wool, confirmed by ITG, dyed and prepped for testing. Wool was the material of interest selected by ITG. The fabric was woven twill, 8.5 oz/yd². The dyes used and the dyeing process to dye the fabric were not disclosed by the company. The merino wool fabric, upon the project's inception, had already been dyed black, which was the only color investigated. Black was chosen for several reasons:

- Its widely known characteristic of fading relatively quickly with exposure to sunlight,
- In terms of the L* axis in the CIELab Color Space, true black is considered to have a low value (near zero) on the L* scale,
- Any increase in L* caused by the treatment would be immediately and easily noticeable, in addition to being measurable. The following section outlines this study's objectives:

After the fabric arrived, samples were cut into 9 x 9" squares. Later, sample sizes were adjusted to 5 x 5" squares to better fit the target liquor ratio for the Aerosil ® chemical treatment. The fabric was measured to determine the initial colorimetric values. The reflectance of the fabric was measured using an XRite Spectrophotometer Model XP64 which is capable of both the 2° and the 10° standard observer. The 10° standard observer was used for color measurements in this study. The low a* and b* values indicate that the fabric is neutral black

In addition to black, a lighter color was given the Aerosil® treatment. The fabric sample was treated and tested under the same conditions as the black wool sample.

4.2 Atmospheric Pressure Plasma Unit

The installation of the APJeT® unit, APPR Model 300-13, in the College of Textiles was completed in September of 2007. Figures 7 and 8 include an R&D scale plasma unit as well as a larger scale pilot plant plasma unit, both manufactured by APJeT®. At the beginning of 2009, the College of Textiles had both an R&D unit and a pilot plant unit. Model 300-13 is a lab scale model, where the substrate is placed on the metal, horizontal electrode. The metal electrode then traverses the plasma volume automatically by motor drive. The unit measures 14 inches by 38 inches and can perform for both an in-situ process or downstream production.

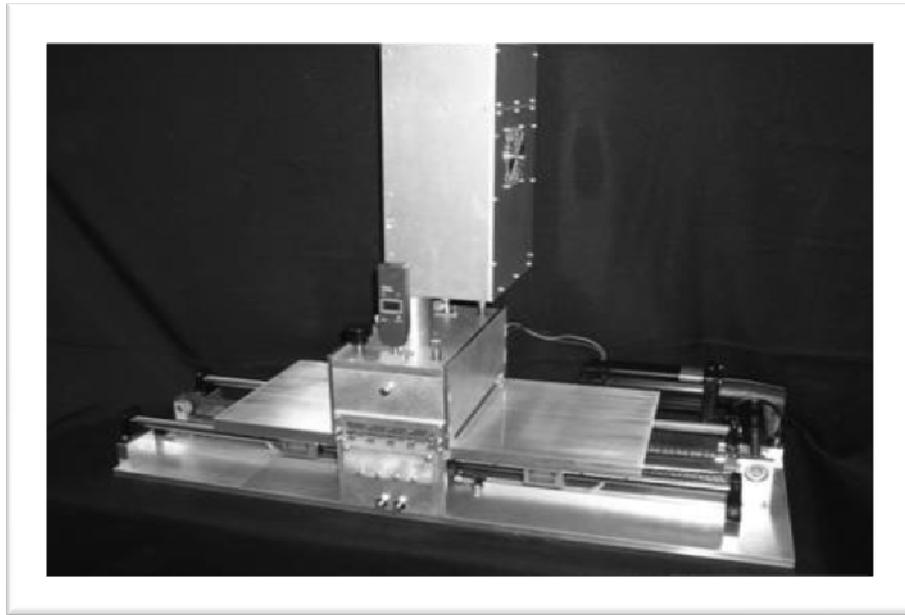


Figure 6. APJeT Laboratory Plasma Unit



Figure 7. Alpha TexJet Unit ^[27]

4.3 Chemicals

Silica was the primary chemical used in this research. Two different sized nano particulates were obtained from Evonik Degussa ®, specifically, Aerosil ® 200 and Aerosil ® 380. Aerosil ® 200 is the larger particle of the two, having a surface area of 200 m²/g and a diameter of 12nm on average. Similarly, Aerosil ® 380 has a surface area of 380 m²/g and a diameter of 7nm on average. These particles were chosen because of their recommended use in coating compositions on both hard and soft surfaces. The Aerosil ® brand was also chosen for its water soluble properties, since most silicas do not dissolve in water easily.

A cationic silicone softener supplied by Dystar under the trade name Silfin SBS was also used during the course of this research. Silfin SBS is described as a cationic silicone macroemulsifying agent. In addition, a wetting agent supplied by the Clariant Corporation under the trade name Leonil EH was also used.

4.3 Ahiba® Texomat Bench Dye Machine

This dyeing machine from Ahiba® was used primarily for applying the nanoparticle finish. It is typically used for exhaust dyeing in a small scale. The Ahiba was chosen because of its ability to treat several small samples at once. It is also capable of treatments that require higher liquor ratios. The Ahiba has positions for 12 beakers (400 ml each), and the unit has a temperature range of 20 to 105°C. This unit is not necessary in order to apply the finish; the finish was also successfully applied using a 2L beaker, a hot plate, and thermometer. For an industrial setting, a jet or winch beck machine may be used. The Ahiba ® Texomat Bench Dyeing Machine is shown in Figure 9.

4.4 Atlas Ci3000+ Xenon Weather-Ometer ®

The Ci3000+ Weather-Ometer ® and Fade-Ometer ® is used to determine the durability of certain materials intended primarily for outdoor use. The Atlas exposes small fabric samples to artificial sunlight, ambient temperatures, rain, snow, and other types of weather. The 3000® Series is approved for use in many fields including textiles, paints & coatings and plastics. In this study it was used to expose the treated fabric to 20 hours of simulated sunlight according to AATCC Test Method 16-2003. Sunlight was simulated using a xenon arc lamp. Instrumental color measurement was used for the assessment of the color change of the exposed treated fabric. The weatherometer is calibrated using a xenon reference lamp supplied by Atlas. The Atlas Ci3000+ Xenon Weather-Ometer ® is shown in Figure 10.

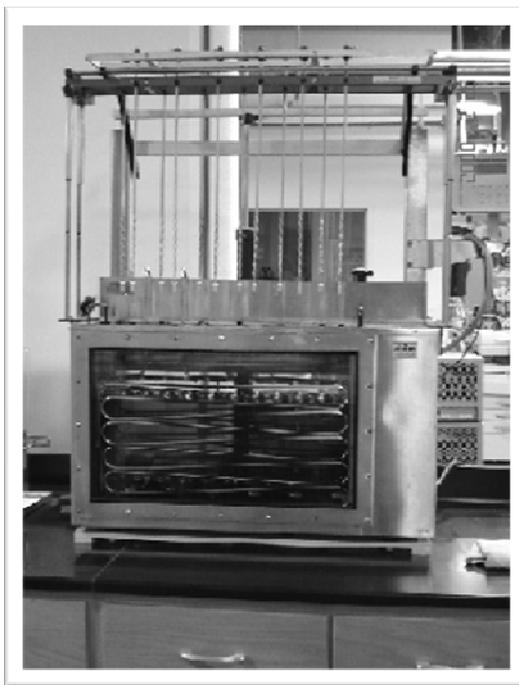


Figure 8. Ahiba ® Texomat Bench Dyeing Machine



Figure 9. Atlas Ci3000+ Xenon Weather-Ometer ®

4.5 Procedure

4.5.1 Nanoparticle Exhaustion

An initial concentration of 1.00g/L Aerosil® was used and a wetting agent was added at 2.00 g/L, which was enough to wet out the fabric. Different concentrations of Aerosil ® were used in order to determine the optimum level of color enhancement. The wetting agent remained constant through the different concentrations tested. The following section outlines the individual process steps taken.

4.5.2 Process Steps

- Fabric was added, X g/L SiO₂ (Aerosil ®), and 2.00 g/L wetting agent following an all-in method. The liquor ratio, depending on the sample, ranged between 10 and 15 to 1.
- The samples were added to a beaker (fabric and chemicals) and placed in the Ahiba ® Texomat bench dyeing machine.
- After the beakers had been mounted, the bath temperature was increased at a rate of 3.0 °C/min to a maximum temperature of 70°C.
- The dwell time at 70 °C was 10 to 15 minutes.
- After time 15 minutes, the samples were removed from the beakers and rinsed immediately with room temperature water.
- The samples were allowed to air dry for a day.

To prevent the loss of dye from the fabric to the bath due to the simultaneous application of the chemical finish, the bath temperature was set to a maximum temperature of 70 °C, which is slightly below the minimum dyeing temperature required for most acid dyeings. When dealing with Aerosil®, pH is not normally controlled since the particles are soluble only in large amounts of water.

4.5.3 Plasma Unit Parameters (pretreatment)

A random selection of samples was selected to include in the plasma pretreatment procedure. Each sample was exposed to plasma for 0.5 sec/in² which was approximately 40 seconds per sample. Each sample was placed individually on the horizontal metal electrode of the plasma unit. The gas composition in the plasma chamber consisted of 40 SLPM (standard liters per

minute) helium and 0.4 SLPM oxygen. This composition is standard and was used throughout this study. The gas mixture was selected based on particular gas flow rates for the plasma unit. The plasma jet's settings were selected based on the optimum stability of the plasma. The power required by the unit is set to 500 W at a radio frequency (RF) of 13.5 MHz. The space between the electrodes, or gap, measured 0.088 mm.

4.5.4 Instrumental Color Evaluation Procedure

The colorimetric properties of each of the samples studied were systematically evaluated using a Portable Sphere XRite SP64 Spectrophotometer. Although a visual change in color was perceived, the samples were not visually assessed in this study due to the subjective experience of color. The reflectance of all the samples was measured using the following steps based on the AATCC Evaluation Procedure 6:

All the samples were conditioned for 24 hours at 70 °F and 65% RH according to evaluation procedure.

Each sample was folded until four layers were obtained. This was done to ensure that there is no interference in the measurement due to intrusion of unwanted reflecting light.

Measurements were taken with specular component excluded and UV excluded. The colorimetric data were calculated using CIE Illuminant D65 and the 10° standard observer. Each measurement was based on an average of 5 readings per sample. The samples were compared and assessed by their measured values. The measured values were then used to calculate color differences.

4.5.5 Weatherometer Evaluation Procedure

- Samples were tested for weathering properties. The weatherometer described earlier was used and calibrated according to AATCC TM16-2003, AATCC TM169, and ASTM G155. The unit was calibrated using a Xenon arc lamp as a D65 reference light source.
- The following instrument settings were used for all samples tested throughout the course of this study:
 - Time: 20 hrs (395.92 kJ)
 - Irradiance: 0.55 w/m² at 340 nm
 - Rack Temperature(black panel): 54 °C
 - Chamber Temperature: 34 °C
 - Relative Humidity: 79%
 - Ground Level Filters: borosilicate/borosilicate
- Samples were loaded into the testing slides as required by the AATCC technical manual. After 20 hours of exposure, the samples were re-evaluated for L*.

The results given by the samples exposed to artificial sunlight in the weatherometer were very interesting. The samples were exposed to 20 hours of sunlight under "Miami" standard conditions, which are 34 °C (average Miami annual high) and 79% relative humidity. The samples were exposed to 395.92 kJ of energy per square meter and an irradiance of 0.55 W/m² at 340 nm. The filters used to simulate ground level light were composed of borosilicate.

4.5.6 Washfastness & Tear Strength Evaluation Procedure

Additionally, samples were evaluated to determine washfastness properties and tear strength followed the proposed treatment.

For washfastness properties, samples were laundered according to AATCC Test Method 61-2006. According to the test method, fifty steel balls are put in a canister with the test sample and laundered for 45 minutes. The reflectance of the samples was subsequently measured to determine any changes in color.

Tear strength was evaluated according to ASTM Test Method D226. The samples were tested for tear strength using an Instron machine located in the College of Textile's Physical Testing Lab. See Appendix D for detailed information regarding the results obtained from tear strength testing. ASTM Test Method D226 is a tensile tear test in which the test sample is subject to a tensile force to the point of rupture. The Instron subsequently measures the minimum amount of force required to tear the test sample.

5. Results and Discussion

A total of 350 samples were treated and evaluated as part of this study, of which 25% of the samples were pretreated with plasma. 50% of the samples were treated with Aerosil®, and 25% of the samples were treated with a silicone softener. After each treatment the samples were measured to determine which color enhancement method provided the best results.

5.1 Silica Treatment (Aerosil®)

Table 1. Aerosil® 200 Silica Concentration and L* (15 minutes)

Particle	Sample	Concentration (g/L)	Average L*
Aerosil® 200	Control	0	14.62
	1	1.50	14.95
	2	1.75	14.10
	3	2.00	14.29
	4	2.25	14.38
	5	2.50	14.04

Table 2. Aerosil ® 380 Silica Concentration vs. L*(15 minutes)

Particle	Sample	Concentration (g/L)	Average L*
Aerosil® 380	Control	0	14.62
	6	1.50	14.27
	7	1.75	14.49
	8	2.00	14.48
	9	2.25	14.35
	10	2.50	14.28

Tables 1 and 2 show the average colorimetric results obtained when applying Aerosil® treatment to the fabric. It can be seen that, both types of Aerosil® darken wool fabric in comparison to the lightness values of the fabric without treatment. The samples treated with Aerosil ® 200 show on average, slightly lower lightness values compared to Aerosil ® 380 for each of the concentrations in the study. This may be due to the fact that Aerosil ® 200 is the larger particle (12 nm compared to 7 nm for Aerosil® 380). The surface of the substrate will be more heterogeneous (i.e. not as fine as the smaller particle). The larger, irregular surface can more effectively scatter light off the fabric's surface compared to the smaller finer particle surface. Producing an irregular surface is more conducive to scattering light, and thus enhancing fabric color. For purposes of calculation, the absolute value was used.

For Aerosil® 200, there are two measurements that are statistically significant. The first is measurement number two, where the Aerosil® concentration was 1.75 g/L and the corresponding L* value was 14.10. The second measurement that is statistically significant is measurement number five, where the Aerosil® concentration was 2.50 and the corresponding L* value was 14.04.

For Aerosil® 380, there are also two measurements that are statistically significant. The first is measurement number six, where the Aerosil® concentration was 1.50 g/L and the corresponding L* value was 14.27. The second measurement that is statistically significant is measurement number ten, where the Aerosil® concentration was 2.50 g/L and the corresponding L* value was 14.28.

Moreover, if the finer particle (Aerosil® 380) is considered, a more homogeneous coating on the surface of the substrate can be accomplished simply because the smaller particles can be packed together more efficiently to create a more uniform surface and coating. In terms of the amount of light reflected, the more homogeneous surface is less conducive to scattering

light. The control sample is incapable of scattering light having a uniform surface. This is why the Aerosil® treatment is applied; it is applied in order to increase the fabric's ability to scatter light by making the surface more irregular at the microscopic level.

Figure 11 illustrates the values 1-5 shown in Table 1. Mathematically the plot indicates a minimum point occurring at 1.75 g/L silica and a maximum point occurring at 2.25 g/L silica. The absolute minimum value for the function yields an L^* value of 13.96 which occurs at 2.50 g/L silica. The maximum shade change given by the tabulated data points is 5% darker on average compared to the untreated samples. The dotted line on the plots represents the untreated standard ($L^* = 14.62$).

On the other hand, the samples treated with a concentration of 1.5 g/L show higher L^* values. This might be due to a more uniform aggregation of particles only achieved at lower concentrations. In order to darken the fabric more particles are required in order to make the surface less uniform.

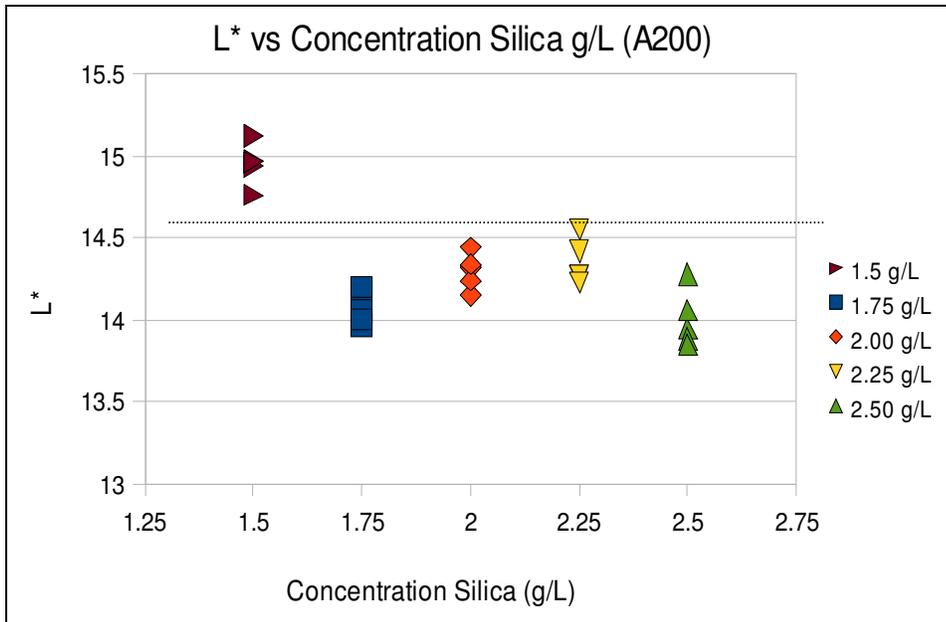


Figure 10. Aerosil® 200 with a dwell time of 15 minutes at 70 °C

In the case of Aerosil® 380, a similar plot (although not as defined as the previous plot) can be generated from the data gathered. Figure 12 illustrates values 6-10 from Table 2.

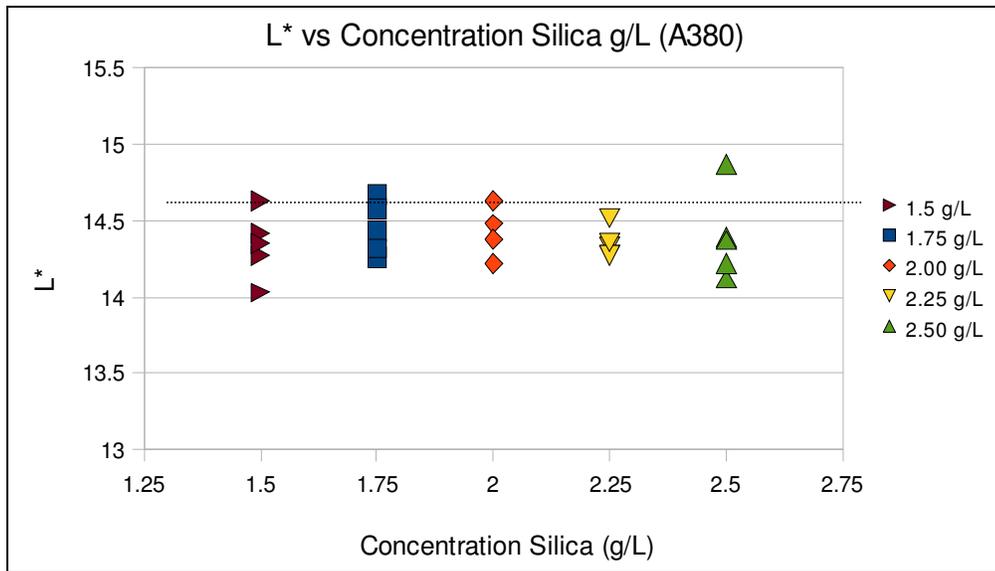


Figure 11. Aerosil® 380 with a dwell time of 15 minutes at 70 °C

The results shown in Tables 1 and 2 represent samples treated with silica for a dwell time of 15 minutes. On the other hand, Table 3 shows the results obtained when the dwell time was shortened to 10 minutes at a constant temperature. The L* values in this set of samples are much lower than the values shown in Tables 1 and 2.

Table 3. Silica Concentration vs. L* (10 minutes)

Particle	Sample	Concentration (g/L)	Average L*
Aerosil ® 200	Control	0.00	14.62
	1	1.50	14.20
	2	1.75	13.27
	3	2.00	13.36
	4	2.25	13.48
	5	2.50	13.92
Aerosil ® 380	6	1.50	13.79
	7	1.75	13.55
	8	2.00	13.63
	9	2.25	13.50
	10	2.50	13.43

Table 4. Aerosil ® 200 Treatments on Colors Other Than Black

Sample	Untreated L*	Aerosil ® Treated L*
1	46.84	45.35
2	46.19	45.64
3	47.00	45.93
4	46.25	45.34
5	46.83	45.76

Notice that the lightness values obtained with a shorter treatment time are approximately 5% lower compared to the values shown in Tables 3 and 4. Overall, by shortening the dwell time, the total shade change from the untreated standard ($L^* = 14.62$) is an average of 10%. Refer to Appendix A for additional information.

Figures 13 and 14 illustrate the difference in L^* as a result of changes in dwell time. Each point represents the mean value for the corresponding dwell time and bath concentration, and the dotted line represents the measured L^* value of the untreated wool fabric. Figure 13 is for the Aerosil® 200 treatment and Figure 14 is for the Aerosil® 380 treatment. The dotted line in each of the following plots represents the untreated standard.

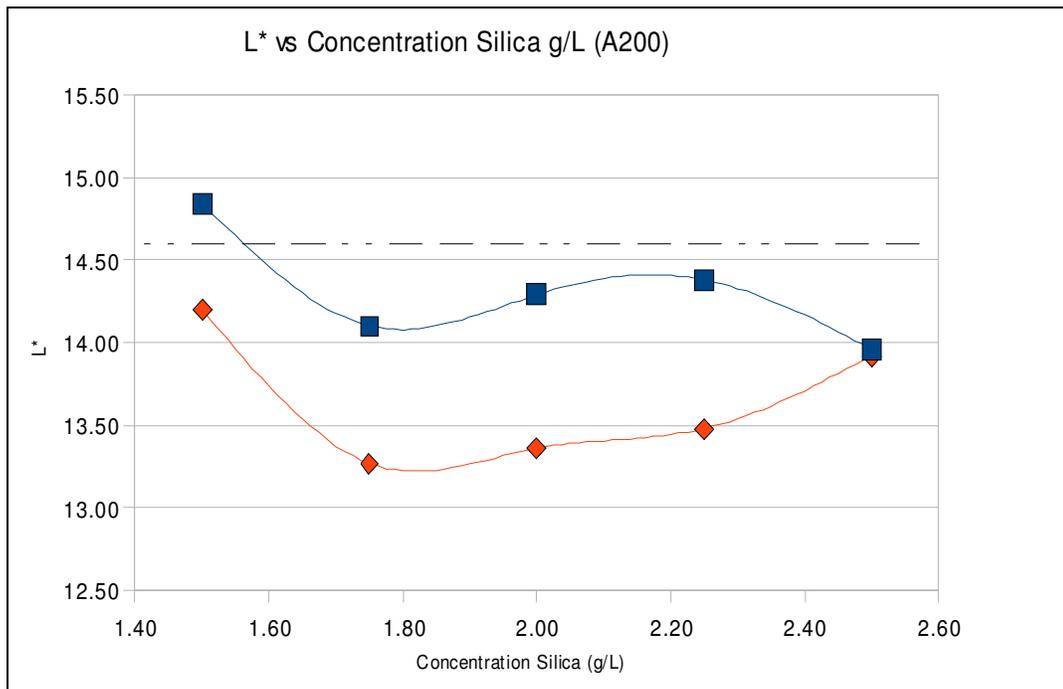


Figure 12. Aerosil® 200 dwell time comparison plot, 15 minutes (\square) and 10 minutes (\diamond) at 70 °C.

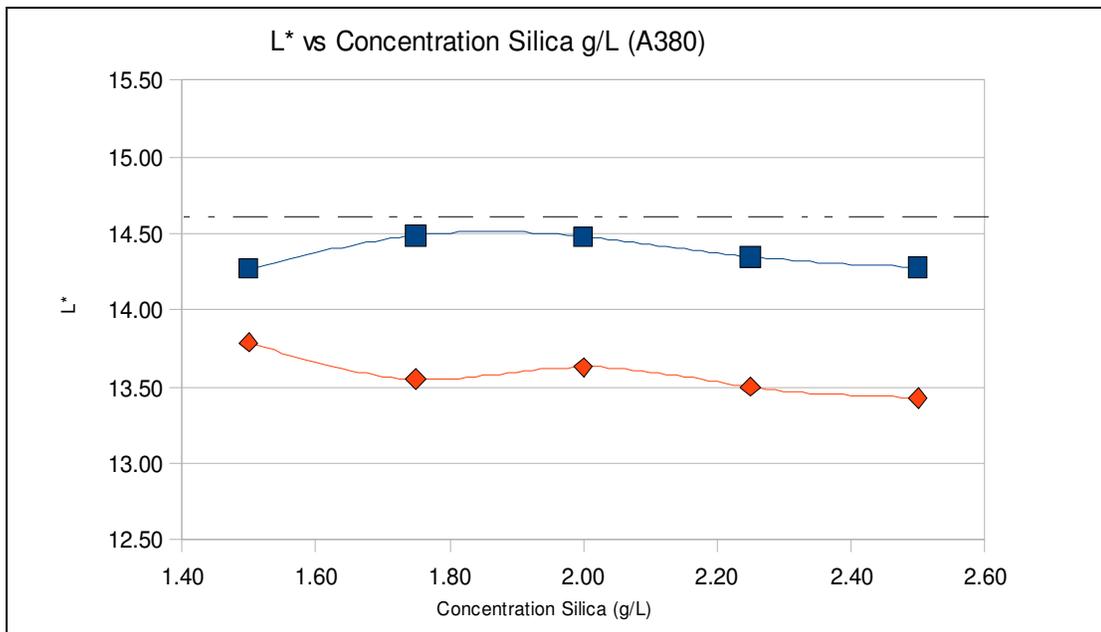


Figure 13. Aerosil® 380 dwell time comparison plot, 15 minutes (□) and 10 minutes (◇) at 70 °C.

The best dwell time for the Aerosil® (both the 200 and 380) fabric treatment, as a result of this study, is 10 minutes with a maximum bath temperature of 70 °C. This conclusion was reached because the ten minute dwell time gave a better result than the fifteen minute dwell time. The bath temperature was not varied throughout the study of the Aerosil® treatment since exhaustion for acid dyes on wool occurs normally at temperatures slightly above 75 °C. Using lower temperatures (i.e. those less than 60 °C) may not apply the treatment effectively enough and were not investigated. With a dwell time 10 minutes at 70 °C, a noticeable difference in L* can be achieved.

5.2 The Effect of Silica Treatment on Colors Other Than Black

In order to determine the limitations of Aerosil® treatments, fabric of a lighter color was given the Aerosil® chemical treatment. The absolute change in shade, in terms of ΔL^* , was consistent and in line with the treated black wool samples; however, the perceived difference in shade was not as noticeable. The perceived difference (i.e. the change in color the eye sees), was not as noticeable because the L^* value of the lighter color is comparatively higher on the L^* scale, and since the treatment provides a constant change in L^* , the overall percent change is not as significant as with the darker color which is lower on the L^* scale.

If we consider ΔL^* as a function of the finish and thus a consistent value, then the percent shade change will be less significant for colors with a higher L^* value and more significant for colors with a lower L^* value. For this treatment to be effective the initial fabric L^* value must be low in order to get the best results possible from the Aerosil® treatment.

5.3 Cost of Applying Aerosil® Treatment

Aerosil® costs approximately \$113.50/kg (\$51.56/lb). In order to treat 91 meters (100 yards) of fabric with the Aerosil® chemical treatment (assuming an optimum concentration of 1.75 g/L), 3.36 kg (8.5 lbs) of Aerosil® is required. To apply the finish at this concentration, a cost of \$3.81 per square yard is incurred. Refer to Appendix B for additional information

5.4 Silicone Softener Treatment

In order to compare the Aerosil® treatment with currently used methods for making fabric color appear darker, a cationic silicone softener was used to exhaust treat several samples at room temperature. Using a cationic silicone softener is a widely accepted method among dyers for darkening the color of certain fabrics. ^{[13][37]}

The softener was added to the treatment solution with a concentration of 3% owb. This concentration was selected because softener is traditionally applied at this concentration. As a result, the silicone softener yielded an average L* value of 12.7.

Compared to the Aerosil® treatment, the silicone softener treatment remains the more effective treatment, reducing the L* by nearly 14%, on average. This is 4% lower than the best Aerosil® treatment method.

5.5 Effect of Plasma Pretreatment

The primary objective of this study was to assess if plasma pretreatment was even necessary for the color enhancement of fabrics. Based on this study, plasma pretreatment has shown to be beneficial for the color enhancement of wool fabrics. Figure 15 shows the effect a plasma pretreatment has on the value of L* before the Aerosil® treatment is applied.

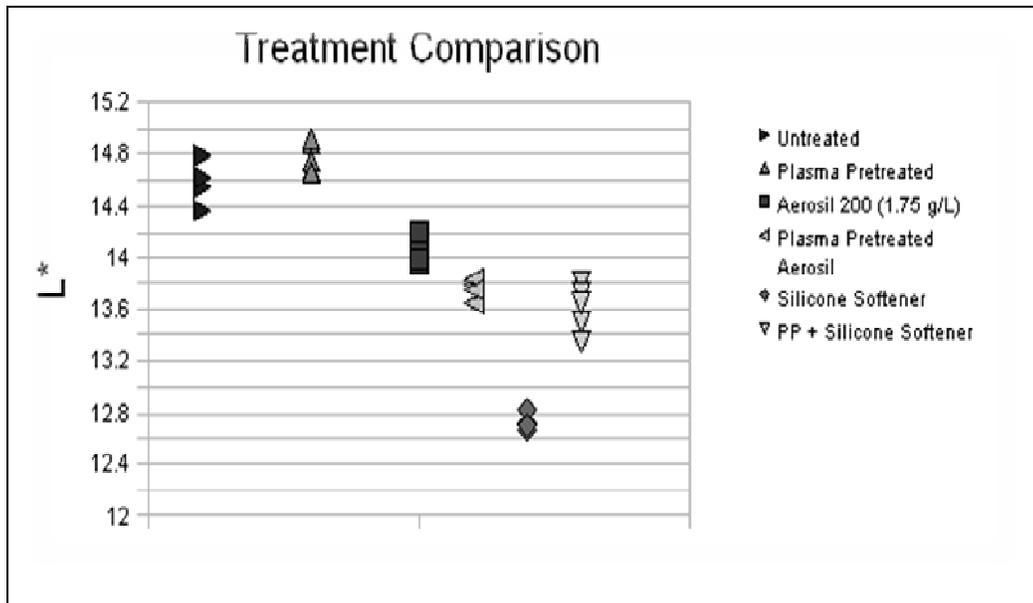


Figure 14. Treatment Comparison (excluding laundered)

The data suggests that the use of a plasma pretreatment decreases the measured L* value by about 2.0% when compared to the Aerosil® 200 (the “best” Aerosil ® treatment) treatment alone (which was 5% darker relative to the untreated standard). Using plasma as a pretreatment for this process, increases the strike rate of silica nanoparticles which increases the fabric's absorbance of the particles and allows for better light scattering.

The plasma exposure parameters for each sample remained constant throughout the study. They are: fabric exposure rate of 0.5 in²/sec, treated at a power of 500 Watts, and a gas content of 0.4 SLPM (Standard Liters per Minute) oxygen, and 40 SLPM helium.

5.6 The Chemical Treatment's Impact on Physical Properties

Washfastness, lightfastness, and tear strength were tested to determine the durability of the

treatment and resulting strength of the fabric. The following subsections detail these results and discuss the impact of each test on the Aerosil® treatment.

5.7 Washfastness

Washfastness of the silica exhaustion treatment was evaluated by AATCC Test Method 61-2006. The samples of utmost interest in the case of both particle types, Aerosil® 200 and Aerosil® 380, are samples 2,3,4 and 7,8,9, respectively, since these are the samples showing the most dramatic change in L* shown by the minimum point in Figure 16. These values are tabulated in Table 5 below.

Table 5. Washfastness Test Results

Particle	Sample	L* Before Laundering	L* After Laundering
Aerosil ® 200	2	13.27	12.68
	3	13.36	12.45
	4	13.48	12.70
Aerosil ® 380	7	13.55	12.72
	8	13.63	12.78
	9	13.50	12.83

Note the laundered L* values in Table 5. When compared to the unwashed untreated standard ($L^* = 14.62$), these values are nearly 15% lower on average. If the laundered L* values are compared to the chemically treated samples, they are 5% lower on average. Overall, the laundered samples, both silica treated and untreated, showed a consistent drop in L* after laundering. The laundered untreated sample summary shown in Table 5 indicates that a fraction of the decrease in L* observed is in part to the dye itself and not due to the

treatment. This control sample decreases in L^* in part to the laundering process, because the configuration and aggregation of the dye molecules within the fabric may be effected by the water temperature, surfactant, or the agitation inherent to laundering. This shows that the silica treated and untreated L^* values will decrease proportionately when laundered.

By laundering both the treated and untreated sample it was shown that the Aerosil® treatment dramatically improves with laundering. Even after multiple launderings (by AATCC Test Method 61), the Aerosil® treatment becomes 10% darker, on average. With the additional agitation and heat supplied by the laundering process, the nanoparticles can become more diffuse within the fabric. Consequently the fabric increases its ability to scatter light more effectively because the particles spread out and create a system more conducive to scattering light. Thus the overall L^* value decreases.

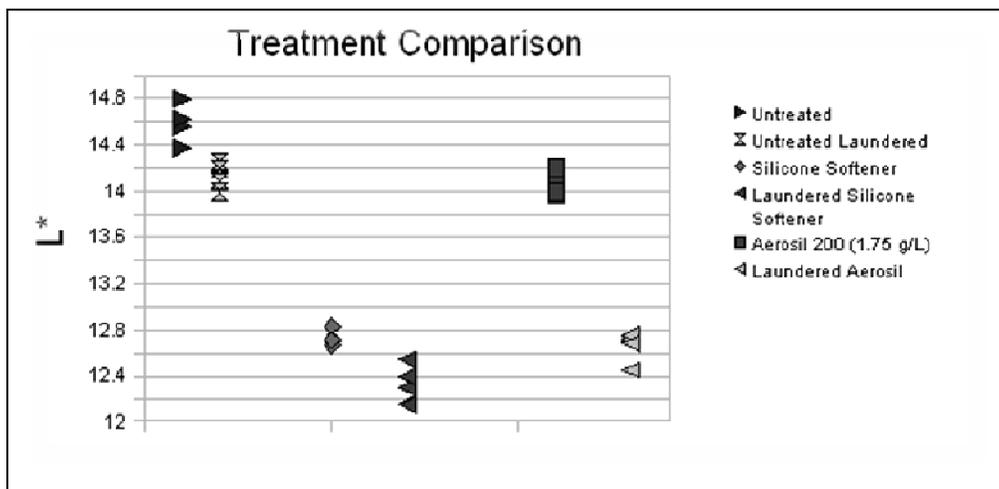


Figure 15. Treatment Comparison (including laundered)

Table 6 organizes the treatments discussed above in terms of percent difference from the untreated standard which had an average L^* value of 14.62.

Table 6. Effectiveness of Each Treatment

Treatment	% Change Control
Control	0.00
Laundered Control	-3.45
Aerosil ® 380	-4.05
Aerosil ® 200	-4.48
Plasma Pretreated + Aerosil ® 200	-6.28
Silicone Softener	-13.90
Laundered Aerosil	-14.37
Laundered Aerosil – Plasma	-16.17
Silicone Softener + Plasma Pretreatment	-16.30
Laundered Silicone Softener	-17.23

In Table 6, negative values indicate a lower L* value. If the % difference were positive, this would indicate an increase in L,* which would mean the fabric became lighter. Negative values mean the fabric became darker in color.

5.8 Lightfastness and Weatherometer Testing

Table 7 Weatherometer Test Results in terms of L* (Aerosil® concentration 2.00g/L)

Sample	Untreated	Aerosil Treated	Plasma Pretreated
Untreated	14.62	14.10	14.20
Aerosil® 200	14.90	13.62	14.70
Aerosil® 200	14.87	13.65	14.71
Aerosil® 200	14.90	13.59	14.68
Aerosil® 200	14.92	13.64	14.69
Aerosil® 200	14.92	13.63	14.67
Aerosil® 380	14.90	13.60	14.72
Aerosil® 380	14.90	13.60	14.68
Aerosil® 380	14.91	13.64	14.67
Aerosil® 380	14.89	13.64	14.70
Aerosil® 380	14.90	13.60	14.70

From the data gathered in this study, the Aerosil® treated samples become darker when exposed to sunlight, and the plasma exposed and treated samples do not. It is evident that pretreating the fabric with plasma influences the Aerosil® treatment directly or the fabric's ability to maintain the treatment when exposed to sunlight. Although the plasma pre-treatment procedure increases the fabric's uptake of silica, it causes the dye to degrade more rapidly, creating free radicals, when exposed to sunlight. The weatherometer test results are shown in Table 7.

Considering the results of this study, the Aerosil® treatment alone yields the best result both

in terms of lower L^* and maintaining the decreased L^* value when laundered and exposed to sunlight.

5.9 Tear Strength

Under standard conditions (STP), treated (Aerosil® 200 or Aerosil® 380) and untreated (UT) wool samples were tested for tear strength according to ASTM Test Method D2261. See data in Appendix C.

Note that the Aerosil® 200 (A200) finish has the greatest effect on fabric tear strength, independent of concentration. Coincidentally, this treatment also produces the best color enhancing effect.

As shown, the silica nanoparticle finish slightly weakened the fabric's inherent rigidity and strength; however, the overall weakening effect on the fabric falls within 3 standard deviations of the untreated mean peak load. This is statistically insignificant. Based on these results, the chemical treatment can be applied without significant loss of fabric tear strength.

5.10 The Best Performers in Terms of ΔE^*_{cmc}

If the bottom three treatments in Table 7 are considered to be the “best” treatments as a result of this study, Table 8 shows the color difference of these three treatments in terms of ΔE^*_{cmc} . Moreover, if the CIEL*a*b* calculation of 1984 is considered, and if a threshold value of at least 2.3 ΔE^*_{cmc} is considered; only the “laundered silicone softener” treatment, has been shown to produce a noticeable change in color. That is to say, only this treatment produces a visual color change.

Table 8. Performance of Top Treatments by ΔE^*_{cmc}

Da^*	Db^*	DE_{cmc}	Treatment
0.09	-0.20	0.74	Laundered Aerosil® - Plasma Treatment
0.01	-0.17	0.85	Laundered Aerosil® - Plasma Treatment
0.00	-0.20	1.52	Laundered Aerosil® - Plasma Treatment
0.08	-0.01	1.40	Laundered Aerosil® - Plasma Treatment
0.03	-0.19	1.31	Laundered Aerosil® - Plasma Treatment
0.04	0.13	0.95	Plasma Pretreated Silicone Softener
0.04	0.29	1.08	Plasma Pretreated Silicone Softener
-0.05	0.30	1.31	Plasma Pretreated Silicone Softener
0.02	0.14	1.05	Plasma Pretreated Silicone Softener
0.02	0.14	1.12	Plasma Pretreated Silicone Softener
-0.18	-0.04	1.41	Laundered Silicone Softener
-0.21	-0.01	2.24	Laundered Silicone Softener
-0.19	0.08	2.48	Laundered Silicone Softener
-0.28	0.02	2.43	Laundered Silicone Softener
-0.18	0.15	2.62	Laundered Silicone Softener

Based on these facts, the Aerosil® nanoparticle treatments provide an interesting method for enhancing fabric color; however, for the purpose of enhancing the fabric color to achieve a change in color the general consumer would notice, the Aerosil® nanoparticle treatments do not perform. In terms of these parameters, the laundered silicone softener is the only treatment that produced a visual change in color, according to CIEL*a*b* of 1984.

6. Conclusions & Future Work

6.1 Conclusions

Color enhancement of fabrics can be achieved using an Aerosil® nanoparticle treatment applied by chemical exhaustion. Both Aerosil® 200 and 380 can be used successfully to treat wool fabric for color enhancement. The plasma pretreatment was determined to improve the darkening effect imparted to the substrate by both Aerosil® nanoparticle treatments, but was determined to degrade the performance of the Aerosil® treatment when exposed to sunlight. Even though the plasma pretreatment negatively affected the Aerosil® treatment's lightfastness, an average maximum achievable darkening effect of 15% is possible with the best Aerosil® treatment (i.e. Aerosil® 200).

To summarize, the following highlight conclusions can be made as a result of this study:

Silicone Softener Treatment:

1. The silicone softener treatment yields the best result in terms of maintaining and improving L^* (decreasing L^*) when subject to laundering.
2. The silicone softener treatment typically cause the substrate to become weaker, unlike the Aerosil® treatment.
3. The laundered cationic silicone softener treatment was the most effective treatment in terms of creating a noticeable (visual) change in color, based on CIEL*a*b* of 1984.

Aerosil ® Treatment:

4. The Aerosil® nanoparticle treatment yields the best result in terms of lightfastness. The darkening effect given by the treatment was enhanced further with exposure to sunlight.
5. The Aerosil® nanoparticle treatment can be applied with no significant loss of fabric strength, in a relatively short amount of time.

6.2 Future Work

Based on the results of this study, further investigation into the application of silica to enhance fabric color and the use of atmospheric plasma to enhance color is necessary. Since wool was the only substrate, the application of both silica and plasma should be investigated for other fabrics.

Future should include the analysis of the fabric's surface using an electron microscope in order to conclude whether either treatment warrants physical changes to the fabric's surface. In addition to studying the changes in surface characteristics before and after applying the experimental treatments, the study should be extended to include the effect of an extended dwell time. Since only ten minutes and fifteen minutes were used as dwell times, evidence is inconclusive as to how the length of exposure to silica changes fabric color.

In this study, plasma was used as a pre-treatment to investigate whether there were any changes to the effect of silica on the fabric. Future work should include a study of a plasma treatment after the chemical treatment has been applied. This study should also incorporate the use of carbon nanoparticles to determine the resulting effect on L*.

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APPENDICES

Appendix A: XRite® Spectrophotometer Data

Trial Name	L*	DL*	DE*
Chemical Treated Laundered	12.68	-2.11	2.12
Chemical Treated Laundered	12.45	-2.34	2.35
Chemical Treated Laundered	12.75	-2.04	2.05
Chemical Treated Laundered	12.72	-2.07	2.08
Chemical Treated Laundered	12.70	-2.09	2.10
A380 Treatment (Plasma) (4)	14.49	-0.29	0.43
A380 Treatment (Plasma) (3)	13.63	-1.15	1.18
A380 Treatment (Plasma) (2)	13.55	-1.23	1.26
A380 Treatment (Plasma) (1)	13.79	-1.00	1.04
A200 Treatment (Plasma) (5)	13.92	-0.86	0.91
A200 Treatment (Plasma) (4)	13.48	-1.31	1.32
A200 Treatment (Plasma) (3)	13.36	-1.43	1.43
A200 Treatment (Plasma) (2)	13.27	-1.52	1.53
A200 Treatment (Plasma) (1)	14.20	-0.68	0.72
A380 Treatment (1)	14.27	-0.52	0.57
A380 Treatment (3)	14.38	-0.41	0.51
A380 Treatment (5)	14.48	-0.31	0.33
A200 Treatment (5)	13.96	-0.83	0.85
A200 Treatment (3)	14.29	-0.49	0.54
A200 Treatment (1)	14.84	0.05	0.16
A200 Treatment + Plasma Pretreatment (5)	14.21	-0.58	0.59
A200 Treatment + Plasma Pretreatment (2)	14.22	-0.57	0.59
A200 Treatment + Plasma Pretreatment (1)	14.22	-0.56	0.60
A200 Treatment + Plasma Pretreatment (5)	14.50	-0.29	0.31
A200 Treatment + Plasma Pretreatment (4)	14.81	0.03	0.40
A200 Treatment + Plasma Pretreatment (3)	14.40	-0.38	0.49
A200 Treatment + Plasma Pretreatment (2)	14.22	-0.57	0.62
A200 Treatment + Plasma Pretreatment (1)	14.08	-0.71	0.72
Nanoparticle Baseline Treatment	14.38	0.14	0.30
Nanoparticle Baseline Treatment	14.22	-0.57	0.57

Plasma + Nanoparticle Baseline Treatment	13.24	-1.55	1.55
Plasma + Nanoparticle Baseline Treatment	13.10	-1.69	1.69
Nanoparticle Pad Application Method	13.84	-0.95	0.96
Nanoparticle Pad Application Method	13.79	-1.00	1.00
Nanoparticle Pad Application Method	14.57	-0.22	0.22
Nanoparticle Pad Application Method	14.71	-0.08	0.12
dNanoparticle Pad Application Method	17.77	2.98	3.19
Nanoparticle Pad Application Method	14.72	-0.06	0.08
Plasma Pretreatment (untreated substrate)	14.94	0.16	0.16
Plasma Pretreatment (untreated substrate)	14.91	0.13	0.14
Plasma Pretreatment (untreated substrate)	14.80	0.01	0.10
Plasma Pretreatment (untreated substrate)	14.75	-0.03	0.06
Plasma Pretreatment (untreated substrate)	14.92	0.13	0.14
Plasma Pretreatment (untreated substrate)	14.89	0.11	0.11
Plasma Pretreatment (untreated substrate)	14.69	-0.09	0.10

**Numbers 1, 2, 3, 4, and 5 in parenthesis denote Aerosil ® concentrations of 1.5, 1.75, 2.0, 2.25, 2.5 g/L respectively.

Appendix B: Estimated Cost of Treatment

The following calculation determines the cost of treating the fabric with the Aerosil® 200 treatment as designed in preceding document. This is only an approximation and must not be considered.

Length of roll = 91 meters

Width of roll = 1.114 meters

Cost of Aerosil® is \$113.50/kg silica

$$91\text{m} \times 1.114\text{m} = 101.4 \text{ m}^2$$

$$1.75\text{g SiO}_2/15\text{g fabric} \rightarrow 11.7\% \text{ owf}$$

$$101.4 \text{ m}^2 \times (0.00175 \text{ kg SiO}_2/0.0529 \text{ m}^2) = 3.36 \text{ kg SiO}_2$$

$$= \$3.76 \text{ per m}^2$$

Based on material costs between August 2007 and June 2008, the treatment, as designed by this study, would cost an estimated \$3.76 per square meter of merino wool fabric.

Tear strength on the treated (but not laundered) fabric was also tested: sample #4 lost roughly 10% of its original untreated tear strength with a variability of $\pm 5\%$.

Appendix C: Instron Data

Reference

2/21/2008

Ref

Sample ID: Eric-Wool-Untreated-Across cross-2-21-08.mss
 Method: Tongue_Tear-ASTM_D2261.msm

Test Date: 2/21/2008
 Operator: Grad

Sample Information:

Name	Value
Client or Class	Eric
Date of Test	2-21-08
Grip Pressure	80 psi
Jaw Face Size	1" x 3"
Lab Conditions	70F, 65% RH
Sample Info 1	Wool
Sample Info 2	Untreated
Test Direction	Across cross

Specimen Results:

Specimen #	Width in	Peak Load lbf	Ave "N" Peaks lbf	Max Ld S-P lbf	Min Ld S-P lbf	Avg Ld S-P lbf	Scatter Ld S-P lbf
1	3.000	6.43	5.93	6.43	3.20	4.47	0.68
2	3.000	6.08	5.87	6.08	2.99	4.54	0.70
Mean	3.000	6.26	5.90	6.26	3.10	4.51	0.69
Std. Dev.	0.000	0.25	0.04	0.25	0.15	0.05	0.01

Specimen #	Load @ Tear lbf						
1	6.21						
2	5.11						
Mean	5.66						
Std. Dev.	0.78						

Specimen Comments:

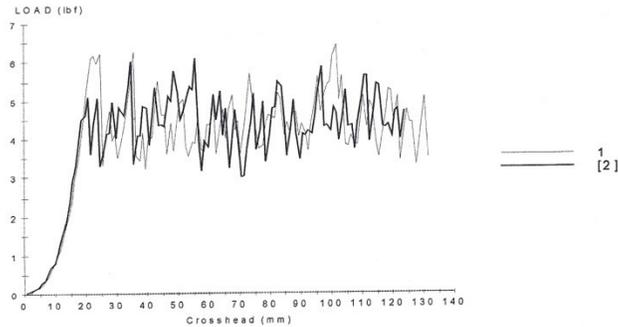
Specimen #	Comments
1	
2	

Calculation Inputs:

Name	Value	Units
"N" peaks	5	
Elong @Mkr "P"	100.00	mm
Elong @Mkr "S"	20.00	mm
Jaw Separation	3.00	in
Peak Criteria	1.0	%

Test Inputs:

Name	Value	Units
Brk Sensitivity	95	%
Crosshead Speed	300.00	mm/min



Aerosil ® 200 Treatment:

2/21/2008

A200

Sample ID: Eric-Wool-treated-Across cross-2-21-08.mss
 Method: Tongue_Tear-ASTM_D2261.msm

Test Date: 2/21/2008
 Operator: Grad

Sample Information:

Name	Value
Client or Class	Eric
Date of Test	2-21-08
Grip Pressure	80 psi
Jaw Face Size	1" x 3"
Lab Conditions	70F, 65% RH
Sample Info 1	Wool
Sample Info 2	treated
Test Direction	Across cross

Specimen Results:

Specimen #	Width in	Peak Load lbf	Ave "N" Peaks lbf	Max Ld S-P lbf	Min Ld S-P lbf	Avg Ld S-P lbf	Scatter Ld S-P lbf
1	3.000	5.34	4.71	5.34	2.38	3.53	0.55
2	3.000	5.54	5.30	5.54	3.44	4.33	0.50
3	3.000	5.27	4.79	5.00	2.74	3.78	0.53
4	3.000	5.59	5.05	5.59	3.32	4.13	0.44
5	3.000	6.31	5.80	6.31	3.89	4.94	0.43
Mean	3.000	5.61	5.13	5.55	3.15	4.14	0.49
Std. Dev.	0.000	0.41	0.44	0.48	0.60	0.54	0.05

Specimen #	Load @ Tear lbf					
1	4.49					
2	5.21					
3	5.27					
4	4.22					
5	4.68					
Mean	4.78					
Std. Dev.	0.46					

Specimen Comments:

Specimen #	Comments
1	
2	
3	
4	
5	

Calculation Inputs:

Name	Value	Units
"N" peaks	5	
Elong @Mkr "P"	110.00	mm
Elong @Mkr "S"	30.00	mm
Jaw Separation	3.00	in
Peak Criteria	1.0	%

Test Inputs:

Name	Value	Units
Brk Sensitivity	95	%
Crosshead Speed	300.00	mm/min

Aerosil ® 380 Treatment:

2/21/2008

A380

Sample ID: Eric-Wool-treated 2-Across cross-2-21-08.mss
 Method: Tongue_Tear-ASTM_D2261.msm

Test Date: 2/21/2008
 Operator: Grad

Sample Information:

Name	Value
Client or Class	Eric
Date of Test	2-21-08
Grip Pressure	80 psi
Jaw Face Size	1" x 3"
Lab Conditions	70F, 65% RH
Sample Info 1	Wool
Sample Info 2	treated 2
Test Direction	Across cross

Specimen Results:

Specimen #	Width in	Peak Load lbf	Ave "N" Peaks lbf	Max Ld S-P lbf	Min Ld S-P lbf	Avg Ld S-P lbf	Scatter Ld S-P lbf
1	3.000	6.39	5.78	6.39	3.92	4.75	0.47
2	3.000	6.82	5.69	5.80	4.33	5.02	0.36
3	3.000	5.23	5.00	5.07	3.74	4.46	0.30
4	3.000	4.81	4.37	4.81	2.32	3.27	0.54
5	3.000	6.85	5.69	6.16	3.65	4.66	0.47
Mean	3.000	6.02	5.31	5.65	3.59	4.43	0.43
Std. Dev.	0.000	0.94	0.61	0.68	0.76	0.68	0.09

Specimen #	Load @ Tear lbf					
1	5.48					
2	6.82					
3	5.06					
4	4.53					
5	6.85					
Mean	5.75					
Std. Dev.	1.05					

Specimen Comments:

Specimen #	Comments
1	
2	
3	
4	
5	

Calculation Inputs:

Name	Value	Units
"N" peaks	5	
Elong @Mkr "P"	110.00	mm
Elong @Mkr "S"	30.00	mm
Jaw Separation	3.00	in
Peak Criteria	1.0	%

Test Inputs:

Name	Value	Units
Brk Sensitivity	95	%
Crosshead Speed	300.00	mm/min