

Abstract

DALTON, EDWARD. Durable Flame Retardant and Antimicrobial Nano-Finishing.
(Under the direction of Dr. Xiangwu Zhang.)

Due to the costs associated with processing, materials, and the inherent difficulties in applying durable flame retardant and/or antimicrobial finishes, alternatives to conventional finishing methodologies are one of the focal points in today's textile research and industry. We, therefore, propose a new nano-finishing, involving the use of conventional flame retardants, titanium dioxide (TiO₂) nanoparticles, and multifunctional silanes, to replace conventional methodologies as this new finishing combines the functionality of flame retardant and antimicrobial performance, each feeding off of the synergistic properties of the other.

In this work, 100% cotton and 80/20 polyester/cotton fabrics were treated with a combination of Degussa P25 TiO₂ nanoparticles, tetrakis(hydroxymethyl)phosphonium chloride and urea flame retardants, and silane cross-linkers (such as tetraethoxysilane). These fabrics were prepared using a conventional pad-dry-cure laboratory-scale methodology. Following the coating process, fabrics were evaluated for flame retardant performance through the use of a vertical flame chamber. Fabrics were also evaluated for antimicrobial performance under varying light conditions (i.e. ultraviolet, visible, and no light) at Aerobiology Labs in Dulles, VA. Fabrics showing most flame resistant promise were further investigated for finish durability by flame retardant testing following a series of 5 washing and drying cycles. These laundered fabrics received further flame retardant

evaluation in the flame chamber and also ICP elemental analysis comparing active ingredient concentrations on the fabrics pre and post-laundering.

Results of this work show that without the addition of TiO_2 , THPC and urea were unsuccessful in imparting flame retardant properties on 80/20 polyester/cotton blended fabrics. However, flame retardant properties of both 100% cotton fabrics and 80/20 polyester/cotton fabrics are enhanced as add-on of titanium dioxide nanoparticles increases, specifically when using the silane cross-linker tetraethoxysilane (TEOS). Properties that were enhanced include char length as well as afterflame time. As on-weight-of-bath percentage of TiO_2 increased to levels of 6% and above, all poly/cotton fabrics self-extinguished. Similar results were observed on 100% cotton fabrics. This, in fact, does show that TiO_2 possesses synergistic effects with the phosphorus-based, condensed phase flame retardant, THPC + Urea.

Flame retardant performance levels following the laundering process were much more variable. In the case of the 100% cotton fabrics, some flame retardant property enhancements were noted, however poly/cotton fabrics showed no improvement over the control.

Antimicrobial properties of un-treated poly/cotton fabrics were compared to fabrics treated with only THPC + Urea flame retardants and a combination of THPC + Urea + TiO_2 . Un-treated poly/cotton fabrics had no resistance to bacteria as each sample exhibited colony growth after 24 hours of incubation. THPC proved to be antimicrobially active against gram positive *S. aureus* under no light and active against gram negative *K. pneumoniae* under no light, visible light, and UV light. THPC + Urea + TiO_2 proved to be antimicrobially active

against both gram positive *S. aureus* and gram negative *K. pneumoniae* under no light, visible light, and UV light. This shows that both THPC + Urea and THPC + Urea + TiO₂ have antimicrobial efficacy, however, the efficacy of THPC + Urea + TiO₂ has higher overall efficacy than THPC + Urea as it is able to effectively eliminate both *S. aureus* and *K. pneumoniae* at all conditions.

It is suggested that in future works, further attempts are needed to increase durability of flame retardant and antimicrobial coatings to the abrasive forces of laundering. Other cross-linkers, flame retardants, and application methodologies should be investigated.

Durable Flame Retardant and Antimicrobial Nano-Finishing

by
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Biography

Edward Dalton grew up in Winston-Salem, North Carolina. He graduated from North Carolina State University's College of Textiles with a B.S. in Textile Engineering. Prior to attending NC State, he was nominated for the Centennial Scholarship and received a Merit Scholarship to the College of Textiles. During his undergraduate studies, Edward was able to gain experience and networking skills in the textile industry through a co-op with Cotton Inc. lasting 3 years and an internship with Milliken and Co. Following graduation, Edward worked at Milliken's apparel dyeing and finishing facility in Barnwell, South Carolina. Edward wore many hats at Barnwell, including process engineering positions in preparation, finishing, face finishing, and a department management position in preparation. Following graduation from ITT, Edward will continue his career with Milliken and Co. at the Pendleton dyeing and finishing facility as a production and process manager.

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1 Introduction

The purpose of this research is to utilize commercially available titanium dioxide (TiO_2) nanoparticles, flame retardants, and multifunctional silanes to obtain durable flame retardant and antimicrobial fabric nano-finishing. Because the use of TiO_2 is employed as the main research ingredient, the literature review will describe the science behind antimicrobials and flame retardants, fabric functionalization mechanisms, and physical characterizations and properties of TiO_2 (nanoparticles in particular).

Because efficient antimicrobial effects and synergistic flame retardant effects are the desired end result of this research, it is very important to understand the photocatalytic process, particularly of TiO_2 , as well as the combustion process and thus, the flame retardant mechanisms. Fabrics used for this coating process will be constructed of 100% cotton as well as 80/20 polyester/cotton. The blended fabric is heavily biased towards synthetic fibers due primarily to industrial interest in coating performance on synthetic fabrics. Secondly, durable flame retardants are so difficult to achieve on synthetic/natural blends primarily due to the “wicking” effect, in which cellulosic fibers char but lock synthetic fibers within the fabric structure, preventing the polymer from melting and dripping; this negatively impacts flame retardant properties of both textile fibers. At present, while most antimicrobials are not light activated, it will be beneficial to understand antimicrobial capabilities of the most promising transition metal photocatalyst, TiO_2 , which also is shown to be synergistic with phosphorus-based flame retardants when applied to textile fabrics. Multifunctional silane cross-linkers will also help to drive the durability performance of these coatings and in specific, the durability of TiO_2 attachment to fabrics. While current research reveals

numerous methods of applying nanosol coatings specifically containing TiO_2 to fabrics to achieve antimicrobial surfaces, there lacks any research implementing TiO_2 – flame retardant nanosols to textile fabrics and further, insufficient data as to the durability of these finishes.

This research will focus on achieving antimicrobial and flame retardant properties simultaneously by employing nano-finishes containing TiO_2 . The durability of these finishes to laundering will also be studied.

2 Literature Review

The need for durable, cost-effective, non-toxic, and efficient antimicrobial and flame-retardant finishes has the textile industry searching for alternative solutions. Recent developments in nanoparticle technologies offer capable solutions to these problems. The primary focus of this research will be to evaluate current antimicrobial and flame retardant finishing technologies and how TiO₂ nanoparticles may be utilized for their effect on the above-mentioned properties to fabrics finished with selected flame retardant treatments.

2.1 Functional Textile Finishes

Although numerous functions may be employed to textile fibers and fabrics such as antimicrobial, flame retardant, repellent, soil-release and antistatic, only two functions (which may somewhat overlap with other functions) will be addressed by this research: antimicrobial and flame retardant.

2.1.1 Functionalization Mechanisms

Textile materials may be functionalized by three primary methods:

- 1) Incorporating functional additives (compounds, particles, polymers) into a polymer melt or polymer solution prior to the spinning or extruding process.

Durability is a huge advantage; however, this procedure is obviously not practical for natural fibers.

- 2) Chemical grafting of additives to fiber surfaces directly or through the means of linkers. This technology is restricted to reactive fibers or additive structures.

- 3) Equipping fabrics with functional coatings. This is a flexible method and fairly independent from fabric types. It is a simple way of combining multiple functionalities (Mahltig, Haufe, & Bottcher, 2005).

Chemical finishes may be durable and forego repeated launderings without losing their effectiveness or non-durable, which means chemical properties are needed only temporarily or when the textile will not be washed or dry-cleaned, for example, outdoor fabrics. However, for the scope of this research, only durable finishing mechanisms will be examined. Chemicals that have no affinity for textile fibers may be applied by continuous processes involving immersing the textile in the chemical solution or by mechanically applying the solution. Following the application step, curing or annealing fixes the chemistry to the surface of the fiber.

In order to achieve uniform chemistry application, a pad with uniform nip pressure across the width of the fabric is necessary. The fabric must move through the pad and chemical trough at a consistent speed with chemistry level and temperature constant. Also, to achieve uniform finish distributions, fabric must be properly prepared and well-absorbent (Schindler & Hauser, 2004).

2.2 Flame Retardant Textiles

A flame retardant may be defined as a chemical compound capable of imparting flame resistance to a material to which it is added, in this case, textiles. Flame resistance is merely a property of exhibiting reduced flammability (Lewin & Sello, Handbook of Fiber Science and Technology: Vol II. Chemical Processing of Fibers and Fabrics. Functional

Finishes. Part B, 1983). Therefore, depending once again on end use, customer specifications, and/or government regulations, a more specific definition of a flame resistant material may be concluded. In order to achieve flame retardant performance, large quantities of chemicals, typically 10-30% of fiber weight must be incorporated into the fabric (Lewin & Sello, Handbook of Fiber Science and Technology: Vol II. Chemical Processing of Fibers and Fabrics. Functional Finishes. Part B, 1983). With add-ons so high, it is expected that physical properties of the fabrics will change, therefore making flame retardant (and specifically durable flame retardant) treatments a challenging undertaking with much room for improvement. Commercially successful flame-retardant textile products typically must meet the following requirements:

- 1) little or no adverse effect on the physical properties of the textile
- 2) retaining the textile's physiological properties and aesthetics
- 3) simple production process with inexpensive chemicals and conventional equipment
- 4) Durable to repeated home launderings, tumble dryings, and dry-cleaning (Schindler & Hauser, 2004).

2.2.1 The Combustion Process

While there remains no true way to “fireproof” textiles, flame retardant finishes play an important role in protecting consumers, workers, and military. Generally speaking, flammability of textile fabrics depends on the fiber type(s), the construction of the fabric, and finally the flame retardant chemistry applied to the fabric. Obviously, some fibers melt while others may burn and looser fabrics may offer more opportunity for oxygen and fuel to be

available during the combustion process, which is merely a feedback mechanism involving a fuel and an oxidizer, illustrated in Figure 2.1.

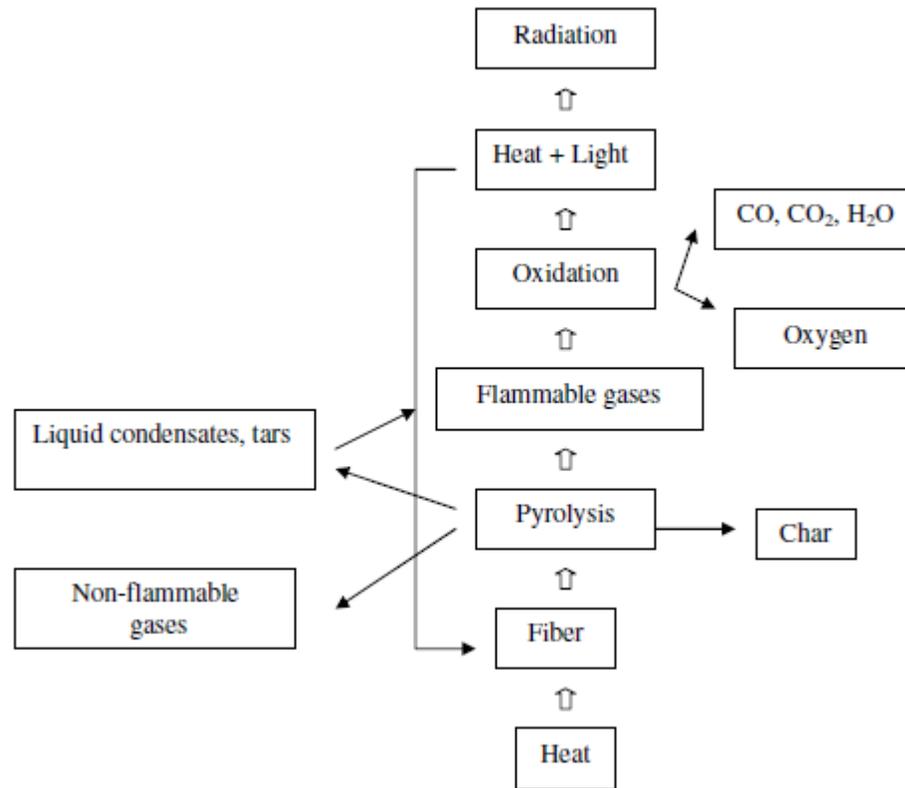


Figure 2.1: The Fiber Combustion Process

Under the influence of an externally applied heat source, the substrate undergoes thermal decomposition, pyrolysis, and generates flammable gases. By combining with oxygen in the atmosphere, a part of these gases are combusted in the flame. The rest remain and can be combusted by an excess of oxygen. Now the flame provides the heat source and thus, the cycle continues. Cotton fibers typically combust the instant the pyrolysis process begins, which occurs at 350°C. Polyester fibers, on the other hand, begin the pyrolysis process at around 430°C but the combustion cycle does not truly begin until the fiber reaches

a temperature of around 480°C (Lewin & Sello, Handbook of Fiber Science and Technology: Vol II. Chemical Processing of Fibers and Fabrics. Functional Finishes. Part B, 1983).

2.2.2 Flame Retardant Mechanisms

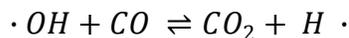
Extensive research has been conducted on performance mechanisms of flame retardants in accompaniment with development of innovational flame retardant systems. Most flame retardant coatings do one or more of the following: 1) flame retardant coating directing thermal degradation to low-fuel pyrolysis paths, 2) coating substrate to exclude oxygen, 3) formation of an internal barrier to prevent release of combustible gases, 4) release of inert gasses to dilute pyrolysis fuels, and 5) heat dissipation away from the flame front (Lewin & Sello, Handbook of Fiber Science and Technology: Vol II. Chemical Processing of Fibers and Fabrics. Functional Finishes. Part B, 1983). These mechanisms usually perform in either the condensed phase or the vapor phase.

2.2.2.1 Condensed-Phase Mechanisms

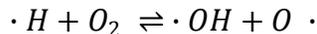
Condensed phase mechanisms can be through fiber insulation, removal of heat from the fiber, or the dehydration and cross-linking of the polymer. In general, condensed-phase retardants alter the substrate's pyrolytic path by promoting char, carbon dioxide, and water formation. The flame retardant effect is concentrated on decreasing fuel production during the pyrolysis process. It has actually been shown that on cotton, polyester, and their blends, low FR levels can be considered "catalytic amounts" and increase flammability rather than decrease flammability due to poor cross-linking or char formation (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983).

2.2.2.2 Vapor-Phase Mechanisms

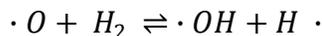
Flame retardants that perform action in the vapor phase do not necessarily change the pyrolysis process; rather, the combustion within the flame itself is changed. Basically, the flame actually consumes less fuel and generates less heat as the amount of vapor-phase flame retardant is increased. In turn, this decreases the amount of heat returned back to the polymer substrate and slows or halts pyrolysis. Because the active chemistry in the flame retardant must reach the gaseous phase in order to be effective, residual flame retardant left on charred surfaces is significantly less than that of a condensed-phase flame retardant. Therefore, it is common to assess types of flame retardant mechanisms through chemical analysis of char. Generally speaking, gas-phase flame retardants interfere with combustion reactions of the flame. Equation 1 illustrates the primary exothermic reaction within the flame. Thus, the focus of vapor-phase flame retardants is to hinder the chain branching reactions illustrated by Equation 2 and Equation 3, which propagate fuel combustion (Lewin & Sello, Handbook of Fiber Science and Technology: Vol II. Chemical Processing of Fibers and Fabrics. Functional Finishes. Part B, 1983).



Equation 1: Flame's Primary Exothermic Reaction



Equation 2: Chain Branching Reaction 1



Equation 3: Chain Branching Reaction 2

Typically, halogen derivatives such as bromine and chlorine operate via the gas phase. However, halogenated flame retardants are also thought to inhibit burning in the solid and/or liquid phases where halogenated molecular fragments help to exclude oxygen from the burning material, thus encouraging char formation (Georlette, 2001).

2.2.3 FR Treatments for Cellulose

Conventionally applied FR treatments for cellulosic fabrics have consisted of either non-durable salts or durable phosphorus-based products. These compounds act on cellulose primarily in the condensed phase. These finishes form resins that surround the fibers. The process typically consists of padding, drying, curing, oxidizing (e.g. in hydrogen peroxide – H_2O_2), and washing the finish. The final add-on of phosphorus should be around 3% owf. In 1953, tetrakis(hydroxymethyl)phosphonium chloride (THPC) was suggested as flame retardant for cellulose and is considered the most important development in this field. THPC, a reducing agent, reacts with many chemicals containing active hydrogens such as phenols and amines to form insoluble polymers on cellulosic substrates. Trimethylol melamine (TMM) is usually applied with a THPC finish as well to create a 3-dimensional insoluble network of polymer in the fiber finish. Conventional finishing methods consist of 25% THPC, 9% TMM, and 15% Urea (added to prevent acid degradation). An add-on of 18-20% is considered sufficient for laundering durability of the flame retardant. THPC is also capable of reacting and cross-linking with cellulose by itself, however this is a slow process and considered non-durable (Lewin & Sello, Handbook of Fiber Science and Technology: Vol II. Chemical Processing of Fibers and Fabrics. Functional Finishes. Part B, 1983).

2.2.4 FR Treatments for Polyester

FR's for polyester are said to be very difficult to durably apply. These finishes may be applied either in exhaust processes or padding processes. The padding process can involve the pad-dry-cure system or the pad-thermosol system. Thermosoling involves elevation of polyester fiber temperatures allowing the additive to penetrate/diffuse into the swollen fiber. Most finish compounds are proprietary phosphorus and halogen containing compounds. Because both condensed and vapor phase mechanisms have proven effective for polyester, most compounds are phosphorus and halogen containing. Prior research has concluded that phosphorus performs on polyester through prohibition of secondary reactions which lead to formation of volatile products. THPC-Urea combinations on polyester are said to perform in both the condensed-phase and the vapor phase (Lewin & Sello, Handbook of Fiber Science and Technology: Vol II. Chemical Processing of Fibers and Fabrics. Functional Finishes. Part B, 1983). Most of these are pad applied and dried/cured at temperatures at the thermosoling level, allowing the flame retardant to physically penetrate inside the amorphous regions within the fiber structure. Upon cooling, the polyester structure "locks in" the phosphorus compounds and the finish is held as durably as the fiber is able to maintain structural integrity. Bromine may also be used as an FR for Polyester. Some FR's are suitable for any fiber type but typically have to be applied in a latex-coating process (such as decabromodiphenyl oxide – DBDPO).

2.2.5 FR's for Natural/Synthetic Blends

Although poly/cotton blends are widely used, minimal commercially acceptable flame retardant systems have been developed. Achieving adequate flame retardant

performance for polyester and poly/cotton blends has proven to be very difficult. Because of the “scaffolding” or “wicking” effect, flame retardant finishing of blend fabrics is very difficult (Yang & Yang, 2005). The wicking effect is described as follows: cotton decomposed at lower temperatures than polyester (PET); therefore, as cotton (which chars) is decomposed and molten polymer (typically melts and drips by itself) tries to drip, it cannot flow away from the flame source due to the charred cellulosic structure present (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983). Recent patents have also covered the use of tetrakis(hydroxymethyl)-phosphonium (THP) and urea to treat 50/50 cotton/nylon blends such as the Battledress Uniform (BDU) (Yang & Yang, 2005). Other finishes involve the use of THPC-amide or THPOH. However, many of these finishes have not yet been commercialized. Donaldson et al. were able to impart flame resistance on light weight 50/50 poly/cotton blend fabrics using a mixture of 26% THPC-Urea (1:1 mole ratio), 4% dibasic sodium phosphate, and 6.4% PVBr (Poly-vinyl Bromide). Fabrics were dried for 5 minutes at a temperature of 85°C and cured for 1.5 minutes at 160°C. In this case, durable flame resistance is defined as self-extinguishing with a char length of 4.5 inches after 50 launderings (Donaldson, Normand, Drake, & Reeves, 1975). Table 2.1 illustrates differences physical and flame retardant properties in fabrics treated in Donaldson’s experiments.

Table 2.1: Effect of THPC Concentration on Char Length and Physical Properties of 50/50 Poly/Cotton Blends (Donaldson, Normand, Drake, & Reeves, 1975)

THPC-Urea % Conc.	PVBr % Conc.	% Add-On	%B.S. Ret.	%T.S. Ret.	Stiff ^{1/} 10 ⁻⁴	Char Length (in) after 50 Launderings
26	4	16.7	93	54	13.1	BEL ^{2/}
26	6.4	17.3	98	51	7.2	4.5
26	10.0	21.1	97	50	19.1	3.7
30	3	19.0	96	50	13.6	4.7
30	4	18.2	93	50	11.9	4.7
30	6.4	18.4	104	55	9.3	4.2

^{1/} Control stiffness 4.2×10^{-4} in.-lb.

^{2/} BEL = burned entire length.

2.2.6 Flammability Test Methods

There is an extensive list of test methods for evaluating textile flammability and flame resistance. These can be issued by governments, industry, scientific societies, and standards institutes, to name a few (Lewin & Sello, Handbook of Fiber Science and Technology: Vol II. Chemical Processing of Fibers and Fabrics. Functional Finishes. Part B, 1983). While many of these methods have similarities, they can be grouped into two segments: tests for fabrics expected to burn (i.e. clothing) and tests for fire resistance of flame-resistant fabrics. Most of the flammability and fire-resistance tests deal with ignition, afterglow, char area/length, flame time, mass loss, rate of flame surface spread, and flaming of drippings (polymer-based fabrics). In developmental chemistries, it is very difficult to achieve statistically significant results without testing multitudes of samples due to common variations in flame time (for example) of 10 to 20 seconds. Typical test methods place fabrics of a known size (length and width) in a sample holder, either horizontal or vertical,

expose to a flame source for a known duration, and measure burning properties of fabrics such as afterflame time (length of time the sample burns following removal of flame source), afterglow time (amount of time sample “glows” red following extinguishment of flame), and char length (measure of visible damage of the sample). Typical test methods are AATCC TM 34: Fire Resistance of Textile Fabrics, and ASTM D6413: Standard Test Method for Flame Resistance of Textiles.

2.3 Antimicrobial Textiles

Because textiles offer large specific surfaces with good adhesion, water-storage properties and in many cases, optimum temperature conditions, they offer optimum conditions for growth and settlement of biological organisms. Therefore, a large demand exists for antimicrobially finished textiles capable of avoiding or limiting microbial fiber degradation or biofouling, bacterial incidence, odor generation and the spreading or transfer of pathogens (Mahltig, Haufe, & Bottcher, 2005). For example, fungus, such as mildew, leads to discoloration of any fiber type and may even damage organic fiber types such as cotton. Bacteria may also grow on any type of fiber causing diseases, odors, and doubled bacterial population growth approximately every 30 minutes. As a result, significant efforts have been made to generate antimicrobial textiles for many different applications. For example, the European market for antimicrobial textiles in 2003 can be broken down in Table 2.2.

Table 2.2: 2003 European Applications of antimicrobial textiles (Mahltig, Haufe, & Bottcher, 2005)

Area	Millions of m ²
Sportswear	21.0
Outerwear	14.0
Footwear	32.0
Underwear	41.2
Home textiles	34.0
Filling materials	21.0

For most applications, an effective antimicrobial finish should offer the following characteristics:

- Quick acting
- Durable to multiple launderings
- Safe for any animal
- Easy application/processing
- Low environmental impact
- Cost effective

2.3.1 Bacteria

Typical antimicrobial testing methods call for two types of bacteria for full evaluation, gram positive and gram negative. For example, *Staphylococcus aureus* (*S. aureus*) is gram positive while *Escherichia coli* (*E. coli*) is gram negative. The gram positive bacteria have a relatively thick wall, which is composed of many layers of peptidoglycan polymer and one plasma membrane. These layers of peptidoglycan are composed of a fairly open network polymer of N-acetylmuramic acid and N-acetylglucosamine polysaccharide chains with peptide bridges (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007). For example, *Staphylococcus aureus*, the most frequently evaluated species, colonizes

approximately 30% of individuals in developed countries, mainly in the nose or on the skin (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007) and is the major cause of cross-infection in hospitals and home or commercial laundry (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983). Methicillin-resistant *S. aureus* (MSRA) can survive up to 9 weeks when dried onto surfaces (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007). Furthermore, *S. aureus* contamination of a surface has been shown to typically be between 4 and 7 colony forming units per cm² (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007).

Gram-negative bacteria only have a thin layer of peptidoglycan but a much more complex cell wall structure with two cell membranes, an outer membrane and a plasma membrane (Fu, Vary, & Lin, 2005). The outer membrane, although semi-permeable, is comprised of a complex layer of lipids, lipopolysaccharides and proteins. Rather than passing through it, many hydroxyl radicals will react with the lipid constituents of the membrane (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007). Therefore, gram-negative bacteria's additional outer membrane influences the permeability of many molecules and makes the bacteria more resistant to many chemical agents than gram-positive cells (Fu, Vary, & Lin, 2005). However, once the membrane has been breached, no further significant obstacles block the approach of the radicals and cell death can then be observed (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007).

2.3.2 Antimicrobial Mechanisms

Antimicrobial finishes may be considered leaching, slowly releasing antimicrobial from fabric surface or interior, or bound through chemical bonding to the surface of the fiber. Bound antimicrobials may be further broken into two distinct categories: regenerative and barrier. Generally speaking, these finishes may be considered biostatic, preventing further growth and spread of microbes, or biocidal, actually killing microbes (Schindler & Hauser, 2004). Controlled release, or leaching, antimicrobials present many processing difficulties when trying to manipulate chemistries to truly slow the rate of release of active agents. Whether textiles are regularly laundered or used outdoors and subjected to weathering, rate of agent leach will continue to be an issue, however, most insecticides and insect repellents, even co-applied to fabrics with film-forming polymers, maintain their effectiveness through a controlled release mechanism (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983). Gagliardi's regenerative mechanism provides that the germicidal species may be regenerated by bleaching agents during the laundering process or ultraviolet light, for example (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983). The final antimicrobial mechanisms are barrier/blocking in which films or coatings may be impervious to transmission of microorganisms through fabrics or films or coatings having direct surface contact activity against the growth of microbials (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983).

2.3.3 Effect of Fiber/Fabric Type on Antimicrobial Properties

There are currently no un-altered fiber types that are inherently resistant to disease/odor causing bacteria or fungi, however, bacterial retention of certain fiber types do vary. One particular study was able to verify that 100% cotton fabrics retain less odor-causing bacteria both before and after laundering than cotton blends or fully synthetic fabrics (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983). However, for cellulosic fabrics, there are four risks that can inherently affect their susceptibility to microbial attack:

- Lowering degree of polymerization (DP) of cellulose chain (through mechanical, photochemical, etc.)
- Decreasing fiber crystallinity or orientation
- Presence of non-cellulosic components (pentosans and pectins increase susceptibility; lignins, waxes, etc decrease susceptibility)
- Tightly woven fabrics are less susceptible to microbial attack (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983)

2.3.4 Common Antimicrobial Finishes

There are six recognized strategies for imparting antimicrobial finishes in/on textile fibers and fabrics:

- Insolubilization of chemical reagents in/on fibers
- Graft polymers, homopolymers, and/or copolymerization onto fiber
- Treat fiber with resins, condensates, cross-linking agents

- Chemical fiber modification through formation of covalent bonds
- Coating of the fiber surface
- Microencapsulation of chemical agent with fiber in a matrix

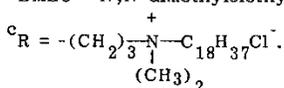
Table 2.3 lists the six mentioned techniques, typical chemistries, types of protection, and types of fibers.

Table 2.3: Textile Multipurpose Antimicrobial Finishing Techniques (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983)

Finishing technique	Chemical agents	Organisms protected against	Fiber type
Insolubilization	$(n\text{-Bu}_3\text{SnO})_2 \cdot \text{TiX}^{\text{a}}$	Gram-positive bacteria, dermatophytic and mildew fungi	Polyamide, acrylic, polypropylene
Homo- and copolymerization	Acrylamido-8-hydroxy-quinolines and metal salts	Bacteria, mildew fungi	Cellulosics
Resin treatment	Hexachlorophene and DMEU ^b	Bacteria, mildew fungi	Cellulosics
Covalent bond formation	5-Nitrofurylacrolein	Bacteria, mildew and yeast fungi	Poly(vinyl alcohol)
Coatings	Hydrolysis product of $(\text{CH}_3\text{O})_3\text{Si}-\text{R}^{\text{c}}$	Bacteria; dermatophytic, yeast, and mildew fungi; algae	All types
Microencapsulation	Any bactericide, pyrethrins, pheromones	Bacteria and insects	Many types

^aX = di(acetylacetonate), diisopropoxide, or dipropyl acetate.

^bDMEU = N,N-dimethylethylene urea.



Insolubilization is the most frequently used technique for imparting antibacterial finishes to textiles, however, durability to laundering usually is not as good as other techniques such as homopolymerization or co-application with resins (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983).

While recent embedded commercial antimicrobials containing bisphenols such as triclosan, biguanids such as poly(hexamethylen)biguanid, colloidal silver, and/or fabrics blended with silver-coated nylon or chitosan fibers exist, simple and highly efficient antimicrobial coatings for any common fiber type with better durability and mechanical properties are in high demand (Mahltig, Haufe, & Bottcher, 2005). Many markets offer grand opportunities for antimicrobially finished textiles: health-care and hospitals, dishcloths and sponges, outdoor or weather-exposed textiles, home furnishings such as upholstery, sportswear, intimate apparel, and towels to name a few. Table 2.4 lists classes of compounds used to impart antimicrobial activity on textiles.

Table 2.4: Commonly Used Textile Antimicrobial Compounds (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983)

Type of compound	Frequently used agents
Inorganic salts	Ag(I), Hg(II), Sn(IV), and Zn(II) salts
Organometallics	(n-Bu ₃ SnO) ₂ and $\text{C}_6\text{H}_5\text{-HgOAc}$
Iodophors	KI or I ₂ ·poly(vinylpyrrolidinone)
Phenols and thiophenols	Hexachlorophene, dichlorophene, and bithionol
Onium salts	(RO) ₃ SiR ₄ N ⁺ X ⁻ , R ₄ N ⁺ X ⁻ , R ₄ P ⁺ X ⁻ ^a
Antibiotics	Neomycin, kanamycin, grisofulvein
Heterocyclics with anionic groups	8-Hydroxyquinoline, 2-mercaptobenzothiazole, substituted triazines, and pyrimidines
Nitro compounds	5-Nitrofurylacrolein
Ureas and related compounds	Halogenated salicylanilides and aryl ureas, and bisbiguanide salts
Formaldehyde derivatives	Polyformaldehyde, urea-formaldehyde resins
Amines	Polyethyleneimine, hexahydropyrimidines
Miscellaneous	Peroxide-containing polymers, reactive dyes

^aR = alkyl for the silicon-containing quaternary ammonium salt, alkyl or aryl for R₄N⁺X⁻ or R₄P⁺X⁻.

Typically, application of a functional finish typically affects other textile properties. For example, antimicrobial finishes usually result in reduction in mechanical properties of the textile such as tensile/tear strength, discoloration, or acceleration of photochemical degradation (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983).

2.3.5 Durability of Antimicrobial Finishes

Depending on the textile environment and end-use conditions, durability requirements for antimicrobial textiles vary considerably. Lewin et al. researched antimicrobial durability and was able to make the following conclusions:

- Textiles requiring durability to laundering should maintain antibacterial activity for 20-50 launderings unless used in hospitals (require activity for the lifetime of the garment)
- Above-mentioned finishes must be bacteriostatic/fungistatic if for aesthetic end use; should be –cidal for hospital or confined environments
- Disposables only need be durable to leaching, not laundering
- Outdoor antimicrobial textiles should be durable to weathering for 2- 3 yr periods (usually accomplished through addition of UV stabilizers)
- Table 2.5 assesses durability of more common antibacterial finishes.

Table 2.5: Typical Durability for Common Antimicrobial Finishes (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983)

Finishing technique	Chemical agents ^a	Organisms protected against	Fiber type	Durability (number of launderings)
Insolubilization	Zn ²⁺ and EDTA	Bacteria	Natural and synthetics	50
Insolubilization	Neomycin sulfate	Bacteria	Cellulosics	Several alkaline ^b
Insolubilization	3,4,4'-Trichlorocarbonyl	<i>Staphylococcus aureus</i>	Various synthetics	25
Homopolymerization	Zn(OAc) ₂ ·H ₂ O—H ₂ O ₂ —HOAc	<i>Staphylococcus aureus</i> and <i>Staphylococcus epidermidis</i>	Cellulosics	50
Resin treatment	Mercurated allyl-triazines	<i>Trichophyton interdigitale</i>	Synthetics	60
Resin treatment	THPC-TMM	Bacteria	Cellulosics	50-100
Covalent bond formation	Carboxymethyl cellulose and Ag ⁺ or Cu ²⁺ salts	Gram-positive bacteria	Cellulosics	30

^aAbbreviations for chemical agents are as follows: EDTA = ethylenediaminetetraacetic acid; THPC = tetrakis-(hydroxymethyl)phosphonium chloride; TMM = trimethylolmelamine.

^bNumber not specified.

2.3.6 Antimicrobial Textile Testing Methods

Obviously, it is very difficult to correlate antimicrobial effectiveness results between the controlled environment of a laboratory with the un-controllable environment of a human user or outdoor interface. Numerous protocols have surfaced over the years, however, industry and researchers must choose/design a test method with chemical capability and end-use in mind. Table 2.6 below gives some general ideas of the methodologies employed by the more common tests.

Table 2.6: Antimicrobial Textile Laboratory Tests (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983)

Test	Analytical capability	Scope and limitations
Agar plate	Qualitative; bacteriostatic	Activity measured indirectly by reagent diffusing off fabric into culture medium; can be run rapidly for screening samples
Parallel streak	Qualitative; bacteriostatic	Same as agar plate, except fabric swatches placed perpendicular to streaks of test organisms
Majors	Semiquantitative; bacteriostatic	Based on amount of titratable acid or alkali produced by organism in presence of treated fiber; reproducibility fair
Quinn	Quantitative; bacteriostatic or bactericidal; fungistatic or fungicidal	Fabric dried, sterilized, inoculated with test organism, and bacterial or fungal colony count made under high-powered microscope; time consuming; some fabrics require special sterilization procedures
AATCC-100	Quantitative; bacteriostatic	Similar to Quinn test, except that fabric not dried before sterilization and percent reduction bacteria in fabric measured by serial dilution techniques; time consuming
Lashen	Quantitative; bacteriostatic	Modification of Quinn test; fabric not dried under special conditions or sterilized; not yet accepted as a general method
Warburg respiration	Qualitative; bacteriostatic	Based on increase of oxygen consumption of bacteria (inhibition of respiration) in presence of treated fibers; rapid screening possible; other bacterial functions not measured
Manometric technique	Qualitative; fungistatic	Same principle as Warburg respiration test applied to fungi
Agar plate	Qualitative; fungistatic	Fabric placed on agar surface, inoculated with test fungus, incubated 14 days, inspected visually for fungal growth
Humidity jar	Qualitative; fungistatic	Fabric inoculated with test fungus is sprayed, suspended in water, incubated, inspected visually for fungal growth weekly (up to a maximum of 28 days)
Perfusion	Qualitative; fungistatic	Various fabric treatments (as strips) fastened to perfusion bed by adhesive, inoculated with agar discs, incubated by immersion in nutrient, inspected for fungal growth; rapid screening
Soil burial	Semiquantitative; fungistatic	Strips of treated fabric buried in soils in trays or beds for a specified period of time, fabric samples then washed and conditioned at standard temperature and humidity, and loss of breaking strength of fabric determined

2.4 TiO₂ Nanoparticles

As particle sizes decrease, specific surface area of a constant mass of particles increases. Therefore, a lot of attention is currently being given to nanoparticle materials

science. If the particle structures retain consistency, yet decrease in size, an enhancement in chemical properties of these particles may be realized when applied to surfaces. For example, commercial TiO₂ nanoparticulates (Degussa P25) offer the following advantages:

- a) Permanent stability under UV exposure (Wang, Han, & Ke, 2006)
- b) Excellent antimicrobial function (Fu, Vary, & Lin, 2005)(Anpo, Shima, Kodama, & Kubokawa, 1987)
- c) Excellent deodorizing effects (Amemiya, 2004)
- d) Excellent thermal stabilizing and flame retardant properties
- e) Positive impact on finish durability (Yoneda & Morimoto, 1999) (Soeno, Inokuchi, & Shiratori, 2004) (Yeadon & Harper, 1979)
- f) Minimal impact on fabric shade (Degussa)
- g) Non-toxic
- h) Low cost (Evonik Degussa - Chemicals)

TiO₂ first came to the scientific community's attention when Fujishima and Honda demonstrated photolysis of water by a TiO₂ – Pt electrochemical photocell in 1972. Thirteen years later, in 1985, the antimicrobial efficacy of TiO₂ semiconductor particles was realized (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007). Literature has shown that TiO₂ demonstrates both antibacterial and flame-retardant properties. These properties, nevertheless, may be enhanced as the particle size of TiO₂ decreases. Nanometer-size TiO₂ particles may exhibit many special features due to the fact that the band gap (the distance between the valence band and conduction electron band) increases with the decrease of their size. Also, small TiO₂ particles offer very large active surface area (Fu, Vary, & Lin, 2005).

Research has shown that the vast majority of studies of TiO₂ antimicrobials are conducted in solution using suspensions or thin films of Degussa P25 (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007),(Verran, Sandoval, Allen, Edge, & Stratton, 2007).

2.4.1 Effect of Nanoparticles on Durability

Research has shown that addition of fine particles to functional films or coatings offer superior wear resistance. This is due to an enhanced surface state. Mahltig et al. reported improved abrasion stability and tensile strength after the treatment of cotton, polyamide and glass fibers with nanosol coatings (Mahltig, Haufe, & Bottcher, 2005). For example, if cotton is treated with ceramic sols and modified epoxysilanes such as glycidylpropyloxytrimethoxysilane (GPTMS), the adhesion of the coating to the fiber is increased, thus mechanical stability is enhanced (Mahltig, Haufe, & Bottcher, 2005). In general, good bonding of the nanosol to the fiber or textile surface will increase mechanical stability. Yoneda applied water repellent films to glass substrates as a starting material and then applied a film using TMOS and fine ceramic particles. His research was able to show that a roughed surface structure of the glass substrate prevented the initial water repellent film from abrasion and improved the durability of that film against abrasion (Yoneda & Morimoto, 1999). Yoneda also found that one of the factors affecting mechanical durability of the coated glass substrate was the density of the surface functional group. It has also been shown that fine particles in coatings increase the surface area of the coated substrate, thus increase the density of the surface functional groups (Yoneda & Morimoto, 1999). As a result, Yoneda's research proves that improvement in mechanical durability should be achieved by coating films that have strong bonding, obviously, high adhesion density, and a

roughed surface. Largely, mechanical durability depends on the surface roughness and density of functional groups on the substrate (Yoneda & Morimoto, 1999). A final factor to consider, in its simplest form, is that inorganic coatings offer improved abrasion stability due to the enhanced solidity of the substrate (Mahltig, Haufe, & Bottcher, 2005).

2.4.2 Toxicity of TiO₂ Powders

TiO₂ is present in many commonly used products today: medicines, cosmetics, paints, paper, plastics, etc. The list is a long one. Nanoparticles, due to their increasing development, have been a particular concern as well as many concerns from the manufacturing segments as to possibilities of TiO₂ being a human carcinogen and increasing the risk of lung cancer. In one particular case, TiO₂ nanoparticles (very similar in structure and characteristic to Degussa P25) were administered intravenously in rats (Fabian, Landsiedel, Ma-Hock, Wiench, Wohlleben, & van Ravenzwaay, 2008). Rats were subjected to 5mg/kg body weight of TiO₂ nanoparticles and were tested for particle concentrations in the lung, spleen, kidney, and liver on 1, 14, and 28 day intervals. Results showed highest concentration of the particles in the liver followed in decreasing order by the spleen, lung, and kidney. Table 2.7 illustrates the findings of this study.

Table 2.7: TiO₂ Organ Distribution over Time

Organ	TiO ₂ on day 1		TiO ₂ on day 14		TiO ₂ on day 28	
	Control	Treated	Control	Treated	Control	Treated
Liver	0.5	133.8 ± 26.0	0.5	99.5 ± 55.8	0.5	111.3 ± 27.3
Spleen	0.8	78.7 ± 19.3	0.9	48.8 ± 27.8	0.7	33.3 ± 28.8
Lung	1.5	8.8 ± 0.6	1.7	2.8 ± 1.4	1.5	2.3 ± 1.0
Kidney	0.3	0.67 ± 0.06	0.3	0.2 ± 0	0.2	0.2 ± 0

In all four areas, highest levels were noted on day one and proceeded to decrease throughout the 28 day test cycle. Exposed rats showed no obvious toxic or adverse health effects at the “low” dose level of 5mg/kg body weight (Fabian, Landsiedel, Ma-Hock, Wiench, Wohlleben, & van Ravenzwaay, 2008). Furthermore, a study was conducted assessing the risk of lung cancer mortality related to on-the-job exposure to TiO₂ in Europe (Boffetta, et al., 2004). The results of the study suggested there was not a carcinogenic effect of TiO₂ dust on the human lung.

2.5 Flame Retardant Effects of TiO₂

2.5.1 TiO₂ as a Polymer Filler

Research has shown that metal oxide nanoparticles (i.e. TiO₂) used as fillers have effects on reducing the thermal degradation of polymers (Laachachi, Leroy, Cochez, Ferriol, & Lopex Cuesta, 2005), (Laachachi, Cochez, Leroy, Ferriol, & Lopez-Cuesta, 2007). Also, besides acting as thermal stabilizers, it has been shown that the nano-sized particles have synergistic effects with organoclays, combining flame resistant performance with enhanced mechanical properties (Laachachi, Leroy, Cochez, Ferriol, & Lopex Cuesta, 2005). Laachachi et al. melt-blended TiO₂ nanoparticles (Degussa P25) with poly(methyl methacrylate), or PMMA, and measured the flame resistant properties of the polymer. Comparing 2 different oxide nanoparticles, TiO₂ and Fe₂O₃, it was found that the thermal

stability of PMMA-TiO₂ samples had a 2% mass loss at 295°C while PMMA-Fe₂O₃ had a 2% mass loss at 275°C, as shown in Figure 2.2. Laachachi also notes that the peak of heat release rate (pHRR) is greatly reduced in the presence of nanoparticles as compared to pure PMMA. At 5%, 10%, 15%, and 20% TiO₂, the pHRR is lowered by 5%, 30%, 45%, and 49% respectively. For TiO₂, the effect is even greater than that of Fe₂O₃. It was also found that the time to ignition (TTI) for PMMA-TiO₂ increases compared to pure PMMA or PMMA-Fe₂O₃ nanocomposites (Laachachi, Leroy, Cochez, Ferriol, & Lopex Cuesta, 2005). At 15 and 20 wt % TiO₂, the total smoke release, a product of incomplete combustion, is also less than that of pure PMMA or PMMA-Fe₂O₃.

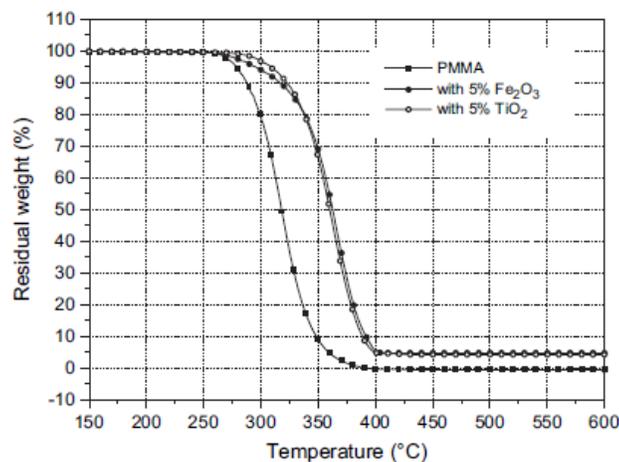


Figure 2.2: TGA Curves for Pure PMMA, PMMA-Fe₂O₃, and PMMA-TiO₂ Nanocomposites

It has also been found that the addition of TiO₂ to a PVC polymer melt strongly inhibits the release of hydrogen chloride (HCl), a highly flammable and toxic gas, during the combustion process (Pi & Guo, 2005). Other transition metal oxides, such as MnO₂ and Fe₂O₃, do not offer this benefit. In fact, they promote the release and combustion process of HCl (Pi & Guo, 2005). It has also been documented that synergistic effects have been found

between nano-fillers and phosphorus-based flame retardants (Laachachi, Cochez, Leroy, Ferriol, & Lopez-Cuesta, 2007).

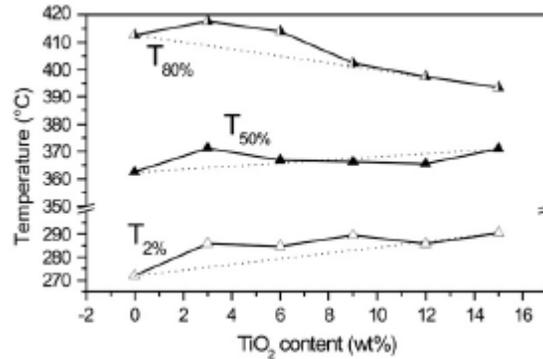


Figure 2.3: Influence of Oxide Content on Thermal Stability of PMMA

When blended with phosphinate-based additives, TiO₂ exhibited some synergistic effects for fiber weight percentages of TiO₂ up to 9%, as shown in Figure 2.3 (Laachachi, Cochez, Leroy, Ferriol, & Lopez-Cuesta, 2007). Still, because TiO₂ was melt-blended into the polymer, these effects were due to mobility restriction in the PMMA polymer chains (Laachachi, Cochez, Leroy, Ferriol, & Lopez-Cuesta, 2007).

2.5.2 TiO₂ as a Particle Coating

Nano-TiO₂ can greatly increase the anti-ageing properties of flame retardants through its UV-absorbing or UV-blocking power. Also, uniformly dispersed nano-scale TiO₂ particle coatings form an interpenetrating network on the surface and enhance the resistance of the coating to moisture in natural weathering. Adsorption or absorption of water has been shown to harm the flame resistant properties of coatings (Wang, Han, & Ke, 2006). Therefore, a coating which increases surface roughness, thus repelling moisture through the lotus effect and also creating a cross-linked particle network (“labyrinth effect”) on the surface of a

fabric, may prevent or delay harm to the functionality of applied flame retardants. It has been shown that SiO₂-TiO₂ nanosol coatings on textile filters can give heat resistance up to temperatures of 300°C. Following exposure to flame, nano-TiO₂ can also lead to the formation of ceramic-like materials on the char surface that protects the substrate during the combustion process and serves as a mechanical reinforcement of the charred layer, leading to better accommodation of future strains (Wang, Han, & Ke, 2006). Combinations of insoluble salts and TiO₂ are said to perform as semi durable flame retardants for cellulose. It is believed that when the TiO₂ is exposed to flame, the particles do not decompose and achieve FR effectiveness through the soluble salts adsorbed to them (Lewin & Sello, Handbook of Fiber Science and Technology: Vol II. Chemical Processing of Fibers and Fabrics. Functional Finishes. Part B, 1983). Nanometer TiO₂ is also shown to be helpful in limiting oxygen diffusion to the coated substrate, thus limiting a much needed fuel source (Wang, Han, & Ke, 2006).

2.5.3 Synergistic Effects of TiO₂ used with other Flame Retardants

Synergism may be defined as observed greater effectiveness of combinations of compounds compared to the sum of the effects of the individual compounds. Non-FR additives that enhance flame retardant effects may also be termed synergists (Lewin & Sello, Handbook of Fiber Science and Technology: Vol II. Chemical Processing of Fibers and Fabrics. Functional Finishes. Part B, 1983). Recent research has shown TiO₂ to have certain synergistic effects when placed with other flame retardants, in addition to maintaining flame retardant properties obtained previous to the addition of TiO₂. For example, magnesium hydroxide, Mg(OH)₂, is commonly used as a flame retardant and smoke suppressor in the

plastics industry, it was found to have varying effects on the colors of polymers during processing ranging from light beige to dark gray shifts. The combination of TiO_2 with $\text{Mg}(\text{OH})_2$ offers synergism in terms of flame retardant performance and also thermal stabilizing of polypropylene (Titelman, Gonen, Keidar, & Bron, 2002). Titelman et al. also found that addition of TiO_2 to $\text{Mg}(\text{OH})_2$ positively impacted length of ignition of polypropylene samples compared to just the use of $\text{Mg}(\text{OH})_2$ (Titelman, Gonen, Keidar, & Bron, 2002). It has also been shown that heat and flame resistance of textiles can be improved by embedding phosphorus-based flame retardants into nanosol coatings on textile fibers (Horrocks, Wang, Hall, Sunmonu, & Pearson, 2000).

Furthermore, it is also possible that synergistic antimicrobial effects may be realized when combining flame retardants with TiO_2 . Certain flame retardants have been shown to exhibit antimicrobial effects by themselves, i.e. THPC and urea-formaldehyde combinations. In 1966, Hoch et al. investigated the bactericidal properties of cotton fabrics with applied THPC resins (Hoch, Wagner, & Vullo, 1966). Cotton fabrics were treated with solutions of 50% THPC owb and 30% urea-formaldehyde owb resins and cured at temperatures from 90-160°C. The resulting finishes were either partially or completely effective against both gram-positive and gram-negative bacteria for 50 to 100 launderings (Hoch, Wagner, & Vullo, 1966). While the active chemical species was not definitively determined, it is likely that the phosphonium salts and formaldehyde, which have been previously reported to show antibacterial activity, are the contributors (Hoch, Wagner, & Vullo, 1966). Table 2.8 illustrates Hoch's findings for cotton fabrics with 5 oz. cotton with 22.4% THPC add-on.

Table 2.8: Mean Bacterial %Reduction of THPC-Resinated Cotton Fabrics with 15 min Exposure (Hoch, Wagner, & Vullo, 1966)

Bacteria	1 Wash	50 Wash	100 Wash
Staphylococcus aureus	92	88	78
Staphylococcus albus	81	79	68
Proteus vulgaris	84	80	71
Salmonella typhosa	89	85	63
Streptococcus faecalis	82	75	58
Escherichia coli	78	66	53
Shigella dysenteriae	87	80	56
Cornybacterium diphtheriae	84	70	67
Diplococcus pneumonia	80	68	46
Pseudomonas aeruginosa	76	70	53
Bacillus ammoniogenes	79	76	53
Bacillus subtilis	38	33	28

These % reductions were also significantly increased as exposure time increased. For example, *Bacillus subtilis* was reduced by 51% for fabrics washed 100 times but exposed to the bacteria for 6 hr compared to 28% reduction of *Bacillus subtilis* exposed for 15 min (Hoch, Wagner, & Vullo, 1966). The antimicrobial benefits of TiO_2 will be discussed in the next section.

2.6 Antimicrobial Benefits of TiO_2

2.6.1 The Photocatalytic Process

TiO_2 can be used as a catalyst for the acceleration of a photoreaction (Photocatalysis, 2009). TiO_2 has three major structural forms: anatase, rutile, and brookite. Two of these forms can exhibit photocatalytic activity: anatase and rutile. The anatase form, consisting of chains of TiO_6 octahedral sharing two edges, has a wider optical band gap of 3.2 eV. Rutile TiO_2 , consisting of chains of TiO_6 octahedral sharing four edges, has a band gap energy of 3.0 eV. This means that UV light of energy greater than 388nm and 413nm is required to activate anatase and rutile TiO_2 , respectively (Amemiya, 2004). Although ultraviolet rays

are present virtually everywhere, there are certainly many factors affecting the intensity of the rays which should have a direct impact on the efficiency of photocatalytic reactions of TiO₂. Table 2.9 illustrates varying ultraviolet intensities in some ordinary surroundings.

Table 2.9: Intensities of Ultraviolet Rays Measured with an Illuminance Meter (TOPCON UVR-2) (Amemiya, 2004)

measurement location		intensity of ultraviolet rays	remarks
outdoors	under direct sunlight	4 to 5mw/cm ²	fair weather
		2 to 2.5mw/cm ²	slightly overcast
		0.7 to 0.8mw/cm ²	cloudy
inside vehicle	through rear window glass	150 to 350 μW/cm ²	fair weather - slightly overcast
	through side window glass	90 to 300 μW/cm ²	
	through front glass	0.5 to 2.0 μW/cm ²	
	rear seat in shade	10 to 30 μW/cm ²	
	ceiling surface	2 to 4 μW/cm ²	
inside of house	immediately below the fluorescent lamp	2 to 3 μW/cm ²	

Even though rutile TiO₂ has lower band gap energy, the anatase form exhibits a higher photocatalytic activity (Fu, Vary, & Lin, 2005). The reason for this difference is in the energy structure between the two forms. In both forms, anatase and rutile, the position of the valence band is deep and resulting positive holes show sufficient oxidating power, however, the conduction band is positioned near the oxidation-reduction potential of the hydrogen, signifying both forms are fairly weak in terms of reducing power (Amemiya, 2004). Because the conduction band of the anatase form is located closer to the negative position than the rutile form, the reducing power of anatase TiO₂ is stronger than that of rutile. Figure 2.4 illustrates this phenomenon.

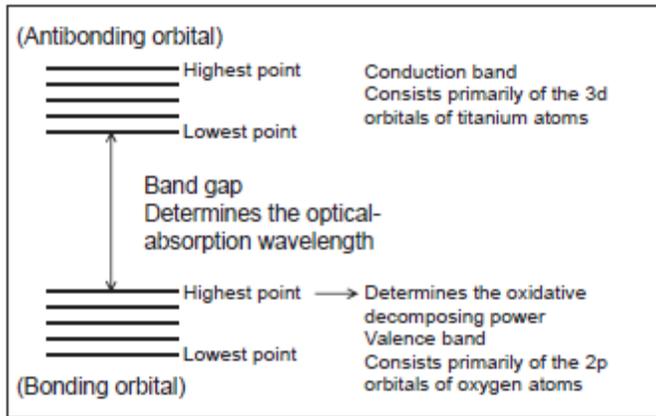


Figure 2.4: The TiO₂ Band Structure (Amemiya, 2004)

When the TiO₂ photocatalyst is irradiated with light of energy greater than or equal to its band gap energy, electron-hole pairs (free electron in the conduction band, hole in the valence band) are generated. These hole pairs induce oxidation reduction reactions at the surface of the TiO₂ particle. Figure 2.5 and Figure 2.6 illustrate these processes:

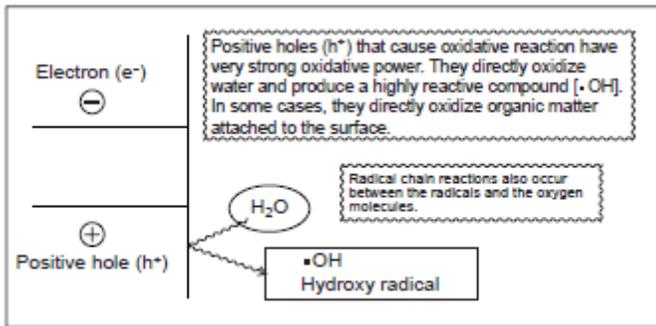


Figure 2.5: Photocatalytic Oxidation Mechanism (Amemiya, 2004)

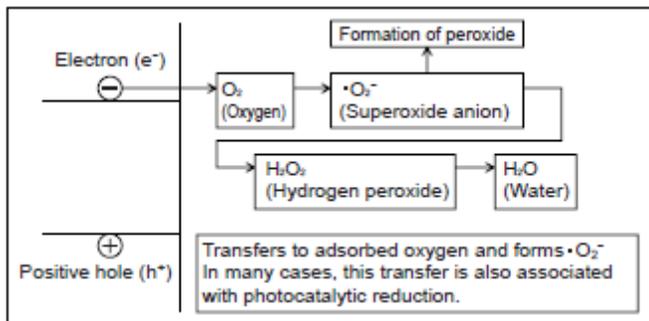


Figure 2.6: Photocatalytic Reduction Mechanism (Amemiya, 2004)

The photocatalytic process of TiO_2 can best be illustrated in three steps:

- 1) Photo-excited TiO_2 produces electron-hole pairs which migrate to the surface of the TiO_2
- 2) The photogenerated holes in TiO_2 react with adsorbed H_2O or OH^- to produce highly reactive hydroxyl radicals, hydrogen peroxide at the catalyst/water interface. Electrons can then react with oxygen vacancies to form superoxide ions.
- 3) The highly active oxygen species generated can then oxidize organic compounds or cells adsorbed on the TiO_2 surface, which results in the death of microorganisms (Fu, Vary, & Lin, 2005).

Figure 2.7 roughly illustrates the valence and conduction electron structures of TiO_2 .

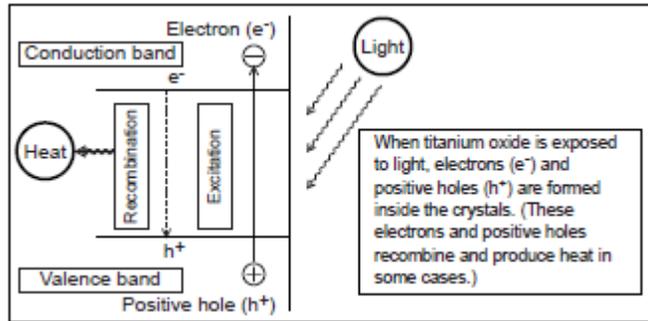


Figure 2.7: The Electron Structure of TiO₂ (Amemiya, 2004)

An important part of resistance for outdoor fabrics is not only their resistance to mildew and rot-producing fungus, but also ability to withstand photodegradation due primarily to ultraviolet light. While textile type, thickness, porosity and color directly affect UV and absorption protection, inorganic UV-absorbers such as TiO₂ can be embedded into coatings to minimize UV penetration through to the fiber, finish, or wearer, for example (Mahltig, Haufe, & Bottcher, 2005). Harper and Yeadon found that the presence of TiO₂ noticeably affected flame resistance at bath concentration levels lower than 3% (Yeadon & Harper, 1979). In conclusion, it was found that the four flame retardants exhibited reasonable flame resistant durability for 12 months of weathering, however, when the fabrics were topped with rutile TiO₂ (sunlight screening agent), excellent flame resistance was obtained for a minimum of 2 years weather exposure (Yeadon & Harper, 1979). Bleached duck fabrics finished without TiO₂ lost flame retardant properties in less than three months of actual weather exposure. Pearl greige duck fabrics finished without TiO₂ lost flame retardant properties in twelve months of actual weather exposure. Table 2.10 lists the results for TiO₂ added to a THPC-Urea fabric finish on 100% Cotton duck fabrics.

Table 2.10: Evaluation of THPC-Urea Finishes after Weathering

Evaluation After Weathering ^{1/}								
TiO ₂ in Topping	0 mo		12 mo		24 mo		100 hr AW	
	VFT	B.S.	VFT	B.S.	VFT	B.S.	VFT	B.S.
	✓	%	✓	%	✓	%	✓	%
(Bleached Duck)								
0	P	59	F ^{2/}	23	-	-	P	50
3.1	P	64	P	16	-	-	P	43
6.9	P	61	P	17	-	-	P	-
6.9 ^{3/}	P	58	P	28	P	13	P	47
0 ^{4/}	P	55	P	15	-	-	P	47
Untreated Bleached Duck								
Duck	-	100	-	32	-	18	-	48
(Pearl Gray Duck)								
0	P	85	P	35	F	21	P	67
2.6	P	87	P	54	P	35	P	75
6.0	P	91	P	62	P	45	P	-
6.2 ^{3/}	P	83	P	66	P	48	P	80
0 ^{4/}	P	96	P	44	P	30	P	79
Untreated Pearl Gray Duck								
Duck	-	100	-	52	-	38	-	78

- ^{1/} AW = Carbon arc accelerated weathering.
- B.S. = Retained breaking strength.
- VFT = Vertical flame test; P = passes; F = fails.
- ^{2/} Failed at 3 months.
- ^{3/} Topping contained pentachlorophenyl laurate and wax.
- ^{4/} Topping of trimethylolmelamine resin.

The mechanism by which TiO₂ functions as an anti-ageing coating is the photocatalytic process. Because anatase TiO₂ has a band-gap energy of 3.2 eV and rutile TiO₂ has a band-gap energy of 3.0 eV and light of energy greater than the band gap energy of TiO₂ is needed to start the photocatalytic UV absorption process, rutile TiO₂ has been determined more suitable as a UV blocker (Wang, Han, & Ke, 2006).

2.6.1.1 Improving the Photocatalytic Process of TiO₂

Photocatalytic efficiency may be improved through several methods: increasing the surface area of TiO₂ through the creation of smaller particle sizes and pore-size distributions, generation of defect structures to induce space-charge separation, and surface modification of TiO₂ with another metal or semiconductor (Fu, Vary, & Lin, 2005). Some researchers have been able to dope various transition metal ions into TiO₂, which extend the excitation wavelength range from UV into the visible region. The transition metal ions absorb visible light and transfer the excited electron to the TiO₂ conduction band. Fu et al. found improved photocatalytic activity of TiO₂ ranging well into the visible region of 396-450 nm through generation of a vanadium-doped TiO₂ nanocolloid (Fu, Vary, & Lin, 2005). Figure 2.8 illustrates the absorption spectra of pure TiO₂ and different percentages of vanadium-doped TiO₂.

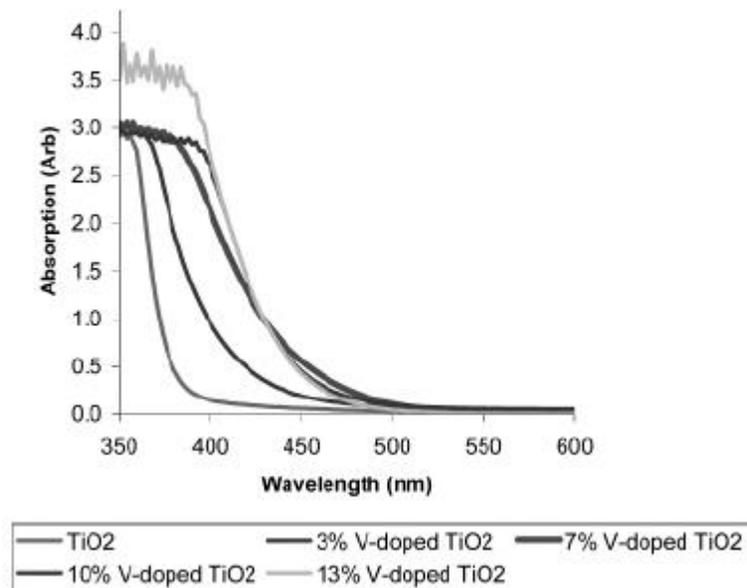


Figure 2.8: Absorption Spectra of Different Percentages of V-Doped TiO₂ Nanoparticle Suspensions (Fu, Vary, & Lin, 2005)

Anpo states that the smaller the particle sizes of the catalyst, the higher the efficiency of photoreaction. This is due to a concentration of unsaturated surface sites such as corners/edges increases and photon energies absorbed by the catalyst will contribute effectively to the surface reactions (Anpo, Shima, Kodama, & Kubokawa, 1987).

Effectiveness of TiO₂ as a photocatalyst is partially dependent upon the production rate of hydroxyl radicals at the particle's surface, which is dependent on the following factors: energy of light illuminating the surface of TiO₂, and competition between electron-hole recombination and the redox process occurring on the surface of the TiO₂ (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007). Through the synthesis of various nano and pigmentary TiO₂ particles in suspension, Verran et al. found that poor crystalline structure and defects play a large role in high electron re-combination rates, thus low photocatalytic activity (Verran, Sandoval, Allen, Edge, & Stratton, 2007). Pigments produced with more defects, thus more recombination centers, generated less reactive species than even slightly larger particles, suggesting that crystallinity of particles may be an even more important factor than particle size when measuring photocatalytic efficiency (Verran, Sandoval, Allen, Edge, & Stratton, 2007).

2.6.2 TiO₂ Size Quantization Effects

While the larger active surface area of TiO₂ is a benefit of smaller particle size, research has also shown that a decrease in particle size, especially below 100 nm, increases photocatalytic activity of TiO₂. This can be referred to as a "blue shift," since blue light is first to appear within the visible wavelength region (beginning at 400 nm). Anpo et al. investigated photocatalytic hydrogenation reactions with TiO₂ catalysts of extremely small

particle sizes and realized this size quantization effect. Anpo states that the different yields on TiO₂ particle diameter suggest that differences in photocatalytic activity are the result of differences in reactivity rather than in surface area according to his research (Anpo, Shima, Kodama, & Kubokawa, 1987). Table 2.11 illustrates how the quantum yield (number of photoformed products / number of incident photons) dramatically increases as the particle size decreases.

Table 2.11: Small-Particle Size Effects upon the BET Surface Area, Wavelength at Band Gap Position, Magnitude of Blue Shift, and Quantum Yields Measured at 300 nm (Anpo, Shima, Kodama, & Kubokawa, 1987)

particle size, Å	BET surface area, m ² /g	wavelength at band gap position, nm	magnitude of blue shift of band gap, eV	quantum yields, ^a %
38	1068	371.5	0.156	7.18×10^{-2}
50	941	375	0.126	7.02×10^{-2}
65	609	380.5	0.079	8.80×10^{-2}
85	430	385	0.041	2.42×10^{-2}
110	312	387	0.024	2.26×10^{-2}
220	137	388	0.016	1.13×10^{-2}
530	26	389.9	0.000	0.264×10^{-2}

Anpo claims that reduction in particle size may result in some electronic modification of TiO₂ to produce an enhancement of the activities of electrons and holes, and/or suppress the radiationless transfer of absorbed photon energies. Basically, nano-scale semiconductors retard the electron-hole recombination process via charge carrier trapping, giving high separation efficiency. Thus the activity of semiconductor nanoparticles may be higher than that of a conventional semiconductor particle because dimensions are so small that diffusion of electrons and holes to the surfaces of the particles is faster than the electron and hole

recombination process (Verran, Sandoval, Allen, Edge, & Stratton, 2007). Particle size has also proven to be a factor in flame retardant properties of TiO₂.

2.6.3 TiO₂ Used as a Sunlight Screener

Although not commonly used as a flame retardant, TiO₂ has been found to show synergism with other flame retardant or fiber dye chemistries, particularly in respect to the durability of the finish. The process of ageing can be defined as the action of atmospheric elements in altering color, texture, composition or form of an exposed object. These agents of weather may be classified as radiation, moisture, thermal conditions, and gasses (Wang, Han, & Ke, 2006). Not only does the addition of nanoparticles to the surface of a substrate increase mechanical durability, but the addition of TiO₂ increases elemental durability. Flame retardant coatings often become moisture sensitive and the sun's ultraviolet rays easily break molecular structures of the coatings (Wang, Han, & Ke, 2006). When ultraviolet rays radiate surface coatings, enough energy will be present to break carbon bonds and numerous functional groups (Wang, Han, & Ke, 2006). Therefore, many traditional coatings are not durable in outdoor environments. In 1979, David Yeadon and Robert Harper (Yeadon & Harper, 1979) applied 4 different phosphonium-based flame retardant treatments to 100% Cotton duck fabrics for use in outdoor applications. The finishes used were THPOH-NH₃, THPOH-Amide, THPC-Urea, and THPC-Amide. In addition to conventional FR treatments, percentages of rutile TiO₂ ranging from 0 to 7 percent were applied. TiO₂ was being used as a sunlight screener because the sun's rays, possessing harmful ultraviolet light, reduced the effectiveness of these tetrakis(hydroxymethyl)phosphonium salt-based flame retardants over

time. TiO_2 possesses photocatalytic abilities meaning not only does it convert ultraviolet light to “ozone” to kill microbes, but first and foremost absorbs UV and some visible rays.

2.6.4 TiO_2 as an Antimicrobial

It has been stated that there should be a regeneration antimicrobial model based on application of chemical finish to fabrics that produce active germicidal species continuously regenerated by ultraviolet light or laundering with bleach, for example (Lewin & Sello, Handbook of Fiber Science and Technology, Vol. II, Chemical Processing of Fibers and Fabrics. Functional Finishes, Part A, 1983). TiO_2 offers a reasonable solution to this suggestion and therefore, has an unlimited reservoir of antibacterial agent. The different morphologies of bacterium (i.e. gram-positive, gram-negative) help us to understand hindering of hydroxyl radicals produced by TiO_2 from penetrating the bacteria's cytoplasmic membrane to different extents (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007). For example, the only barrier for *S. aureus* is the peptidoglycan layer and periplasmic space, thus, *S. aureus* is given little protection from the hydroxyl radicals. However, gram-negative *E. coli* is protected by both a thin layer of peptidoglycan as well as an outer membrane (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007). Thus, the killing of *E. coli* by TiO_2 thin films may be carried out in a 2 step process in which the outer membrane is breached first followed by the compromise of the cytoplasmic membrane (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007).

The reactive oxygen species as mentioned in the photocatalytic process of TiO_2 are responsible for the killing of bacteria. TiO_2 thin films have been shown to be especially efficient under sunlight or black light (UV) irradiation (Page, Palgrave, Parkin, Wilson,

Savin, & Chadwick, 2007). The hydroxyl radicals (OH) are highly reactive and therefore, shorter-lived. Superoxide ions, though relatively longer lived, cannot penetrate the cell membrane due to their negative charge. Therefore, they must directly contact the outer bacterial surface unless the TiO₂ particle has entered the cell (Fu, Vary, & Lin, 2005). While hydrogen peroxide is less harmful compared to hydroxyl radicals and superoxide ions, it can enter the cell. It is still under investigation as to which species contributes more to the oxidative reactions with organic compounds, however, research has proven that TiO₂ possesses excellent antimicrobial ability (Fu, Vary, & Lin, 2005).

The Sunada research group has shown that irradiation of a thin transparent TiO₂ film destroys the outer membrane of the E. coli cell, causing leakage of minerals, proteins, and genetic materials, leading to cell death (Fu, Vary, & Lin, 2005). It was also noted that at a concentration of TiO₂ suspension an order of magnitude higher than that used to kill B. megaterium was required to kill E. coli, which is probably due to changes in cell wall structures (E. coli is gram-positive with a single membrane, B. megaterium is gram-negative with two membranes). Fu was also able to prove qualitatively that a smaller particle size of TiO₂ exhibits better bacterial inhibition results.

K. Page et al. applied TiO₂ and silver-doped TiO₂ nanoparticulate films using the sol-gel process. Thin films were irradiated with 365 nm (UV) light and also placed in total darkness. Samples were tested against gram-positive, gram-negative, and spore-forming bacteria. While it was noted that the silver-doped titanium films were more photocatalytically efficient, no activity was noted in the dark, which leads to the conclusion that the silver eased the stabilization of the photo-generated electron-hole pair. The silver

also donated extra electrons to the conduction band, producing more reactive species at the surface of the catalyst (TiO₂). However, these findings do indicate that the mode of action is not due to silver ion diffusion into the bacteria (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007). Page found that coatings made up of silver-doped TiO₂ were 99.997% effective against inoculums of $\sim 2.15 \times 10^9$ cfu ml⁻¹ (colony forming units * ml⁻¹) of *S. aureus*. The coating made of solely TiO₂ showed an effectiveness of 49.925% against that same inoculum (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007).

TiO₂ has also been studied in its solution form. In the absence of stirring, most solutions have an inherent tendency to sediment. In an absence of stirring, it was found that a Degussa P25 pigment is the most effective antimicrobial (Verran, Sandoval, Allen, Edge, & Stratton, 2007). However, solutions or pigments with the best dispersion have always been as much as 10,000 times more effective (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007),(Verran, Sandoval, Allen, Edge, & Stratton, 2007). In general, Verran's experiments showed that the antimicrobial effectiveness of TiO₂ solutions increased as concentrations increased up to 0.04%. A leveling-off, and in some cases, reduction in effectiveness, was noted as percentages continued to increase. This is because of a balance between the increase in available pigment surface area and a decrease in light transmission due to light scattering as concentration of pigment increases (Verran, Sandoval, Allen, Edge, & Stratton, 2007).

2.7 TiO₂ Application Techniques

TiO₂ thin films have been formed on numerous surfaces such as glass and steel using a wide range of techniques, particularly sol-gel and chemical vapor deposition (Page,

Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007). Surfaces of TiO₂ nanoparticles usually contain high concentrations of remnant un-saturable bonds and hydroxyl groups, which form agglomerates of nanoparticles by van der Waals force (Wang, Han, & Ke, 2006). Therefore, Wang et al. used dispersing agents to decrease interface force and total energy of the system. Well dispersed nanoparticles are necessary to exhibit all beneficial capabilities to the fullest.

2.7.1 The Sol-Gel Functionalization Process

Sols based on nanoparticulate modified metal oxides offer the following benefits:

- 1) Use of particles with diameters < 50 nm form durable transparent oxide layers
- 2) Oxide layers are stable against heat, light, chemical and microbial attacks
- 3) Layers improve mechanical properties such as mechanical strength, wear and abrasion resistance while offering methods of varying surface properties
- 4) Oxide coatings can carry embedded functional additives such as biological compounds, inorganic particles and polymers and the degree of immobilization of these embedded compounds is easily controlled
- 5) Coatings may be prepared at room temperature and applied under conventional textile process such as padding, exhaust dyeing, dip-coating or spraying

Ideally, as these functionalizations are incorporated into textiles, durability (to laundering, abrasion, etc.) should be maintained and may be achieved through new production technologies or improved fiber/coating (surface) materials (Mahltig, Haufe, & Bottcher, 2005).

2.7.2 Preparation and Modification of Nanosol Coatings

Inorganic sols of nanoparticles may be prepared by acid or alkali hydrolysis of the corresponding silicon or metal alkoxides in water or another organic solvent, typically ethanol, miscible with water.

They are typically nano-dispersions with solids content between 4 and 20 wt% and again, particle sizes of less than 50 nm (Mahltig, Haufe, & Bottcher, 2005). Following treatment of the textile substrate, the nanoparticles condensate and aggregate into a 3-dimensional network and form a lyogel-layer, still containing the solvent. During the drying process, solvent is removed from the lyogel and a xerogel layer with a porous structure, free of solvent, is formed (Mahltig, Haufe, & Bottcher, 2005).

Coating properties such as density, porosity, thickness and mechanical properties of the layers may be governed by processing conditions such as hydrolysis and drying. For example, nanosols hydrolyzed under acidic conditions result in weakly cross-linked condensation products having a denser condensation layer; basic hydrolysis conditions form particle aggregates with larger pores. Unfortunately, most textiles cannot undergo thermal treatments much higher than 180°C due to thermal destruction, however, the higher the duration and degree of annealing, the higher the mechanical properties and stability during washing of coated fabrics (Mahltig, Haufe, & Bottcher, 2005).

During an attachment reaction, silane oligomers form hydrogen bonds with the substrates' functional groups which are then converted to covalent bonds during the drying and curing steps (Arkles, Barry; Larson, Gerald, 2008).

2.8 Cotton and Polyester/Cotton Blended Fabrics

Analysis of the chemical structure of fabrics is very important when using the approach of functionalized surface coatings. Poly(ethylene terephthalate), which is commonly known as polyester or PET, contains the ester functional group in the main chain. Illustrated in Figure 2.9 is the structure for polyester.

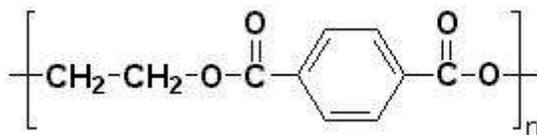


Figure 2.9: Chemical Structure of PET (Polyester)

The structure of cellulose, which makes up a majority of cotton, contains functional hydroxyl groups. The structure of cellulose is illustrated in Figure 2.10.

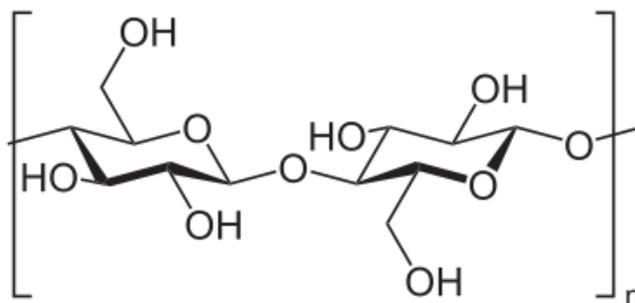


Figure 2.10: Chemical Structure of Cellulose

2.9 Test Methods

Because the objectives of this research are to impart a durable textile finish, consisting of both antimicrobial and flame retardant characteristics, one must understand current test methods and procedures to measure efficacy of the above-mentioned properties. While there are multitudes of methods measuring these properties, a thorough investigation of test methods and procedures would be beyond the scope of this research, therefore, a

simple understanding should be gained about the methods of quantitative assessment currently employed. Standard testing methods have been provided by ASTM and AATCC. In some cases, due to the complexity of the finish, the AATCC protocol for antimicrobial analysis has been modified.

2.9.1 Flame Retardant Test Methods for TiO₂-Based Finishes

TiO₂ possesses flame retardant properties as a thermal stabilizer and oxygen inhibitor through generation of cross-linked particle networks on substrate surfaces. Therefore, testing flame retardant finishes on textiles that contain TiO₂ is no different than testing any other flame retardant fabric finish. Light sources such as those mentioned in Section 2.9.2 may be disregarded when conducting FR testing. Therefore, similar test methods to those listed in Section 2.2.6 may be used to analyze flame retardant effects of TiO₂-based finishes: AATCC TM34 and ASTM D6413.

2.9.2 Antibacterial Test Methods and Procedures for TiO₂-Based Antimicrobials

Standard test methods for antimicrobial textile finishes are published within AATCC's technical manual annually. Commonly used methods consist of TM100: a quantitative bacterial analysis, TM147: a qualitative bacterial analysis, TM30: a fungal analysis, and TM174: quantitative/qualitative test method for carpets. Antimicrobial research with TiO₂ has brought up some difficulties with current textile testing methods. Due to the UV activation of TiO₂ particles, it seems insufficient to test fabrics under AATCC's standard protocol involving only visible and no light sources. When assessing antimicrobial activity, Page *et al.* irradiated sample coatings under a 254 nm germicidal UV lamp for 30 minutes to activate and disinfect the TiO₂ films. Then, samples were irradiated with a black light UV

lamp, 365 nm light for the desired length of time so as not to kill bacteria by the wavelength of light alone (Page, Palgrave, Parkin, Wilson, Savin, & Chadwick, 2007). Page used a system of controls:

- 1) active substrate in UV light
- 2) inactive substrate in UV light
- 3) active substrate in the dark
- 4) inactive substrate in the dark

A comparison of active substrate in UV light with inactive substrate in the dark enables kill levels to be calculated. Page also notes that exposure to UV light by itself may have a microbicidal effect, depending on bacterium type being investigated.

3 Methodology and Experimental Procedures

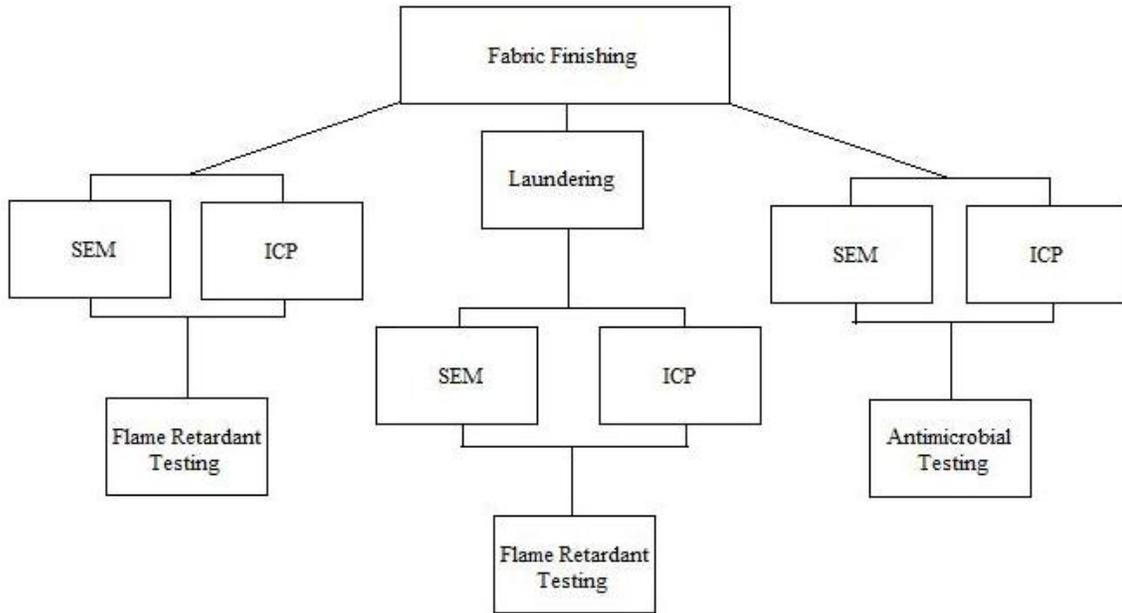


Figure 3.1: Methodology Process Flow Diagram

3.1 The Intent and Advantages of this Research

The approach of this research involves using TiO₂ nanoparticles, flame retardants, and crosslink-able silanes to treat both cotton and polyester/cotton blended fabrics to obtain durable antimicrobial and flame-retardant textiles. The main objectives were to generate a finishing technology having: (1) excellent antimicrobial efficacy, (2) enhancement of existing flame retardant treatments, (3) excellent durability to laundering, and (4) easy process-ability. A process flow diagram of fabric evaluation methodologies is given in Figure 3.1. Following chemical treatment, flame retardant and antimicrobial properties of fabrics were quantified. Selected fabrics were then laundered and flame retardant properties were analyzed as an attempt to assess the durability of finish attachment to the fiber surfaces.

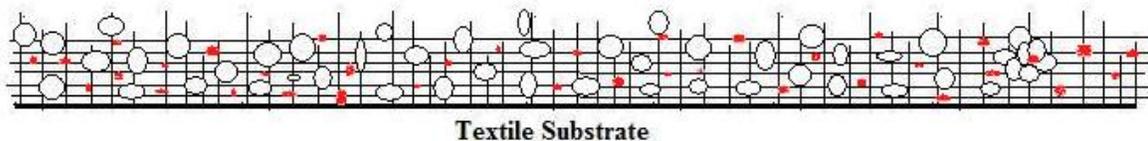
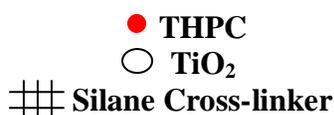


Figure 3.2: Surface Morphology of Applied Finishes



The above-mentioned properties are achieved through TiO₂ nanoparticles because of their photocatalytic activity (antimicrobial), synergistic effects with phosphorus-based flame retardants, and ability to form large numbers of covalent bonds (Degussa). All of these effects are only multiplied due to such small TiO₂ particle diameters (21nm for P25), thus larger surface area for equal particle masses applied. The ability to form large amounts of covalent bonds not only helps to strongly attach TiO₂ to the fabric surface, but also provides further bonding sites for dyes or other finishes, such as flame retardants.

While some TiO₂ nanoparticles attach directly to the fabric as single particles, most are attached to fibers as clusters at random intervals. The silane cross-linkers, however, may create a three-dimensional network between fabric surface, flame retardant, and TiO₂ nanoparticles as illustrated in Figure 3.2.

3.2 Fabric Selection

Due to the complexity and variability of performance associated with both flame retardant and antimicrobial fabrics (Schindler & Hauser, 2004) (Heywood, 2003), 100% cotton and 80/20 polyester/cotton blend fabrics were chosen with relatively simple structures.

Both fabrics were plain woven, light weight (cotton 2.5 oz/yd², poly/cotton 4.5 oz/yd²), sheeting material.

3.3 Finishing Variables

Based on previous research (Schindler & Hauser, 2004), finishing equipment selections included equipment types that would provide the most consistent pad application, drying, and curing oven processes feasible. Equipment used to mix, apply, dry, and cure fabrics developed in this research is given in Table 3.1.

Table 3.1: Machinery Used during Application Process

Equipment	Model	Manufacturer	Notes
Pad	HVF	Werner Mathis A.G.	Lab Scale
Curing Oven	LTF	Werner Mathis A.G.	Lab Scale
High Speed Mixer	Tissuemiser	Fisher Scientific	10,000 - 33,000 RPM

3.3.1 Padding Equipment

Fabrics may be introduced to the pad either vertically or horizontally on the Werner Mathis HTF (adjustable nip configuration). The instrumentation panel on the left allows an operator to adjust nipping pressure and pad roll speed (Figure 3.3).



Figure 3.3: Werner Mathis HVF Lab Scale Pad

The pictured configuration of the machine allows for small chemical sample sizes to be placed between the two rubber-coated rolls once they are pressed together (nipped). This keeps the chemistry “troughed” between the nip rollers and ensures even coating onto fabric surfaces.

3.3.2 Drying/Curing Equipment

In many cases, researchers air or oven dry sample fabrics in a process separate from the curing process. However, in an attempt to replicate a true fabric finishing drying/curing process, finished fabrics were both dried and cured in a single step in a lab scale Werner Mathis LTF horizontal curing oven (Figure 3.4). Although the fabric does not move over burners lined from the entry to the exit end of a conventional finishing oven, the fabric was placed in a closed, controlled environment, which provided very consistent drying and curing conditions. The fabric was only allowed to come into contact with the pins, which kept the fabric suspended above the heating element or any other points of contact.



Figure 3.4: Werner Mathis LTF Horizontal Oven

This configuration allows for fabrics to be pinned onto the sliding rack, shown protruding from the camera-facing side of the machine. Oven temperatures and dwell times may be set on the instrument panel to the right, allowing for consistent drying/curing. Setting dwell time and temperature can be translated to setting temperature and speed in conventional textile drying/curing processes.

3.3.3 Chemical Components

At the start of this research, numerous chemicals were acquired. All chemicals fall into one of the previously mentioned categories: TiO₂ nanoparticles, flame retardants, and multifunctional silanes (Table 3.2).

Table 3.2: Chemicals Used in Experimental Procedures

Titanium Dioxide Nanoparticles	Multifunctional Silane Crosslinkers	Flame Retardants
Aeroxide® P25	Tetraethoxysilane	Tetrakis(hydroxymethyl)-phosphonium-chloride
	Tetramethoxysilane	Urea
	Bis(triethoxysilyl)ethane	
	Bis(trimethoxysilyl)ethane	
	Bis(trimethoxysilyl)hexane	
	1,4-Bis(trimethoxysilyl)ethylbenzene	

It is important to note that the flame retardant used in this research was a mix of tetrakis(hydroxymethyl)-phosphonium-chloride and urea. This FR is a well-known, durable treatment for 100% cotton fabrics and research has shown that it performs reasonably well with cotton/man-made fiber blends (Lewin & Sello, Handbook of Fiber Science and Technology: Vol II. Chemical Processing of Fibers and Fabrics. Functional Finishes. Part B, 1983) (Heywood, 2003). However, where the conventional process calls for pad application, dry, cure, and wash, this research called for a pad, dry, cure procedure because the phosphorus-based flame retardant was intended to bond with the cross-linked network of TiO₂ and silanes on the surface of both cotton and polyester/cotton fabrics.

3.4 Chemical Structures, Properties, and/or Compositions

3.4.1 Multifunctional Silane Cross-Linkers

Six silanes were used in experimentation (usually individually) to compare effects on overall finish durability. The multifunctional silanes serve as cross-linking centers and allow for three-dimensional polymer networks of both flame retardants and TiO₂ to form on the fabric structures through linking with cellulose and polyester functional groups. These six silanes are:

- Tetraethoxysilane (TEOS), illustrated in Figure 3.5

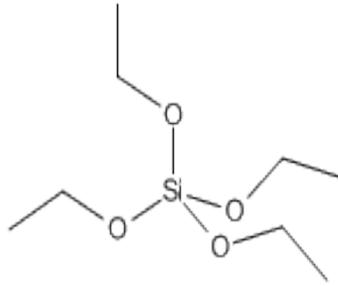


Figure 3.5: Chemical Structure of Tetraethoxysilane

- Tetramethoxysilane (TMOS), illustrated in Figure 3.6

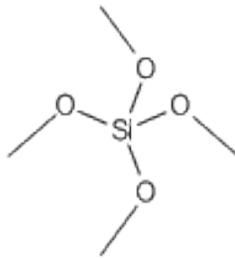


Figure 3.6: Chemical Structure of Tetramethoxysilane

- Bis(triethoxysilyl)ethane (BTESE), illustrated in Figure 3.7

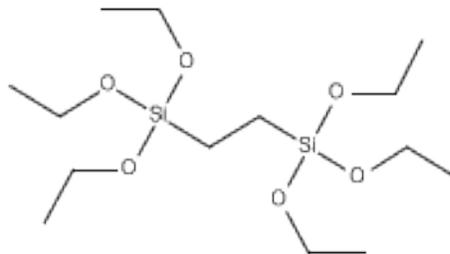


Figure 3.7: Chemical Structure of Bis(triethoxysilyl)ethane

- Bis(trimethoxysilyl)ethane (BTMSE), illustrated in Figure 3.8

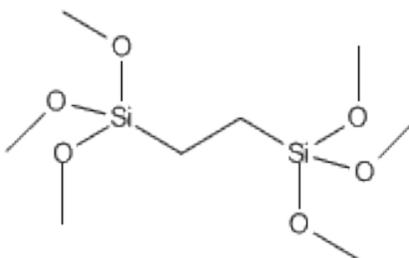


Figure 3.8: Chemical Structure of Bis(trimethoxysilyl)ethane

- Bis(trimethoxysilyl)hexane (BTMSH), illustrated in Figure 3.9

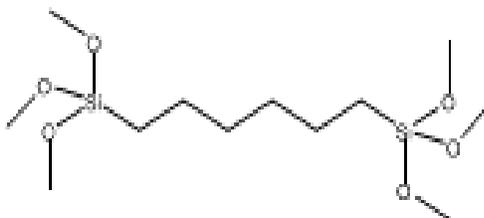


Figure 3.9: Chemical Structure of Bis(trimethoxysilyl)hexane

- 1,4-Bis(trimethoxysilylethyl)benzene (BTMSEB), illustrated in Figure 3.10

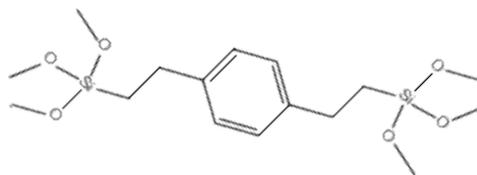


Figure 3.10: Chemical Structure of 1,4-Bis(trimethoxysilylethyl)benzene

3.4.2 Flame Retardants

The primary FR's are, tetrakis(hydroxymethyl)-phosphonium-chloride (THPC) + Urea. THPC + Urea based FR's have been applied to cellulosic, polyester, and poly/cotton blend fabrics since the 1950's. Research has concluded that THPC + Urea provide durable

flame retardant performance to cotton and poly/cotton fabrics as a phosphorus-based retardant, to which TiO_2 is a proven synergist. THPC has also shown microbicidal action (killing bacteria) by itself, due to phosphorus content. Urea, used as a pH stabilizer in THPC + urea finishes, has also shown antimicrobial efficacy (Hoch, Wagner, & Vullo, 1966).

- Tetrakis(hydroxymethyl)-phosphonium-chloride (THPC), illustrated in Figure 3.11

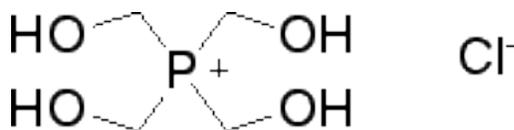


Figure 3.11: Chemical Structure of Tetrakis(hydroxymethyl)-phosphonium-chloride

- Urea, illustrated in Figure 3.12

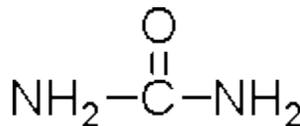


Figure 3.12: Chemical Structure of Urea

3.4.3 TiO_2 Nanoparticles

TiO_2 P25 nanoparticles selected for this research were manufactured by Evonik-Degussa. The manufacturer has claimed that these particles have high purity due to the Aerosil manufacturing process, illustrated in Figure 3.13 performed on TiCl_4 , as well as heat stabilizing properties which result in improved ageing properties under high temperatures as well as positive impact on flammability protection (Evonik Degussa - Chemicals).

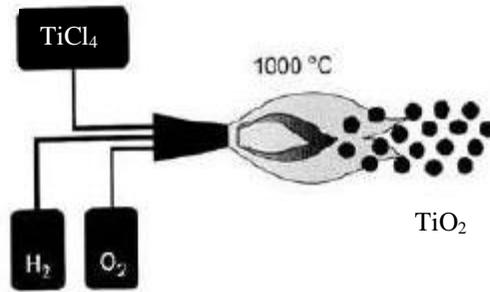


Figure 3.13: The Aerosil Process

These properties may be beneficial in the following applications: active photocatalytic component, catalyst carrier, and heat stabilizer. Table 3.3 provides manufacturer data for this commercially available nano- TiO_2 . The particles consist of approximately 80% anatase structural TiO_2 while the remaining 20% are of the rutile structure.

Table 3.3: Physio-Chemical Data for Degussa P25 (Evonik Degussa - Chemicals)

Properties	Unit	Typical Value
Specific Surface Area (BET)	m ² /g	50 ± 15
Average primary particle size	nm	21
Tapped density (approx.)	g/l	approx. 130
Moisture (2hr at 105 oC)	wt. %	≤ 1.5
Ignition Loss (2 hr at 1000 oC, based on matl dried for 2hr at 105 oC)	wt. %	≤ 2.0
pH (in 4% dispersion)		3.5-4.5
Titanium dioxide	wt. %	≥ 99.5
Al ₂ O ₃ - content	wt. %	≤ 0.300
SiO ₂ - content	wt. %	≤ 0.200
Fe ₂ O ₃ - content	wt. %	≤ 0.010
HCl - content	wt. %	≤ 0.300
Sieve residue (by Mocker, 45µm)	wt. %	≤ 0.050

3.5 Design of Experiments

In order to determine the effects of the chemical and mechanical variables mentioned in Section 3.3, several DOE's (Design of Experiments) were conducted in order to realize effects of adjustment of the parameters associated with these variables.

3.5.1 Cure Time and Temperature Experiments

Due to differences in fabric structures as well as chemical properties, precautions must be taken when selecting optimum finishing conditions for future experiments. For

example, cotton fabrics are typically yellowed or degraded when cured at temperatures of 160°C or above. Also, in order to more accurately reflect true finishing within a textile finishing facility, the drying and curing steps were combined into one overall procedure. Therefore, 80/20 polyester/cotton blended fabrics finished with 6.0% TiO₂, 0.5% TEOS, 25.0% THPC + 15.0% Urea, and 53.5% H₂O were dried/cured at the conditions listed within Table 3.4 and evaluated for flame retardant performance to determine the optimum dry/cure conditions for both 100% cotton and 80/20 poly/cotton fabrics. This experiment was conducted only on polyester/cotton blended fabrics because the 20% cotton within these blended fabrics should be a sufficient amount of cotton fiber to show any degradation or yellowing that would also be seen on 100% cotton fabrics under identical conditions.

Table 3.4: Dry/Cure Variables

Cure Procedures		
Procedure	Time (min)	Temp. (°C)
A	5	120
B	20	120
C	5	150

Upon contacting a technical services representative for Gelest, the manufacturer of the six multifunctional silanes used in totality within this research, the decision was made to reduce curing time to a minimum of five minutes due to the determination that 10-20 minute cure-time was stated to be “overkill” by the representative. Cure times of 5 minutes also better reflect actual dry/cure times in average conventional textile processes. Gelest’s technical manual also recommended cure temperatures of 110°C – 120°C. However, the representative mentioned that 150°C would be an acceptable maximum. Also, a single experiment was conducted using the suggested maximum time and temperature to quantify an effect of more-than-sufficient curing on durability and performance. The curing time and

temperature that produced the best results following flame resistance testing was used for all further experimentation.

3.5.2 Generation of Control Fabrics

In order to assess the effects of TiO₂ nanoparticles, two different control fabrics of each construction, 100% cotton and 80/20 poly/cotton (donated by Jeff Krauss, NCSU COT Pilot Plant Manager), were generated. The first controls were merely un-finished fabrics of cotton and poly/cotton. The second controls were finished with 25.0% THPC, 15.0% Urea, 0.5% TEOS, and 59.5% H₂O on weight of bath (owb). TEOS was chosen as the cross-linker due to its common application in textile sol-gel experimental finishing processes.

3.5.3 Silane Type Experiments

Fabrics were then evaluated for an optimum silane type depending on results from FR testing. Although silanes play an important role in the durability of applied finishes, this experiment was conducted in order to see if actual silane type has either a positive or negative effect on fabric flammability performance as well as finish durability. The following are chemistries applied to both 100% cotton and 80/20 polyester/cotton fabrics to evaluate the effect of silane type on flame retardant performance of 100% cotton and 80/20 poly/cotton fabrics:

- 25.0% THPC + 15.0% Urea + 3.0% TiO₂ + 0.5% TEOS + 56.5% H₂O
- 25.0% THPC + 15.0% Urea + 3.0% TiO₂ + 0.5% TMOS + 56.5% H₂O
- 25.0% THPC + 15.0% Urea + 3.0% TiO₂ + 0.5% BTESE + 56.5% H₂O
- 25.0% THPC + 15.0% Urea + 3.0% TiO₂ + 0.5% BTMSE + 56.5% H₂O

- 25.0% THPC + 15.0% Urea + 3.0% TiO₂ + 0.5% BTMSH + 56.5% H₂O
- 25.0% THPC + 15.0% Urea + 3.0% TiO₂ + 0.5% BTMSEB + 56.5% H₂O

The only variable adjusted within these finishes was silane type, which ranged across each of the six individual types highlighted in Section 3.4.1. The resulting silane with the least negative impact on flame retardant performance was to be used in all further experimentation.

3.5.4 TiO₂ Concentration Experiments

Following the generation of optimum curing conditions and optimum silane type, the main research ingredient, TiO₂, was evaluated through a series of experiments. Holding all other chemical concentrations constant on-weight-of-bath at 25.0% THPC, 15.0% Urea, 0.5% TEOS, and a balance of H₂O, TiO₂ concentrations were adjusted from 0% to 9.0% owb using the following concentrations: 0%, 0.5%, 1.0%, 1.5%, 3.0%, 6.0%, and 9.0%. These concentrations of TiO₂ were evaluated on both 100% cotton fabrics as well as 80/20 polyester/cotton fabrics. Flame retardant properties of all finished fabrics were quantified and selected fabrics were analyzed for antimicrobial testing as well due to TiO₂ being considered the primary active antimicrobial ingredient.

3.5.5 Durability to Laundering Experiments

Due to observations of limited poor durability of flame retardant performance as seen in the results to follow, particularly with polyester/cotton blend fabrics, an experiment was designed to quantify the loss of flame retardant performance with laundering. 80/20 polyester/cotton fabrics were finished with elevated concentrations of silanes (3% and 6%

owb) and 6% TiO₂ owb, which was shown to significantly increase flame resistance of these fabrics when finished with 25% THPC + 15% Urea owb. The experiment may be outlined as follows in Table 3.5.

Table 3.5: Laundering DOE Outline

Silane Type	% Silane	Launderings
TEOS	3	0
TEOS	3	1
TEOS	3	2
TEOS	3	3
TEOS	3	4
TEOS	3	5
TEOS	6	0
TEOS	6	1
TEOS	6	2
TEOS	6	3
TEOS	6	4
TEOS	6	5

TEOS was an obvious selection for this experiment due to its superior performance to other silane types in the previous experiment comparing flame retardant performance of finishes utilizing each of the six silane types.

3.5.6 Silane Concentration Experiments

To further assess the impact of multifunctional silanes on finish durability, a series of experiments were conducted through the manipulation of silane concentration. Since the purpose of the silanes is to cross-link TiO₂ nanoparticles and FR chemistry to substrate surfaces (i.e. poly/cotton fabrics), it is intuitive to think that much greater percentages of silanes are needed to impart more durable flame retardant performance on the polyester/cotton blended fabrics. Therefore, the following experiments, highlighted in Table 3.6, were conducted.

Table 3.6: Silane Concentration Experiment Outline

% TiO ₂	% Silane	Silane Type	% FR	FR Type
6	10	TEOS	25 + 15	THPC + Urea
6	20	TEOS	25 + 15	THPC + Urea
6	10 + 2	TEOS + BTESE	25 + 15	THPC + Urea

The solution containing 10% TEOS + 2% BTESE was prepared according to Gelest's literature suggesting a 5:1 ratio of short-chain to long-chain silanes for enhanced durability under agitating aqueous conditions such as laundering (Arkles, Barry; Larson, Gerald, 2008).

3.5.7 Flame Retardant Concentration Experiments

Due to observed stiffness of hand in 80/20 polyester/cotton fabrics in previous experiments, the concentration of THPC + Urea was split in half and applied to poly/cotton fabrics to compare the fabric hand and flame retardant performance. THPC + Urea are a major contributing factor to fabric stiffness, which is one of the major negative impacts associated with the use of large amounts of this finish (Schindler & Hauser, 2004). Therefore, half of the initial concentration was applied to determine whether or not the phosphorus content would be great enough to maintain the levels of flame retardant performance observed in fabrics finished with 25% THPC + 15% Urea. The experiment is highlighted in Table 3.7.

Table 3.7: FR Concentration Experiment Outline

% TiO ₂	% Silane	Silane Type	% FR	FR Type
6	0.5	TEOS	25 + 15	THPC + Urea
6	0.5	TEOS	25.5 + 7.5	THPC + Urea

3.5.8 pH Experimentation

As discovered through the review of current literature, when applying sol-gel films, pH of chemistry can play a significant effect. As stated by Mahltig et al, sols applied under

acidic conditions create densely concentrated particle condensates on the substrate's surface. Therefore, an experiment was conducted using the standard solution pH of ~3 and an identical chemical solution with the pH adjusted to 5.5 with 0.5 g NaOH (caustic) and applied to polyester/cotton fabrics. In their technical literature, Gelest recommends a hydrolysis pH of silanes to be adjusted to 5.5 as well. Therefore, it seems logical to adjust total bath pH to 5.5 prior to application. Table 3.8 gives details of the experimental chemistries.

Table 3.8: pH Experiment Outline

% TiO ₂	% Silane	Silane Type	% FR	FR Type	pH
6	0.5	TEOS	25 + 15	THPC + Urea	3
6	0.5	TEOS	25 + 15	THPC + Urea	5.5

Mahlting et al. also states that as the acidity of sol-gel mixes is decreased, the 3-dimensional network is modified to more of a porous structure. That is the reasoning outlining this experiment. The THPC + Urea should be able to better penetrate and cross-link within the network structure. There should be better overall cross-linking of TiO₂ particles, THPC, and Urea, which would increase the durability of the finish to polyester/cotton blend fabrics.

3.6 Solution Preparation

Solutions were prepared by hydrolyzing the multifunctional silanes in water overnight by using a magnetic stirrer. pH was adjusted to a level of 5.5 using 0.01N hydrochloric acid (HCl) if necessary. At the same time, a second solution was prepared mixing TiO₂ nanoparticles with flame retardants and water. This solution was also allowed to magnetically stir overnight. Approximately 5 minutes prior to pad application, the

hydrolyzed silane solution was added to the TiO₂/FR solution and vigorously mixed using the Tissuemiser Hi RPM mechanical stirrer for 1-3 minutes to ensure proper dispersion of nanoparticles and other active ingredients within the solution.

3.7 Fabric Coating, Drying, and Curing

3.7.1 Coating Process

Again, fabric coating was performed with the Werner Mathis HVF pad in horizontal configuration. The following machine variables were held constant through the course of this research:

- Roll Speed → 1.5 m/min
- Nip Pressure → 1 Bar

3.7.2 Calculation of Fabric Wet Pick-Ups (WPU) and Finish Add-On

Prior to the coating process, all fabrics were conditioned and weighed. Then, following the coating process, fabrics were then weighed again in order to determine WPU. Equation 4 outlines the mathematical formula for calculation of WPU.

$$\% WPU = \frac{(Wet Fabric Weight - Dry Fabric Weight) * 100}{Dry Fabric Weight}$$

Equation 4: % Wet Pick-Up Calculation

WPU's were calculated for both 100% cotton and 80/20 poly/cotton fabrics. Average wet pick-up for 100% cotton fabrics was determined to be 73.07% with a standard deviation of 3.1 while average wet pick-up for 80/20 poly/cotton fabrics was determined to be 94.74% with a standard deviation of 3.9. Differences in wet pick-ups are due to differences in woven fabric structures. While cotton fabrics typically are more hydrophilic, due to the looseness of

structure of the poly/cotton blend fabric used in this research, wet pick-ups were higher for the blended fabric which possessed greater interstitial space for solution pick-up.

From the WPU formula, add-on may be mathematically calculated as shown in Equation 5.

$$\% \text{ Add - On} = \frac{\% \text{ WPU} * \% \text{ Chemical Concentration (o.w.b.)}}{100}$$

Equation 5: % Add-On Calculation

The add-on's of TiO₂ and THPC were calculated and are provided in Table 3.9.

Table 3.9: Finish Add-On Data

% TiO ₂ owb	% THPC owb	Cotton TiO ₂ % Add-On	Cotton THPC % Add-On	Poly/Cotton TiO ₂ % Add- On	Poly/Cotton THPC % Add-On	Cotton % Add-On	Poly/Cotton % Add-On
0.00	25.00	0.00	18.27	0.00	23.69	18.27	23.69
0.50	25.00	0.37	18.27	0.47	23.69	18.63	24.16
1.00	25.00	0.73	18.27	0.95	23.69	19.00	24.63
1.50	25.00	1.10	18.27	1.42	23.69	19.36	25.11
3.00	25.00	2.19	18.27	2.84	23.69	20.46	26.53
6.00	25.00	4.38	18.27	5.68	23.69	22.65	29.37
9.00	25.00	6.58	18.27	8.53	23.69	24.84	32.21

While the add-on calculation process is a useful exercise in the developmental phases of a textile coating chemistry, it is useful to determine add-on via more scientific methods such as ICP elemental analysis than the mathematical method described above. For example, while TiO₂ nanoparticles may be present as 9% of a finish bath, it should be scientifically verified that 9% of the bath picked-up by the fabric during the coating process consists of TiO₂, hence Section 3.13.

3.7.3 Drying/Curing Process

In order to further replicate conventional textile processes, applied finishes were dried and cured in the same step. The effect of multiple dry/cure configurations on finish durability was evaluated in this research. This portion of the application methodology is very important because the cure of the finish plays an important role in finish durability. It is primarily the cure, which drives out remaining solvent during the sol-gel process and converts hydrogen bonds to covalent bonds between the nanoparticles and the substrate surface, in this case the fabric. However, temperature and duration of heat exposure can affect fabric properties in significantly undesirable ways, such as yellowing fabrics or increasing stiffness or brittleness. Therefore, it only seems feasible to conduct an additional DOE to determine optimum dry/cure temperature associated with these fabrics, this chemistry, and in general, this process, as described above in Section 3.5.1.

3.8 Fabric Laundering Process

In 1991, the American Association of Textile Chemists and Colorists (AATCC) developed a “Standard Laboratory Practice for Home Laundering Fabrics Prior to Flammability Testing to Differentiate Between Durable and Non-Durable Finishes.” This standard is useful either in determining FR durability or simply to establish flammability classifications of textiles before and/or after laundering. The laundering procedure applied in this research was modified due to machine limitations, however, it follows the above-mentioned standard as closely as possible. To avoid sample deterioration in the laundering process, fabrics were serged prior to undergoing any laundering cycle. Serging, in this case,

consists of sewing a commercial seam around all four sides of the fabric sample, which helps hold warp and weft yarns of woven fabrics together during vigorous laundering processes.

Due to the limitations of the equipment used, actual protocol may differ slightly from the standard's recommended practice. To wash fabrics, a General Electric Company (GE) home washing machine, model number WCSR2090DAWW, was used. A matching model GE dryer, model number DBXR463ED2WW, was used in tandem. AATCC recommends using either 1993 AATCC Standard Reference Detergent OR the recommended amount of TIDE detergent. 2x Ultra TIDE original scent laundering detergent was used. For each laundering cycle, the cap was filled to line 2. The washing machine was set for the most extreme laundering conditions available: hot/cold wash/rinse temperatures, super load size, whites-medium wash cycle. The dryer was set for cottons - regular heat and a timed cycle of 45 minutes. This protocol was repeated for each individual laundering cycle. Following completion of the laundering process, fabrics were once again allowed to condition at standard laboratory conditions prior to conducting any further testing.

3.9 Fabric Sample Abrasion

Textile material abrasion resistance is one of several factors which contribute to wear performance or durability experienced in actual use of the material. While both abrasion resistance and durability may be related, this relationship varies with end use. In many cases, fabrics are abraded until the actual textile structure begins to deteriorate. In this case, abrasion testing was conducted to compare deterioration of the finish rather than the fabric structure. Therefore, fabrics were exposed to a relatively low number of abrasion cycles and differences were measured qualitatively via SEM imaging. Selected fabrics were exposed to

abrasion via ASTM test method D4966. A Nu-Martindale Abrasion and Pilling tester, model 403 (s/n 403/97/2073), was used to abrade fabrics. Figure 3.14 represents a typical piece of Martindale abrasion equipment.



Figure 3.14: Nu-Martindale Abrasion/Pilling Tester (TexLabs - Equipment Detail, 2009)

Various fabrics were cut into single 1.5 inch diameter fabric specimens and placed into numbered Martindale specimen holders. Typically, weights of 9kPa for apparel and 12kPa for upholstery are applied. However, no additional weight was applied for these tests as the end use of this finish has not been determined. Each abrasion cycle is a single rotating elliptical movement, 16 of which bring the Martindale abrasion surface back to its neutral position. Fabrics were exposed to a total of 500 abrasion cycles and then held for further analysis.

3.10 Flame Resistance Testing

The modified method used to test flame resistance of pre- and post-laundered fabrics is documented in AATCC Test Method 34-1969 (method has since been taken out of service) and American Society for Testing and Materials (ASTM) Method D 6413-99. The testing protocol replicates that listed in AATCC TM34 except the sample length was increased from 10 in. to 12 in. (as specified by ASTM D6413-99). Three 3 in. x 12 in. fabric swatches were cut from each finished sample to conduct flame resistance testing. Fabrics were cut as pictured in Figure 3.15 below and burned in the warp direction.

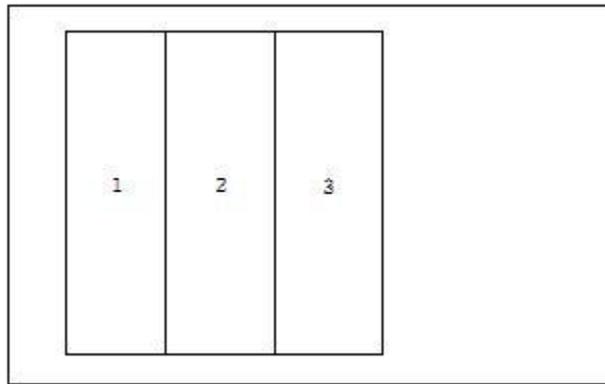


Figure 3.15: Fabric Cutting Diagram for FR Testing

Fabrics were then put into mounting brackets and placed into a vertical flame chamber as pictured in Figure 3.16. Following the mounting of fabrics, the burner is placed into the chamber. Burner flame height was pre-adjusted to 1.5 inches. The lower $\frac{3}{4}$ in. of fabric is in the flame for a total of 12 seconds. The burner is then removed and the fabric is allowed to burn for its natural duration.

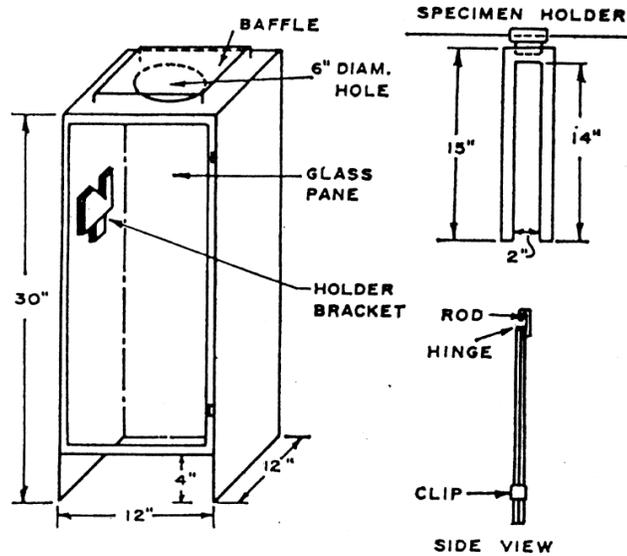


Figure 3.16: Schematic of a Vertical Flame Chamber and Specimen Holder (AATCC Co., 1969)

Data received from conducting these tests consists of afterflame time and char length (as there was no afterglow time). Afterflame time is defined as the length of time a material continues to flame after the ignition source has been removed. Char length is defined as the distance from the fabric edge exposed to the flame to the furthest visible point of fabric damage after a specified tearing force has been applied. While afterflame time may be self-explanatory, Figure 3.17 illustrates how to apply tearing force and thus, measure char length. Figure 3.18 is an image of a self-extinguishing poly/cotton sample following vertical flame testing.

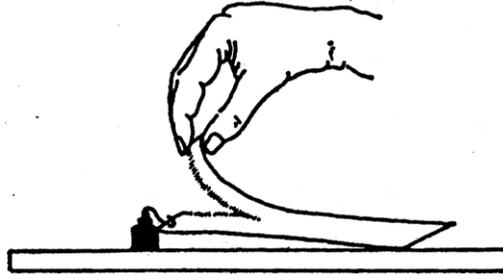


Figure 3.17: Methodology for Tearing Charred Fabrics to Determine Char Length (AATCC Co., 1969)

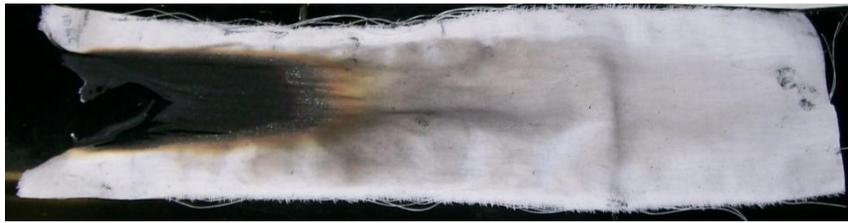


Figure 3.18: Self-Extinguishing Poly/Cotton Sample

The weight in Figure 3.17 is 113 grams according to specifications of TM 34, which classify fabrics with square weights less than 6 oz/yd². Results of flame resistance testing were recorded, charted, and analyzed via Excel spreadsheet software.

3.11 Fabric Antimicrobial Testing

A commonly used test method for testing the antimicrobial properties of textile fabrics is AATCC's quantitative Test Method 100 (TM 100), "Antibacterial Finishes on Textile Materials: Assessment of." Within this protocol, fabrics are inoculated with a predetermined amount of test organisms and, following incubation, bacteria are eluted from swatches by shaking in known amounts of neutralizing solution. The number of bacteria present in the liquid is determined and a % reduction is calculated.

Due to a deviation from standard antimicrobial finishes through the use of light-activated TiO₂ nanoparticles, this methodology must be modified, however, the principles of determining % reduction and bacterial application remain the same. Antimicrobial testing was conducted at Aerobiology Laboratory Associates, Incorporated. Contact information is as follows:

www.aerobiology.net

Suzanne S. Blevins, Laboratory Director

43760 Trade Center Place, Suite 100

Dulles, VA 20166

Phone: (877) 648-9150

Email: Suzanne@aerobiology.net

The following outlines test protocol used to determine % reduction of bacteria on research fabrics. Due to monetary and time constraints, a restricted number of fabrics were evaluated under the following conditions:

- Light Conditions:
 - No Light
 - White Light (20 Watt / MR 16 halogen bulb)
 - UV Light (G8T5 germicidal, 8 watt, 245 nm)
- Contact Time: 0 hours and 24 hours
- Incubation: Ambient temperatures

- Bacteria
 - Gram Positive - Staphylococcus aureus
 - Gram Negative - Klebsiella pneumonia

3.12 SEM Characterization of Finished Fabrics

Following functionality testing of pre- and post-laundered fabrics, selected fabrics were photographed using a scanning electron microscope (SEM) model S-3200N manufactured by Hitachi. The SEM was located in North Carolina State's Analytical Instrumentation Facility (AIF). Sample preparation included coating with gold-palladium (approximately 8 nm) to accurately view sample morphologies under the microscope. Selected magnifications were 100x, 250x, 1000x, and 5000x. Due to the surface roughness of fabrics as well as natural surface inconsistencies characteristic of fibrous samples, the SEM was run in charge reduction mode.

3.13 ICP Elemental Analysis

Although FR testing provides useful insight into the durability of applied flame retardants, it is very difficult to measure durability of TiO₂ attachment. Therefore, Inductively Coupled Plasma (ICP) Elemental Analysis was conducted on selected fabrics. The Sequential ICP - AES equipment, manufactured by Liberty AX, was used to determine concentrations of titanium and phosphorus on acid-digested fabrics. Figure 3.19 is a picture of the ICP machine.



Figure 3.19: Liberty ICP Elemental Analysis Equipment

In order to begin ICP analysis, fabrics were cut into approximately 0.3g weights. A strong solution of acid was prepared by mixing a 2:1 volume ratio of nitric acid (HNO_3) and sulfuric acid (H_2SO_4). Twenty mL of acidic solution was added to each individual fabric sample and placed into a microwave-safe container. Fabrics were then microwave digested using a MARS 5 microwave, manufactured by CEM Corporation, under the following controlled conditions:

- Power: 1200 Watts (W)
- Temperature Ramp/Time: From ambient (22°C) to 180°C over 10 minutes
- Hold Temperature/Time: 180°C for 30 minutes
- Hold Pressure: ~ 800 psi

Following microwave digestion of the fabrics, the individual chemical baths were added to 50 mL flasks and topped-up to 50 mL again with the acidic solution prepared earlier. Fabrics then underwent ICP analysis. Fabrics were evaluated for content of two

elements, titanium (from TiO₂ content) and phosphorus (from THPC content). As a result of these tests, a % concentration of titanium and phosphorus was determined on selected samples and provided useful data in determining add-on and durability of experimental finishes. Table 3.10 lists fabrics selected for ICP elemental analysis.

Table 3.10: Fabrics Selected for ICP Elemental Analysis

Fiber Type	Launderings	% TiO ₂ owb	% THPC owb
Cotton	0	0.0	25.0
Cotton	0	0.5	25.0
Cotton	0	3.0	25.0
Cotton	0	6.0	25.0
Cotton	0	9.0	25.0
Cotton	5	0.5	25.0
Cotton	5	3.0	25.0
Cotton	5	6.0	25.0
Cotton	5	9.0	25.0
Poly/Cot	0	0.0	25.0
Poly/Cot	0	0.5	25.0
Poly/Cot	0	3.0	25.0
Poly/Cot	0	6.0	25.0
Poly/Cot	0	9.0	25.0
Poly/Cot	5	0.5	25.0
Poly/Cot	5	3.0	25.0
Poly/Cot	5	3.0	25.0
Poly/Cot	5	6.0	25.0
Poly/Cot	5	9.0	25.0

4 Results and Discussion

4.1 Cure Time and Temperature Effects on Flame Resistance

In order to assess the effects of changes in processing parameters such as curing time and temperature, a series of experiments were performed to determine optimum cure parameters for all further experimentation. Polyester/cotton blended fabrics were finished with 6.0% TiO₂, 0.5% TEOS, 25.0% THPC, 15.0% urea, and 53.5% H₂O owb. Three different fabrics were then cured under the procedures A, B, and C (defined in bullets below Figure 4.1) and evaluated for flame retardant performance. Figure 4.1 shows percentages of self-extinguishing fabrics obtained from these experiments.

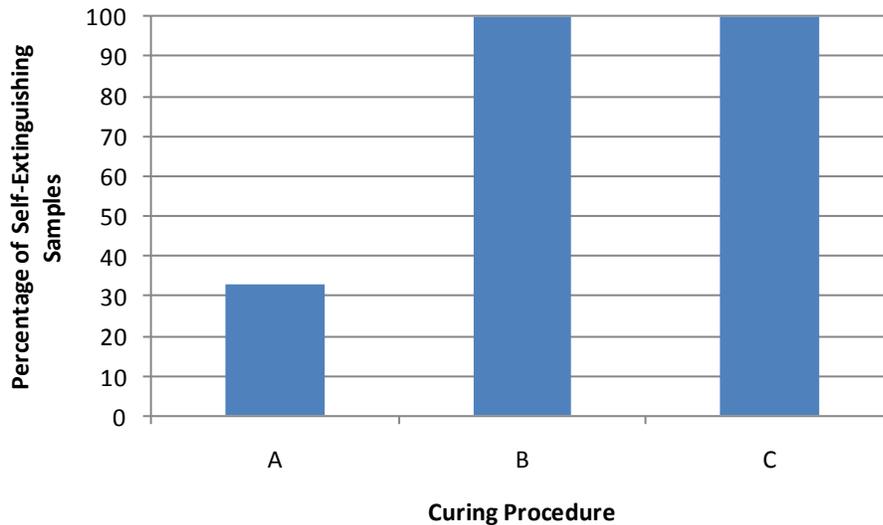


Figure 4.1: Percentage of Self-Extinguishing Poly/Cotton Fabrics Finished with 6.0% TiO₂ + 0.5% TEOS + 25.0% THPC + 15.0% Urea Using Different Curing Procedures

- **Procedure A: 5 minute cure at 120°C**
- **Procedure B: 20 minute cure at 120°C**
- **Procedure C: 5 minute cure at 150°C**

All fabrics cured under procedures B and C self-extinguished, while only 33% of samples cured under procedure A self-extinguished. Average char lengths of self-

extinguished samples are plotted in Figure 4.2 and were compared in order to determine an optimum curing procedure.

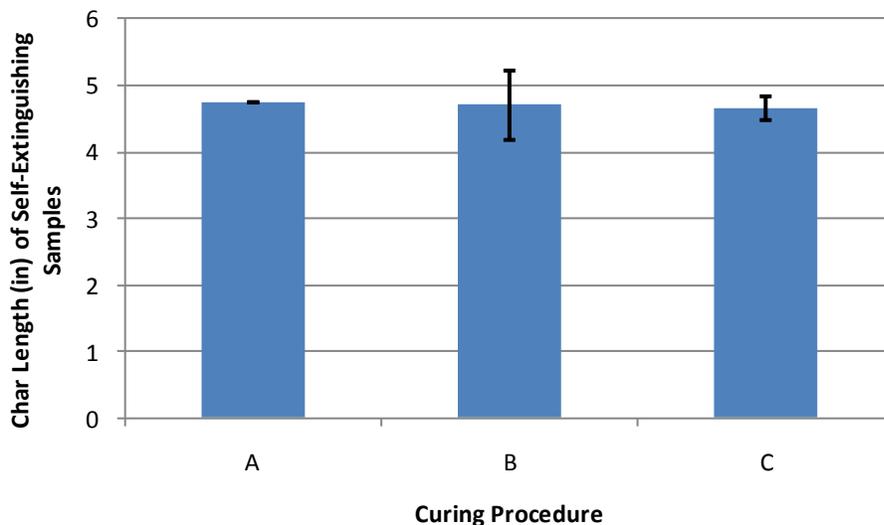


Figure 4.2: Char Lengths of Self-Extinguishing Poly/Cotton Fabrics Finished with 6.0% TiO₂ + 0.5% TEOS + 25.0% THPC + 15.0% Urea Using Different Curing Procedures

Although there is no difference in the percentage of self-extinguishing fabrics cured under procedures B and C, procedure C produced self-extinguishing fabrics with the lowest char length, which translates to the least amount of sample damage following exposure to flame. However, these differences in char lengths are small.

4.1.1 Effects of Laundering

To further justify the positive effects of curing procedure C, fabrics were also laundered according to methodology outlined in Section 3.8, which specifies five consecutive wash and drying cycles. Afterflame times of these fabrics are plotted in Figure 4.3.

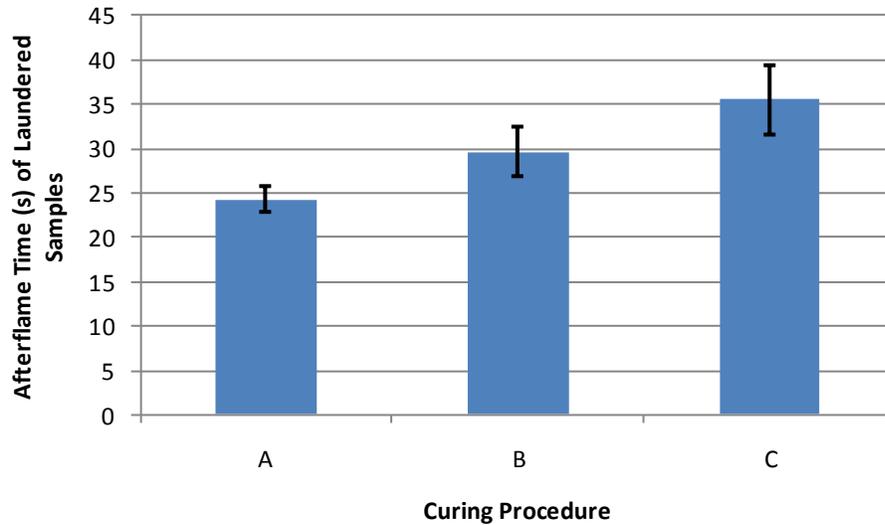


Figure 4.3: Afterflame Times of Poly/Cotton Fabrics Finished with 6.0% TiO₂ + 0.5% TEOS + 25.0% THPC + 15.0% Urea Using Different Curing Procedures after 5 Launderings

Although no fabrics exhibited self-extinguishing characteristics after laundering, it is evident that the afterflame times of fabrics cured under procedure C took the longest amount of time to combust completely, an average of 35.5 seconds. Therefore, all future experiments were cured under procedure C, a dwell time of 5 minutes at a temperature of 150°C.

4.2 Flame Retardant Performance of Finished Cotton Fabrics

For this research, flame retardant chemistry consisting of 25.0% THPC and 15.0% Urea owb was applied to 100% cotton. Rather than using the conventional trimethylol melamine (TMM) to create a three dimensional FR polymer network around the fabric structures, a commonly-used multifunctional silane, 0.5% TEOS owb was used as the cross-linking mechanism and thereby creating a comparable 3-dimensional finish network. Table

4.1 provides initial data regarding un-finished cotton fabrics as well as those with the FR chemistry described above applied to their surfaces.

Table 4.1: FR Performance 100% Cotton Un-Finished Control and 25.0% THPC + 15.0% Urea + 0.5% TEOS-Finished Fabrics

Sample	Combustion	Afterflame Time (s)	Char Length (in)
Un-finished 1	Complete	19.00	BEL
Un-finished 2	Complete	20.42	BEL
Un-finished 3	Complete	17.81	BEL
Finished 1	S/E	0.00	3.75
Finished 2	S/E	0.00	4.25
Finished 3	S/E	0.00	3.75

For clarification, “S/E” is an abbreviation for self-extinguishing and “BEL” abbreviates “burned entire length.” Thus, as noted by the combustion column and afterflame time column, it is evident that the 25.0% THPC + 15.0% Urea + 0.5% TEOS owb finish is enough to impart a notable improvement in flame retarding performance of 100% cotton fabrics. All finished fabrics extinguished themselves prior to the conclusion of initial 12 seconds of flame exposure as called for by AATCC TM34. Future experimentation will compare results to those in this table, which will be used as a benchmark.

4.2.1 Effects of Silane Applied with TiO₂ and FR’s

100% cotton fabrics were finished with 25.0% THPC, 15.0% urea, 3.0% TiO₂, 56.5% H₂O, and 0.5% silane. Each of the six silane types, TEOS, TMOS, BTESE, BTMSE, BTMSH, and BTMSEB were used in six individual experiments. Upon flame retardant testing of un-laundered cotton fabrics, it was evident that all fabrics self-extinguished prior to completing the 12 seconds of gas burner flame exposure. All fabrics yielded afterflame time averages of 0. Therefore, char length of those self-extinguishing fabrics were measured and compared. Results are summarized in Figure 4.4.

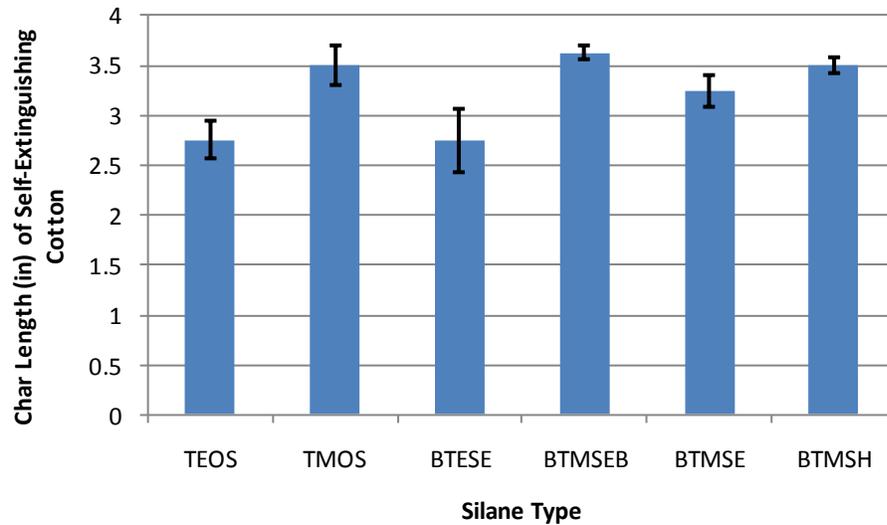


Figure 4.4: Char Lengths of Cotton Fabrics Treated with 3.0% TiO₂ + 0.5% Silane + 25.0% THPC + 15.0% Urea Using Different Silanes

The un-finished control sample is not shown since it burned completely and no char length was obtainable. However, silane types yielded drastically differing results. Optimum FR performance with respect to char length was achieved through the use of TEOS followed by BTMSE, BTESE, TMOS, BTMSH, and BTMSEB respectively. Although this data gives no direct correlation with finish durability, it does successfully represent that TEOS-containing finishes provide the best FR performance with respect to the char lengths of un-laundered cotton fabrics.

4.2.2 Effects of TiO₂ Applied with FR's

100% cotton fabrics were prepared with 25.0% THPC, 15.0% urea, 0.5% TEOS, varying percentages of TiO₂, and a balance of H₂O owb. It was expected that prediction of trends would be difficult due to the fact that THPC + Urea-based fabric finishes already provide good FR performance on cellulosic fabrics. However, data recovered from testing

allowed results to be viewed in terms of both afterflame time as well as char length. Figure 4.5 summarizes the effect of increasing percentages of TiO_2 on afterflame time.

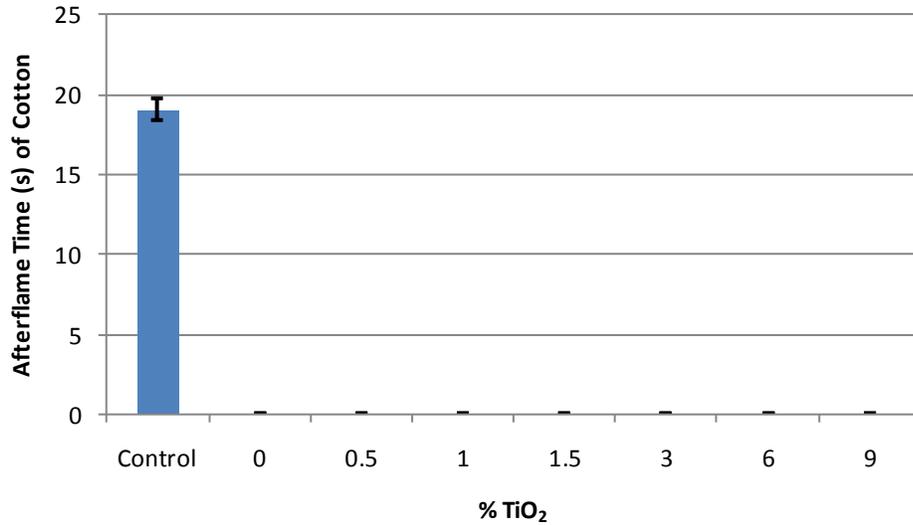


Figure 4.5: Afterflame Times of Cotton Fabrics Treated with Finishes Containing 0.5% Silane + 25.0% THPC + 15.0% Urea Using Different TiO_2 Concentrations

From the above chart, it is obvious that the experimental FR finish performs well on 100% cotton fabrics with or without TiO_2 . The data-point labeled “control” is completely un-finished 100% cotton. The control is the only fabric showing an actual afterflame time due to its undergoing complete combustion. Thus, within approximately 20 seconds after the gas flame was removed (12 second exposure), the control had undergone complete combustion. The data suggests that the THPC + Urea + TiO_2 + TEOS finishes are sufficient to prevent cotton fabrics from igniting any longer than the initial 12 seconds of flame exposure provided by the gas burner. In most cases, the combustion of fabrics ceased well before the 12 seconds of flame exposure was over.

Therefore, an ideal way to measure the effect of TiO_2 on un-laundered cotton fabrics is to measure the resulting char lengths of the exact same fabrics. Figure 4.6 illustrates resulting char lengths.

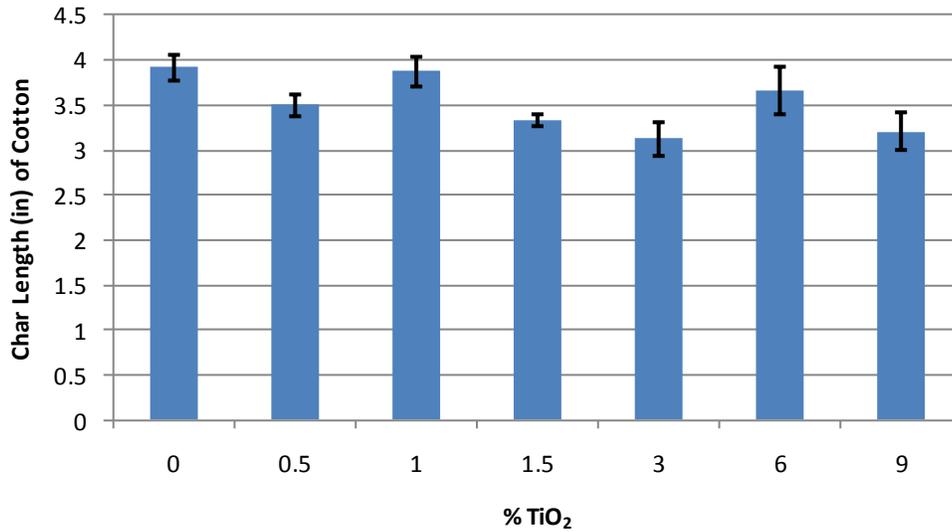


Figure 4.6: Char Lengths of Cotton Fabrics Treated with Finishes Containing 0.5% TEOS + 25.0% THPC + 15.0% Urea Using Different TiO_2 Concentrations

In this case, it becomes obvious that char length has the tendency to decrease with increasing percentages of TiO_2 . Decreasing char lengths suggest that the flame is not allowed to propagate as far as fabrics with longer char lengths. This suggests that P25 TiO_2 nanoparticles act as synergists with the phosphorus-based THPC + Urea flame retardant finish on cotton fabrics.

4.2.3 Durability to Laundering of Finished Cotton Fabrics

Following the analysis of the above results, replicate fabrics finished with varying percentages of TiO_2 were laundered according to the methodology outlined in Section 3.8 (5 consecutive wash and dry cycles). Following laundering procedures, fabrics were again

tested in the vertical flame chamber and analyzed for flame retardant performance.

Laundrying of fabrics exposes topical coatings to significant abrasive forces, thus providing a source for measurement of durability of finish attachment.

A loss of flame retardant properties was noted. Figure 4.7 represents afterflame time data obtained from testing 100% cotton fabrics for flame retardant properties post-laundrying.

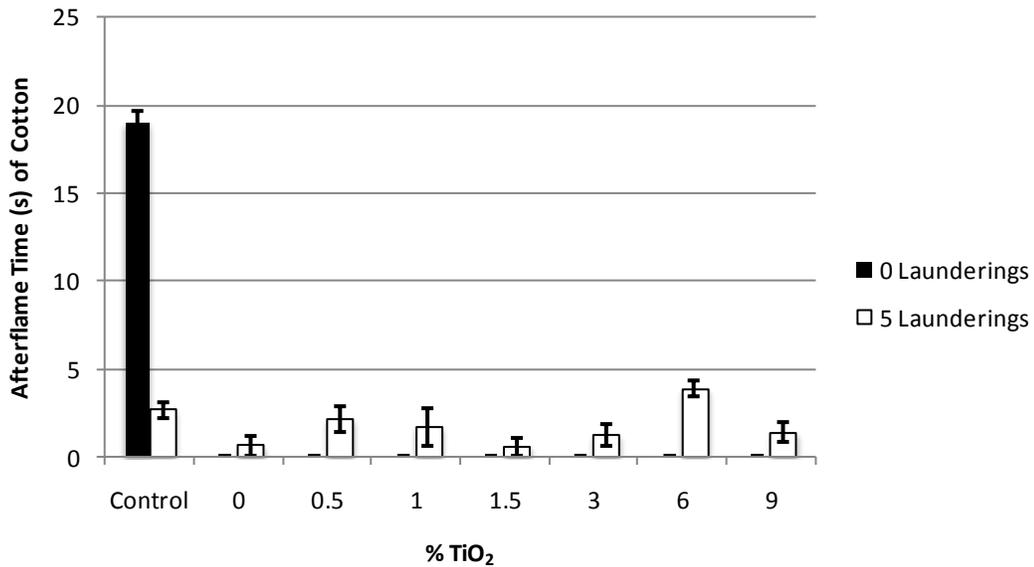


Figure 4.7: Comparison of the Afterflame Times of Un-Laundered and Laundered Cotton Fabrics Treated with Finishes Containing 0.5% Silane + 25.0% THPC + 15.0% Urea Using Different TiO₂ Concentrations

Although fabrics did not technically undergo complete combustion, measured char lengths, in fact, increased to the entire length of the 12 inch fabric sample as illustrated in Figure 4.8.

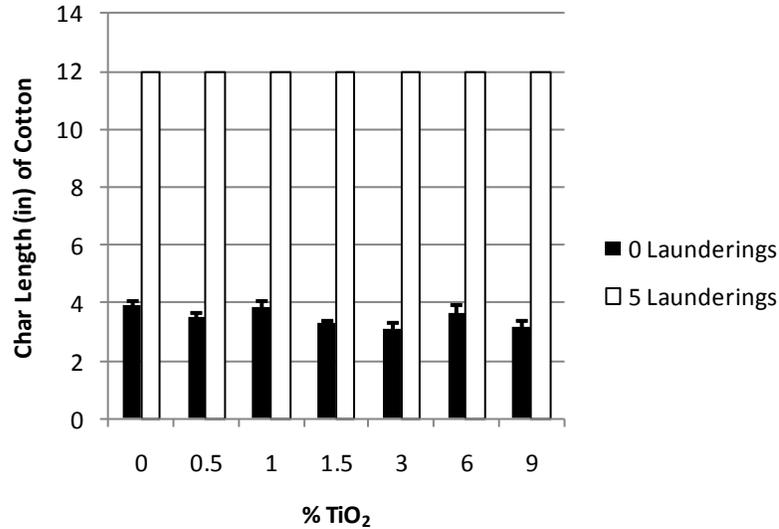


Figure 4.8: Comparison of the Char Lengths of Un-Laundered and Laundered Cotton Fabrics Treated with Finishes Containing 0.5% Silane + 25.0% THPC + 15.0% Urea Using Different TiO₂ Concentrations

The un-finished control samples, however, did completely combust leaving no residual at an average ignition time of less than 3 seconds. Because other fabrics finished with the THPC FR treatment did maintain some structural integrity, significant differences may be noted between the control data-point and the other fabrics finished in this research. According to Schindler and Hauser (Schindler & Hauser, 2004) and Lewin et al (Lewin & Sello, Handbook of Fiber Science and Technology: Vol II. Chemical Processing of Fibers and Fabrics. Functional Finishes. Part B, 1983), even without the use of trimethylol melamine (TMM), typically used to cross-link THPC with cellulose, some cross-linking of THPC with cellulose may be noted. In the case of researched finishes, multifunctional silanes were used to cross-link THPC and TiO₂ with 100% cotton fabrics. In this case, silane cross-linkers were not able to sufficiently retain THPC chemistry after 5 launderings.

Therefore, the researched finishes may be considered non- or semi-durable flame retardants as some fabric properties were retained following partial combustion, however, significant differences in flame retardant performance pre and post-laundering may be noted.

4.3 Flame Retardant Performance of Finished Polyester/Cotton Fabrics

As proven by this research, it is extremely difficult to obtain reliable data from FR tests conducted on natural/synthetic fiber blends. While 100% polyester has a tendency to melt and drip, natural/synthetic blend fabrics are different. This is primarily due to the wicking effect; charred/decomposing natural fibers prevent the burning/melted polymer to drip, thus allowing the flame to slowly propagate up the fabric structure. The polymer is also able to wick upwards, resulting in a partially-melted “glob” of polymer reinforced by natural fibers. In this case, depending on how the polymer or flame “chooses” to melt or wick along the fabric sample’s structure, the length of ignition of similarly finished fabrics can have an excessive amount of variation. Unfortunately, this leaves the possibility of having two distinctly different sets of data for an individual sample. Each of these data sets must be analyzed individually of the other. One of two conditions is likely to occur:

- A sample may self-extinguish. The shorter the char length, the better.
- A sample may combust completely. The longer the afterflame time, the better.

Though THPC + Urea are a well-known FR for cellulosic fabrics, as discussed in Chapter 2, many researchers have used THPC + Urea-based FR treatments on both polyester and polyester/cotton blends and have noted positive results. Table 4.2 summarizes results of un-finished and THPC + Urea-finished poly/cotton fabrics.

Table 4.2: FR Performance of 80/20 Poly/Cotton Control Fabrics

Sample	Combustion	Afterflame Time (s)	Char Length (in)
Un-finished 1	Complete	46.06	BEL
Un-finished 2	Complete	32.50	BEL
Un-finished 3	Complete	28.00	BEL
Finished 1	S/E	2.30	6.25
Finished 2	Complete	28.93	BEL
Finished 3	S/E	1.00	6.75

From the data depicted in Table 4.2, it is evident that the un-treated poly/cotton blend fabrics combust completely (shown as “burned entire length” or BEL) with the afterflame time of 46.06 being an outlier due to polyester melt clumping together and combusting for a period of time long after the remaining fabric had burned away. Therefore, a suitable average combustion time of un-finished poly/cotton would be 30 seconds (by excluding the 46.06 outlier from the average). The majority of fabrics with the THPC + Urea FR treatment, however, showed a difference by self-extinguishing (shown as S/E in Table 4.2) prior to combustion of half the 12 inch sample (shown by the 6.5 inch average char length). It should also be noted that there is much opportunity for improvement in the FR performance of poly/cotton fabrics.

4.3.1 Effects of Silane Applied with TiO₂ and FR’s

A replication of the experiments performed on the 100% cotton fabrics was also conducted on 80/20 poly/cotton fabrics and evaluated: 80/20 poly/cotton fabrics were finished with 25.0% THPC, 15.0% urea, 3.0% TiO₂, 56.5% H₂O, and 0.5% silane. Each of the six silane types, TEOS, TMOS, BTESE, BTMSE, BTMSH, and BTMSEB were used in six individual experiments. It is possible that changing silane type could positively impact flame retardant performance, as one sample underwent complete combustion when finished

using the TEOS silane cross-linker. Illustrated in Figure 4.9 are the percentages of poly/cotton fabrics which self-extinguished.

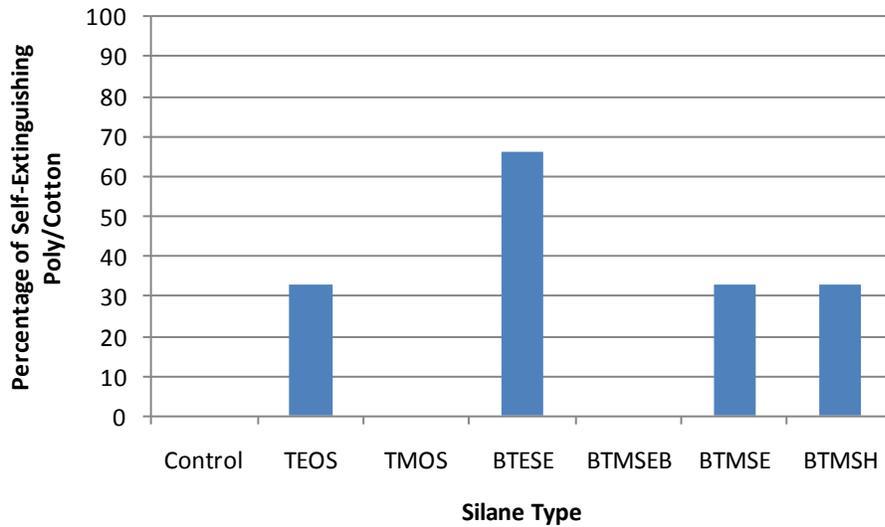


Figure 4.9: Percentage of Self-Extinguishing Poly/Cotton Fabrics Treated with Finishes Containing 3.0% TiO₂ + 0.5% Silane + 25.0% THPC + 15.0% Urea Using Different Silanes

Once again, the control sample in this case is completely un-finished polyester/cotton fabric. It can be seen that two of the six silane types yielded no self-extinguishing fabrics while the other four silane types generated at least one self-extinguishing sample, BTESE being the best by generating two. Results of these self-extinguishing fabrics were then quantified based on char average char lengths and compared once again in Figure 4.10.

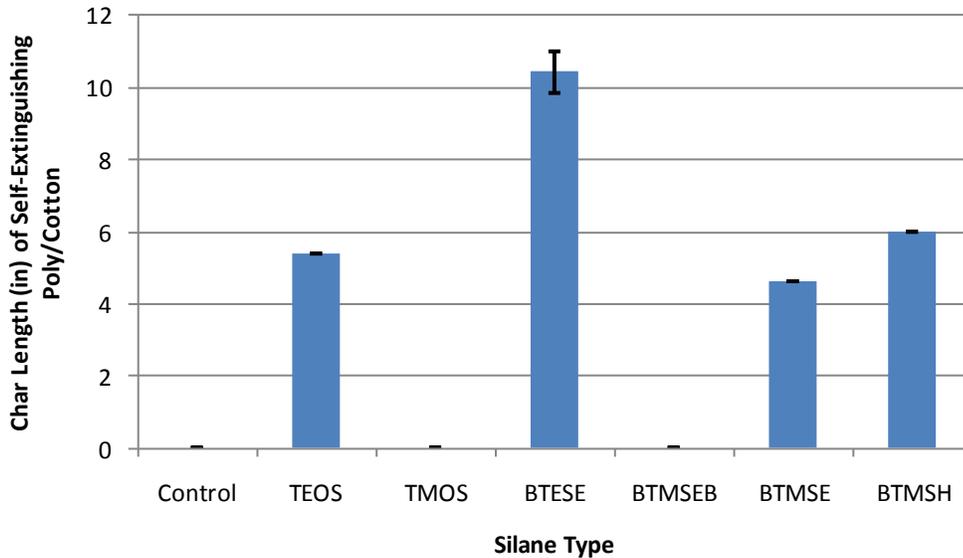


Figure 4.10: Char Lengths of Self-Extinguishing Poly/Cotton Fabrics Treated with Finishes Containing 3.0% TiO₂ + 0.5% Silane + 25.0% THPC + 15.0% Urea Using Different Silanes

When BTESE was used as cross-linker, 66% of fabrics self-extinguished. However, it is obvious that the average char length makes up almost the entire sample length of 12 inches, whereas the char lengths of BTMSE, TEOS, and BTMSH are significantly less, half or less of the actual sample length. Of the fabrics that did undergo complete combustion during these experiments, afterflame time was measured and compared as shown in Figure 4.11.

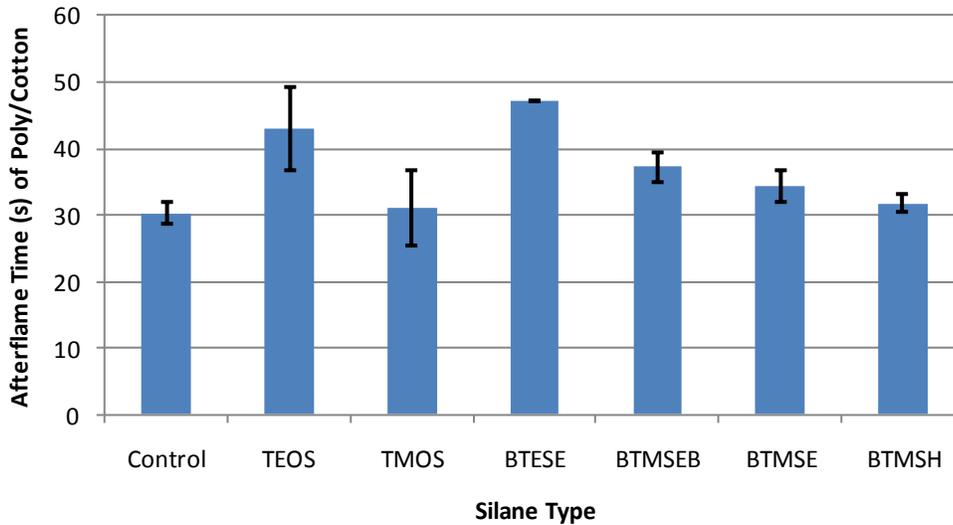


Figure 4.11: Afterflame Times of Completely Combusted Poly/Cotton Fabrics Treated with Finishes Containing 3.0% TiO₂ + 0.5% Silane + 25.0% THPC + 15.0% Urea Using Different Silanes

As shown, all experimental average afterflame times were greater than that of the control sample's average. This, again, is a characteristic of enhanced flame retardant performance. As the length of ignition increases over a controlled amount of sample, the rate of flame propagation thus decreases, which is technically the definition of a flame "retardant." However, in this case, TMOS and BTMSH average afterflame times are nearly equal to that of the control. BTESE and TEOS both held average afterflame times of more than 10 seconds longer than that of the control, making them stand out as possible selections of silanes with which to conduct further experiments on polyester/cotton blended fabrics. As a result of compared burn rates, TEOS was selected as optimum silane type to use in all further experimentation involving polyester/cotton sample types.

4.3.2 Effect of TiO₂ Applied with FR's

Again, much like the 100% cotton fabrics, ranging percentages of TiO₂ owb was applied to 80/20 poly/cotton fabrics alongside 0.5% TEOS, 25.0% THPC, 15.0% Urea, and a balance of H₂O. Percentages of TiO₂ were applied ranging from 0.0% to 9.0% owb and analyzed for their effect on the flame retardant performance of the poly/cotton blend fabric.

Figure 4.12 portrays the percentage of self extinguishing fabrics by % TiO₂.

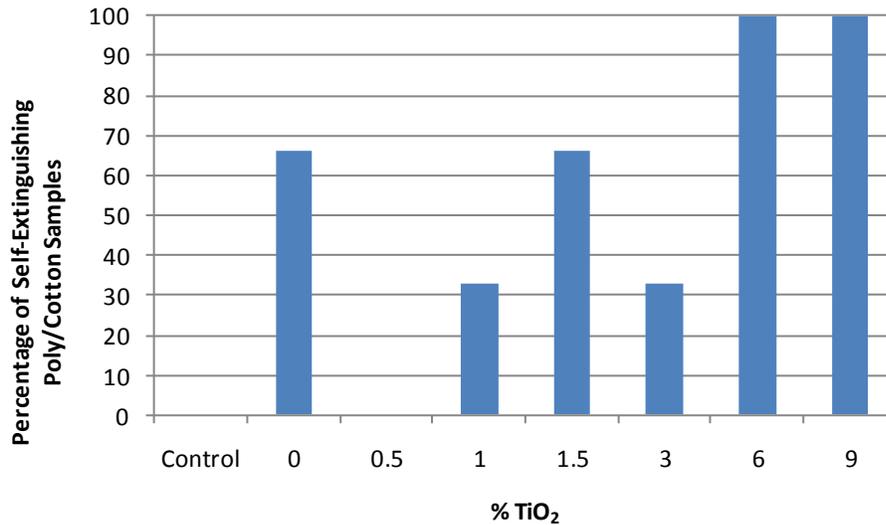


Figure 4.12: Percentage of Self-Extinguishing Poly/Cotton Fabrics Treated with Finishes Containing 0.5% Silane + 25.0% THPC + 15.0% Urea Using Different TiO₂ Concentrations

The percentage of self-extinguishing fabrics increases as the percentage of TiO₂ owb increases. While a trend could not be seen in fabrics ranging from 0.0% to 3.0% TiO₂, all fabrics finished with 6.0% TiO₂ owb or greater self-extinguished. It was observed during the flame retardant testing process that fabrics finished with greater percentages of TiO₂ exhibited a flickering effect in which the flame would extinguish and ignite multiple times within a fraction of a second. A hypothesis was made that the improved flame retardant

performance with an increase in TiO_2 add-on came primarily due to the difficulties in supplying the flame with sufficient oxygen in more concentrated areas of cross-linked TiO_2 (i.e. agglomerates) on the fabric surfaces. These self-extinguishing fabrics were then evaluated according to their respective char lengths and analyzed for further trends in Figure 4.13.

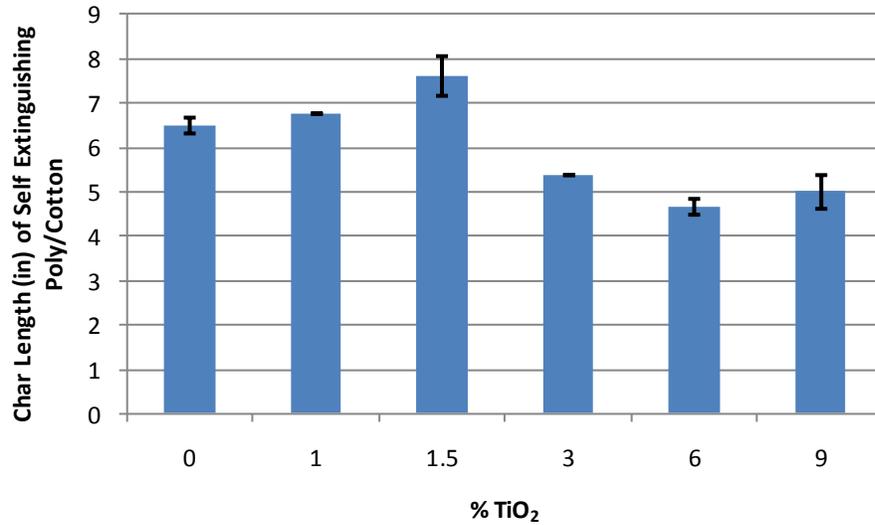


Figure 4.13: Char Lengths of Self-Extinguishing Poly/Cotton Fabrics Treated with Finishes Containing 0.5% Silane + 25.0% THPC + 15.0% Urea Using Different TiO_2 Concentrations

When comparing average char lengths of these self-extinguished fabrics, there is a significant improvement as % TiO_2 owb increases. In particular, fabrics finished with % TiO_2 owb ranging from 3.0-9.0% exhibit shorter char lengths than those finished with less than 3.0% owb.

As described earlier in this section, not all poly/cotton fabrics with % TiO_2 owb less than 6.0% self-extinguished. Data received from fabrics that underwent complete

combustion could not be included in the above analysis of results. Afterflame time results of these fabrics are plotted in Figure 4.14.

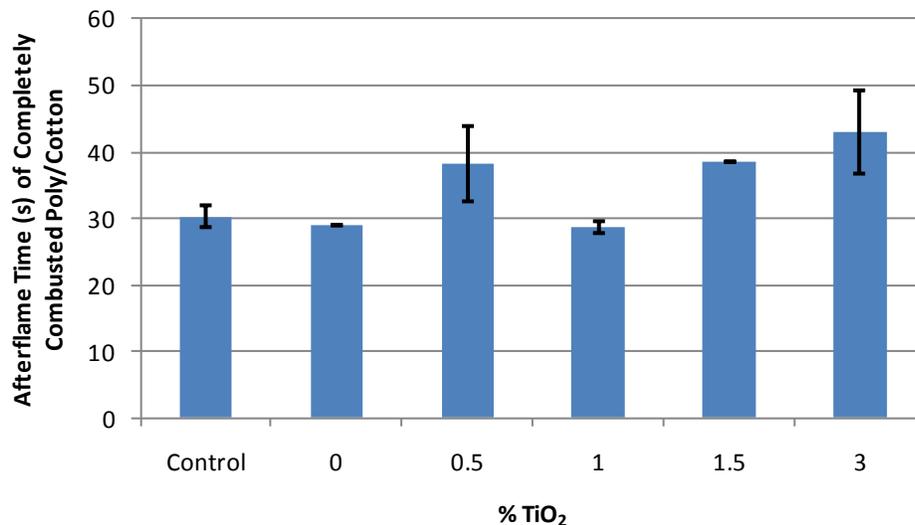


Figure 4.14: Afterflame Times of Completely Combusted Poly/Cotton Fabrics Treated with Finishes Containing 0.5% Silane + 25.0% THPC + 15.0% Urea Using Different TiO₂ Concentrations

Afterflame times have the tendency to increase with increasing %TiO₂ suggesting the rate of combustion is slowed as %TiO₂ is increased on the poly/cotton fabric. As a result of this analysis, TiO₂ can be said to possess synergistic effects with the phosphorus-based flame retardant THPC on 80/20 polyester/cotton blended fabrics.

4.3.3 Durability to Laundering of Finished Poly/Cotton Fabrics

Polyester/cotton blended fabrics also received 5 consecutive washing and drying cycles and were evaluated for durability of flame retardant performance. Much like 100% cotton fabrics, results between pre and post-laundered fabrics displayed noticeable differences. Figure 4.15 summarizes these results.

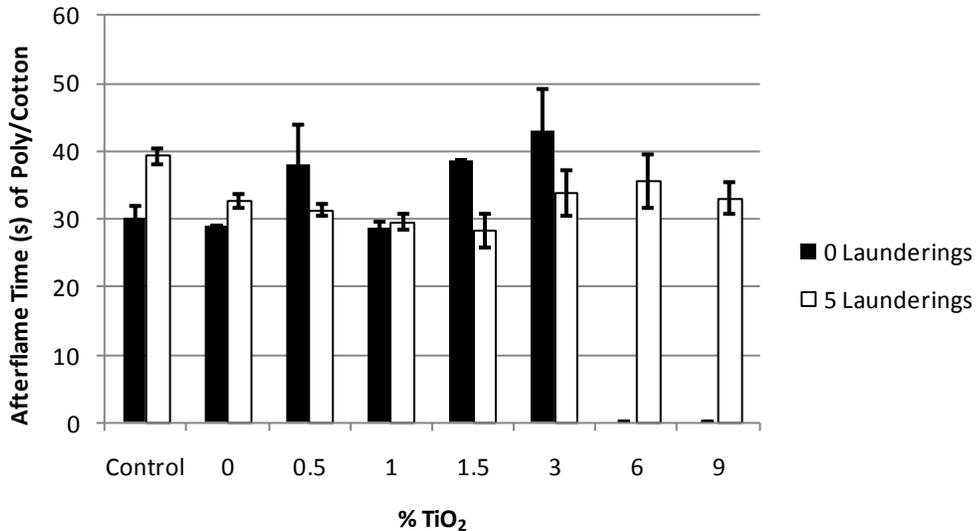


Figure 4.15: Comparison of the Afterflame Times of Un-Laundered and Laundered Poly/Cotton Fabrics Treated with Finishes Containing 0.5% Silane + 25.0% THPC + 15.0% Urea Using Different TiO₂ Concentrations

Flame retardant performance of laundered poly/cotton is fairly flat-lined compared to that of un-laundered poly/cotton. No specific trends showing decrease in rate of flame propagation on laundered fabrics could be identified. Ideally, should any flame retardant characteristics of these fabrics be seen, the afterflame time trend for laundered fabrics (completely combusting) should show a positive slope, indicating that the time taken to completely combust fabrics increases as %TiO₂ increases. Unfortunately, results indicate that the researched finish is not durable to laundering.

4.4 Antimicrobial Efficacy of Finished Fabrics

Selected fabrics were sent to Aerobiology Laboratory Associates in Dulles, Virginia for antimicrobial performance evaluation. Polyester/cotton fabrics finished with 25.0% THPC, 15.0% Urea, 0.5% TEOS, 0.0% or 9.0% TiO₂, and a balance of H₂O were analyzed

and compared to an un-finished poly/cotton control sample. Fabrics were challenged with two bacteria types, gram positive *S. aureus* and gram negative *K. pneumonia*. Fabrics were also challenged under three lighting conditions, no light, visible light, and UV light.

4.4.1 Gram Positive - Staphylococcus Aureus

4.4.1.1 No Light Source

Table 4.3 presents initial and 24 hour colony count data of all fabrics challenged with *S. aureus* under no light.

Table 4.3: Colony Counts under No Light

Type of fabric	Contact time					
	0 hrs			24 hrs		
	Colony count	Dilution read	Final count	Colony count	Dilution read	Final count
Control fabric (polycotton)	4	0.001	4.0×10^5	43	0.001	4.3×10^9
	6	0.001	6.0×10^5	34	0.001	3.4×10^9
	11	0.001	1.1×10^6	88	0.001	8.8×10^9
	19	0.001	1.9×10^6	36	0.001	3.6×10^9
	4	0.001	4.0×10^5	28	0.001	2.8×10^9
0% TiO ₂ (finished)	3	0.001	3.0×10^5	NG	0.1	NG
	3	0.001	3.0×10^5	NG	0.1	NG
	2	0.001	2.0×10^5	NG	0.1	NG
	2	0.001	2.0×10^5	NG	0.1	NG
	3	0.001	3.0×10^5	NG	0.1	NG
9% TiO ₂ (finished)	2	0.001	2.0×10^5	NG	0.1	NG
	3	0.001	3.0×10^5	NG	0.1	NG
	4	0.001	4.0×10^5	NG	0.1	NG
	3	0.001	3.0×10^5	NG	0.1	NG
	3	0.001	3.0×10^5	NG	0.1	NG

Control fabrics exhibited significant bacterial growth following the 24 hour incubation time with an average growth of 4.5×10^9 colonies. Both the THPC + 0.0% TiO₂ and the THPC + 9.0% TiO₂ fabrics showed no bacterial growth (complete elimination or 100% reduction) after 24 hours of incubation under no light. Thus, it is concluded that both

THPC and THPC + TiO₂ provide significant antimicrobial efficacy to the poly/cotton fabrics exposed to *S. aureus* for 24 hours under no light source.

4.4.1.2 Visible Light Source

Table 4.4 presents initial and 24 hour colony count data of all fabrics challenged with *S. aureus* under visible light.

Table 4.4: Colony Counts under Visible Light

Type of fabric	Contact time					
	0 hrs			24 hrs		
	Colony count	Dilution read	Final count	Colony count	Dilution read	Final count
Control fabric (polycotton)	4	0.001	4.0x10 ⁵	2	0.001	2.0 x10 ⁸
	6	0.001	6.0 x10 ⁵	2	0.001	2.0 x10 ⁸
	11	0.001	1.1 x10 ⁶	32	0.001	3.2 x10 ⁹
	19	0.001	1.9 x10 ⁶	1	0.001	1.0 x10 ⁸
	4	0.001	4.0 x10 ⁵	3	0.001	3.0 x10 ⁸
0% Ti O ₂ (finished)	3	0.001	3.0 x10 ⁵	NG	0.1	NG
	3	0.001	3.0 x10 ⁵	NG	0.1	NG
	2	0.001	2.0 x10 ⁵	NG	0.1	NG
	2	0.001	2.0 x10 ⁵	1	0.001	1.0 x10 ⁸
	3	0.001	3.0 x10 ⁵	NG	0.1	NG
9% TiO ₂ (finished)	2	0.001	2.0 x10 ⁵	NG	0.1	NG
	3	0.001	3.0 x10 ⁵	NG	0.1	NG
	4	0.001	4.0 x10 ⁵	NG	0.1	NG
	3	0.001	3.0 x10 ⁵	NG	0.1	NG
	3	0.001	3.0 x10 ⁵	1	0.001	1.0 x10 ⁸

Control fabrics exhibited significant bacterial growth following the 24 hour incubation time with an average growth of 8×10^8 colonies, lower than the final count for fabrics incubated under no light. This suggests that the visible light used, a 20 W MR 16 halogen bulb, contains wavelengths of light that may be harmful to *S. aureus*. Both the THPC + 0.0% TiO₂ and the THPC + 9.0% TiO₂ fabrics showed no bacterial growth on four replicates (complete elimination or 100% reduction) after 24 hours of incubation under

visible light. One replicate under each condition also resulted in final colony counts of 8×10^8 . Thus, it is concluded that both THPC and THPC + TiO₂ provide significant antimicrobial efficacy to the poly/cotton fabrics exposed to *S. aureus* for 24 hours under a visible light source.

4.4.1.3 Ultraviolet Light Source

Table 4.5 presents initial and 24 hour colony count data of all fabrics challenged with *S. aureus* under UV light.

Table 4.5: Colony Counts under UV Light

Type of fabric	Contact time					
	0 hrs			24 hrs		
	Colony count	Dilution read	Final count	Colony count	Dilution read	Final count
Control fabric (polycotton)	4	0.001	4.0×10^5	88	0.001	8.8×10^8
	6	0.001	6.0×10^5	96	0.001	9.6×10^8
	11	0.001	1.1×10^6	35	0.001	3.5×10^8
	19	0.001	1.9×10^6	13	0.001	1.3×10^8
	4	0.001	4.0×10^5	41	0.001	4.1×10^8
0% Ti O ₂ (finished)	3	0.001	3.0×10^5	23	0.001	2.3×10^8
	3	0.001	3.0×10^5	2	0.001	2.0×10^7
	2	0.001	2.0×10^5	2	0.001	2.0×10^7
	2	0.001	2.0×10^5	NG	0.1	NG
	3	0.001	3.0×10^5	NG	0.1	NG
9% TiO ₂ (finished)	2	0.001	2.0×10^5	NG	0.1	NG
	3	0.001	3.0×10^5	NG	0.1	NG
	4	0.001	4.0×10^5	NG	0.1	NG
	3	0.001	3.0×10^5	NG	0.1	NG
	3	0.001	3.0×10^5	NG	0.1	NG

Control fabrics exhibited significant bacterial growth following the 24 hour incubation time with an average growth of 5.5×10^8 colonies. Three fabrics finished only with THPC + 0.0% TiO₂ also showed an increase in final colony count. The 25.0% THPC + 9.0% TiO₂ fabrics showed no bacterial growth (complete elimination or 100% reduction)

after 24 hours of incubation under UV light. Thus, it is concluded that THPC + TiO₂ provide significant antimicrobial efficacy to the poly/cotton fabrics exposed to *S. aureus* for 24 hours under a UV light source, with TiO₂ being the active antimicrobial agent.

4.4.2 Gram Negative – *Klebsiella Pneumoniae*

4.4.2.1 No Light Source

Table 4.6 presents initial and 24 hour colony count data of all fabrics challenged with *K. pneumoniae* under no light.

Table 4.6: Colony Counts under No Light

Type of fabric	Contact time					
	0 hrs			24 hrs		
	Colony count	Dilution read	Final count	Colony count	Dilution read	Final count
Control fabric (polycotton)	14	0.001	1.4 x 10 ⁶	2	0.001	2.0 x 10 ⁸
	15	0.001	1.5 x 10 ⁶	1	0.001	1.0 x 10 ⁸
	13	0.001	1.3 x 10 ⁶	2	0.001	2.0 x 10 ⁸
	12	0.001	1.2 x 10 ⁶	1	0.001	1.0 x 10 ⁸
	14	0.001	1.4 x 10 ⁶	13	0.001	1.3 x 10 ⁸
0% Ti O ₂ (finished)	19	0.001	1.9 x 10 ⁶	NG	0.1	NG
	19	0.001	1.9x 10 ⁶	NG	0.1	NG
	18	0.001	1.8 x 10 ⁶	NG	0.1	NG
	18	0.001	1.8x 10 ⁶	NG	0.1	NG
	13	0.001	1.3 x 10 ⁶	NG	0.1	NG
9% TiO ₂ (finished)	17	0.001	1.7 x 10 ⁶	NG	0.1	NG
	19	0.001	1.9 x 10 ⁶	NG	0.1	NG
	17	0.001	1.7 x 10 ⁶	NG	0.1	NG
	16	0.001	1.6 x 10 ⁶	NG	0.1	NG
	19	0.001	1.9 x 10 ⁶	NG	0.1	NG

Control fabrics exhibited significant bacterial growth following the 24 hour incubation time with an average growth of 1.5 × 10⁸ colonies. Both the THPC + 0.0% TiO₂ and the THPC + 9.0% TiO₂ fabrics showed no bacterial growth (complete elimination or 100% reduction) after 24 hours of incubation under no light. Thus, it is concluded that both

THPC and THPC + TiO₂ provide significant antimicrobial efficacy to the poly/cotton fabrics exposed to *K. pneumoniae* for 24 hours under no light source.

4.4.2.2 Visible Light Source

Table 4.7 presents initial and 24 hour colony count data of all fabrics challenged with *K. pneumoniae* under visible light.

Table 4.7: Colony Counts under Visible Light

Type of fabric	Contact time					
	0 hrs			24 hrs		
	Colony count	Dilution read	Final count	Colony count	Dilution read	Final count
Control fabric (polycotton)	14	0.001	1.4 x 10 ⁶	19	0.001	1.9 x 10 ⁹
	15	0.001	1.5 x 10 ⁶	34	0.001	3.4 x 10 ⁹
	13	0.001	1.3 x 10 ⁶	51	0.001	5.1 x 10 ⁹
	12	0.001	1.2 x 10 ⁶	29	0.001	2.9 x 10 ⁹
	14	0.001	1.4 x 10 ⁶	25	0.001	2.5 x 10 ⁹
0% Ti O ₂ (finished)	19	0.001	1.9 x 10 ⁶	NG	0.1	NG
	19	0.001	1.9x 10 ⁶	NG	0.1	NG
	18	0.001	1.8 x 10 ⁶	NG	0.1	NG
	18	0.001	1.8x 10 ⁶	NG	0.1	NG
	13	0.001	1.3 x 10 ⁶	NG	0.1	NG
9% TiO ₂ (finished)	17	0.001	1.7 x 10 ⁶	NG	0.1	NG
	19	0.001	1.9 x 10 ⁶	NG	0.1	NG
	17	0.001	1.7 x 10 ⁶	NG	0.1	NG
	16	0.001	1.6 x 10 ⁶	NG	0.1	NG
	19	0.001	1.9 x 10 ⁶	NG	0.1	NG

Control fabrics exhibited significant bacterial growth following the 24 hour incubation time with an average growth of 3.2×10^9 colonies. Both the THPC + 0.0% TiO₂ and the THPC + 9.0% TiO₂ fabrics showed no bacterial growth (complete elimination or 100% reduction) after 24 hours of incubation under visible light. Thus, it is concluded that both THPC and THPC + TiO₂ provide significant antimicrobial efficacy to the poly/cotton fabrics exposed to *K. pneumoniae* for 24 hours under a visible light source.

4.4.2.3 Ultraviolet Light Source

Table 4.7 presents initial and 24 hour colony count data of all fabrics challenged with *K. pneumoniae* under UV light.

Table 4.8: Colony Counts under UV Light

Type of fabric	Contact time					
	0 hrs			24 hrs		
	Colony count	Dilution read	Final count	Colony count	Dilution read	Final count
Control fabric (polycotton)	14	0.001	1.4×10^6	37	0.001	3.7×10^8
	15	0.001	1.5×10^6	42	0.001	4.2×10^8
	13	0.001	1.3×10^6	34	0.001	3.4×10^8
	12	0.001	1.2×10^6	41	0.001	4.1×10^8
	14	0.001	1.4×10^6	32	0.001	3.2×10^8
0% TiO ₂ (finished)	19	0.001	1.9×10^6	NG	0.1	NG
	19	0.001	1.9×10^6	NG	0.1	NG
	18	0.001	1.8×10^6	NG	0.1	NG
	18	0.001	1.8×10^6	NG	0.1	NG
	13	0.001	1.3×10^6	NG	0.1	NG
9% TiO ₂ (finished)	17	0.001	1.7×10^6	NG	0.1	NG
	19	0.001	1.9×10^6	NG	0.1	NG
	17	0.001	1.7×10^6	NG	0.1	NG
	16	0.001	1.6×10^6	NG	0.1	NG
	19	0.001	1.9×10^6	NG	0.1	NG

Control fabrics exhibited significant bacterial growth following the 24 hour incubation time with an average growth of 3.7×10^8 colonies. Both the THPC + 0.0% TiO₂ and the THPC + 9.0% TiO₂ fabrics showed no bacterial growth (complete elimination or 100% reduction) after 24 hours of incubation under UV light. Thus, it is concluded that both THPC and THPC + TiO₂ provide significant antimicrobial efficacy to the poly/cotton fabrics exposed to *K. pneumoniae* for 24 hours under a UV light source.

As a result of antimicrobial testing, it was found that finishes consisting of 25.0% THPC + 15.0% Urea as well as finishes consisting of 25.0% THPC + 15.0% Urea + 9.0%

TiO₂ provide antimicrobial effects on compared to un-finished fabrics under all three lighting conditions. Furthermore, it was discovered that fabrics finished with 25.0% THPC + 15.0% Urea + 9.0% TiO₂ are more antimicrobially active against S. aureus fabrics finished with 25.0% THPC + 15.0% Urea.

4.5 SEM Characterization of Finished Cotton and Poly/Cotton Fabrics

Surface morphologies of selected fabrics were measured qualitatively via scanning electron microscopy (SEM). Pre- and post-laundering fabrics of 100% cotton and 80/20 poly/cotton fabrics were selected. The following fabrics were analyzed:

- Un-finished
- 25.0% THPC + 15.0% Urea + 0.5% TEOS + 59.5% H₂O
- 25.0% THPC + 15.0% Urea + 0.5% TEOS + 3.0% TiO₂ + 56.5% H₂O
- 25.0% THPC + 15.0% Urea + 0.5% TEOS + 9.0% TiO₂ + 50.5% H₂O

Images were gathered at 100x, 250x, 1000x, and 5000x magnifications, however, it was determined that a magnification of 250x offered the most accurate representation of fabrics as a whole. Fabrics finished with 3.0% TiO₂ owb showed little evidence of particle agglomeration on the surface, suggesting that particles were evenly distributed on fiber surfaces. A magnification of 20000x or higher would be required to view individual TiO₂ nanoparticles and is outside of the mechanical capability of the SEM used to gather these images.

4.5.1 Un-Laundered Cotton Fabrics

The first image, Figure 4.16, is of un-finished cotton. It is clear from the image that there is no obvious damage to the fiber/fabric structure. Figure 4.17 is an image of the same fabric, but finished with 25.0% THPC + 15.0% Urea, + 0.5% TEOS owb. A comparison of the two figures shows no difference, suggesting that the THPC + urea flame retardant coating is evenly applied, forming a resin that surrounds the fibers, and certainly enough to provide self-extinguishing properties to the fabric, as proven in Section 4.2.2.

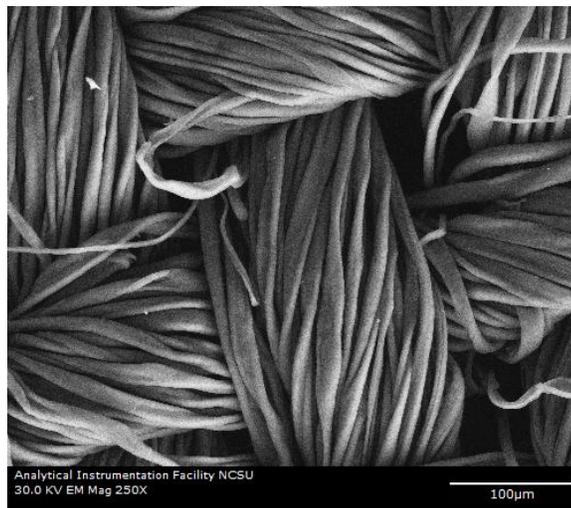


Figure 4.16: SEM Image of Un-Finished Cotton Fabric

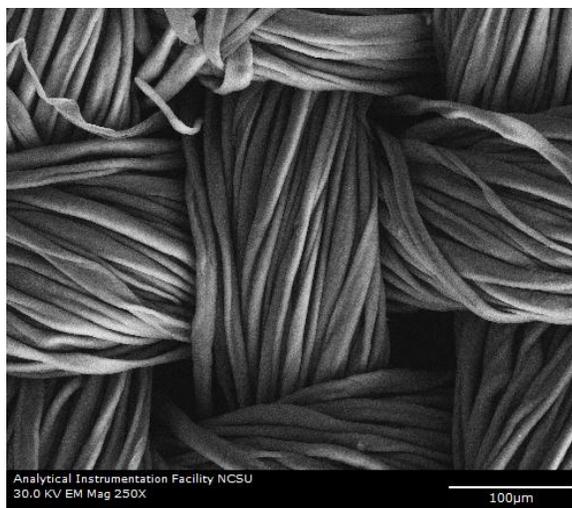


Figure 4.17: SEM Image of 25.0% THPC + 15.0% Urea + 0.5% TEOS + 0.0% TiO₂ Cotton Fabric

Cotton fabrics finished with 3.0% and 9.0% TiO₂, Figure 4.18 and Figure 4.19, give slightly different results. The THPC coating still seems even on the cotton sample finished with 3.0% TiO₂. However, in the middle of the image in Figure 4.19, the THPC coating containing 9.0% TiO₂ starts to peel off of the fiber. TiO₂ agglomerates can also be seen on surface fibers as well as fibers deeper within the fabric structure on cotton finished with 9.0% TiO₂.



Figure 4.18: SEM Image of 25.0%THPC + 15.0% Urea + 0.5% TEOS + 3.0% TiO₂ Cotton Fabric

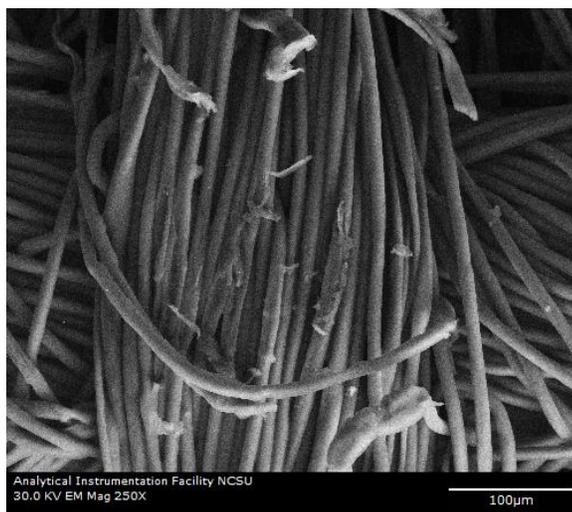


Figure 4.19: SEM Image of 25.0%THPC + 15.0% Urea + 0.5% TEOS + 9.0% TiO₂ Cotton Fabric

4.5.2 Laundered Cotton Fabrics

Fabrics were then exposed to 5 consecutive washing and drying cycles. Following the laundering process, images were gathered of replicate cotton fabrics finished with identical chemistries to the section above. The brighter contrast of images of laundered

fabrics is due to fabrics being coated with gold-palladium a second time to minimize sample charging. From the images, it appears that surface morphologies have changed significantly. This may be due to the abrasive forces of laundering or the peeling of THPC coatings. In Figure 4.20, it is obvious that much of the finish has or is in the process of being abraded off. It also appears that actual fiber surfaces have been abraded (see broken fiber in upper-left quadrant of the image).

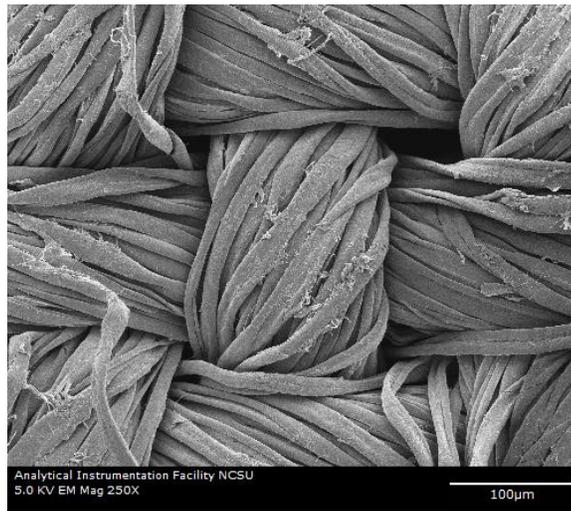


Figure 4.20: SEM Image of 25.0%THPC + 15.0% Urea + 0.5% TEOS + 0.0% TiO₂ Laundered Cotton Fabric

Fabrics finished with 3.0% and 9.0% TiO₂ appear to have less finish and/or surface abrasion, particularly the 9.0% TiO₂ sample. These images are displayed in Figure 4.21 and Figure 4.22. Upon closer inspection of the imagery, TiO₂ agglomerates may also be seen within the fabric structure of the sample finished with 9.0% TiO₂ and much smaller amounts on the 3.0% TiO₂ sample.

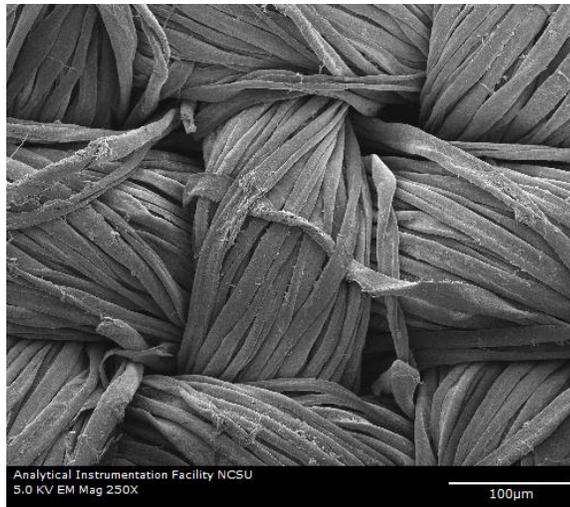


Figure 4.21: SEM Image of 25.0%THPC + 15.0% Urea + 0.5% TEOS + 3.0% TiO₂ Laundered Cotton Fabric

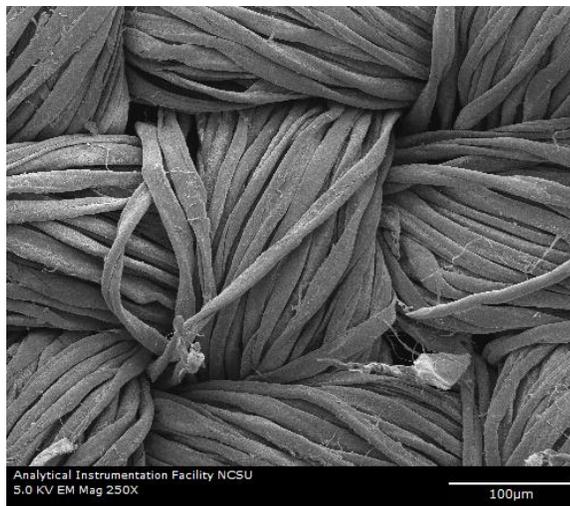


Figure 4.22: SEM Image of 25.0%THPC + 15.0% Urea + 0.5% TEOS + 9.0% TiO₂ Laundered Cotton Fabric

4.5.3 Un-Laundered Poly/Cotton Fabrics

Figure 4.23 is an image of un-finished 80/20 poly/cotton blended fabric. An analysis of fiber morphologies shows that approximately 20% of fiber cross-sections are lumen-

shaped (cotton). The other 80% are round (polyester). While some variations in fiber morphologies are evident, no visible damage is shown to the fiber/fabric structures.

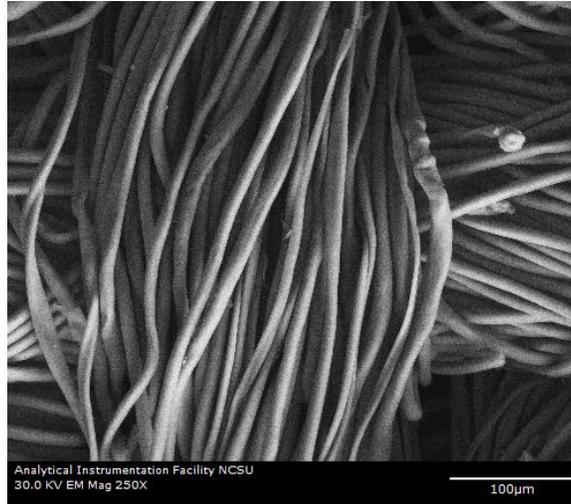


Figure 4.23: SEM Image of Un-Finished Poly/Cotton Fabric

Figure 4.24 displays poly/cotton blended fabric finished with 25.0% THPC + 15.0% Urea + 0.5% TEOS. There are virtually no differences between this fabric and the un-finished fabric, indicating an even coating around the fiber surfaces.

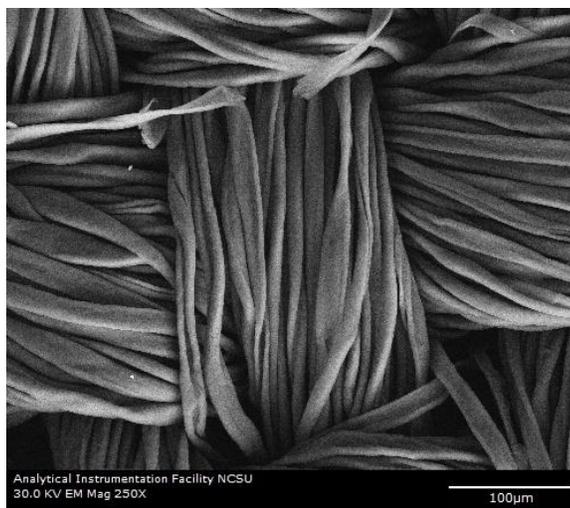


Figure 4.24: SEM Image of 25.0%THPC + 15.0% Urea + 0.5% TEOS + 0.0% TiO₂ Poly/Cotton Fabric

Much like the 100% cotton fabrics, poly/cotton fabrics finished with 9.0% TiO₂, as displayed in Figure 4.26 show some agglomerates of TiO₂ within the fabric structure as well as on fibers on the outer surface. However, the image displayed in Figure 4.25 of poly/cotton fabric finished with 3.0% TiO₂ shows no visible agglomeration. The agglomerate found on the center of the 9.0% TiO₂ sample is micro-scale, approximately 50 µm. From the SEM images, it can be concluded that the majority of TiO₂ nanoparticles are evenly distributed along the fiber surfaces.



Figure 4.25: SEM Image of 25.0%THPC + 15.0% Urea + 0.5% TEOS + 3.0% TiO₂ Poly/Cotton Fabric

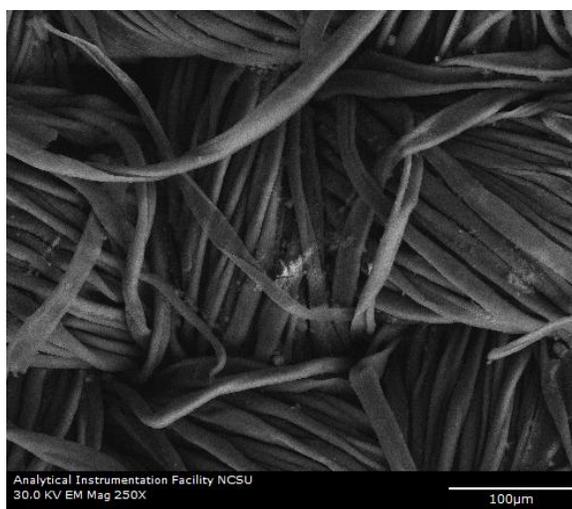


Figure 4.26: SEM Image of 25.0%THPC + 15.0% Urea + 0.5% TEOS + 9.0% TiO₂ Poly/Cotton Fabric

4.5.4 Laundered Poly/Cotton Fabrics

Alongside 100% cotton fabrics, 80/20 poly/cotton fabrics finished with the previously-mentioned chemistries were also subjected to 5 consecutive washing and drying cycles and submitted for SEM imaging. Much like the cotton sample, Figure 4.27 illustrates

poly/cotton finished with THPC and TEOS only. Again, fibers and finish showed signs of abrasion. While parts of the sample appear as though nanoparticles are present, it is merely the abrasion and “pilling” of the THPC.

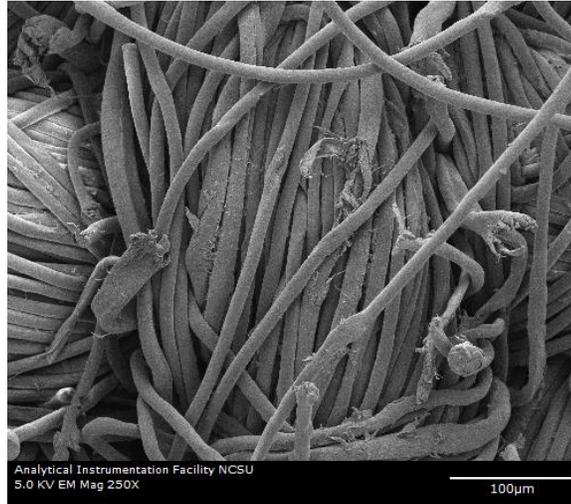


Figure 4.27: SEM Image of 25.0%THPC + 15.0% Urea + 0.5% TEOS + 0.0% TiO₂ Laundered Poly/Cotton Fabric

Although high levels of contrast are present in the 3.0% and 9.0% TiO₂ poly/cotton fabrics, shown in Figure 4.28 and Figure 4.29, it is still clear that much of the THPC is beginning to abrade off. However, it is also clear that a significant proportion of TiO₂ is still present on the sample finished with 9.0% TiO₂.

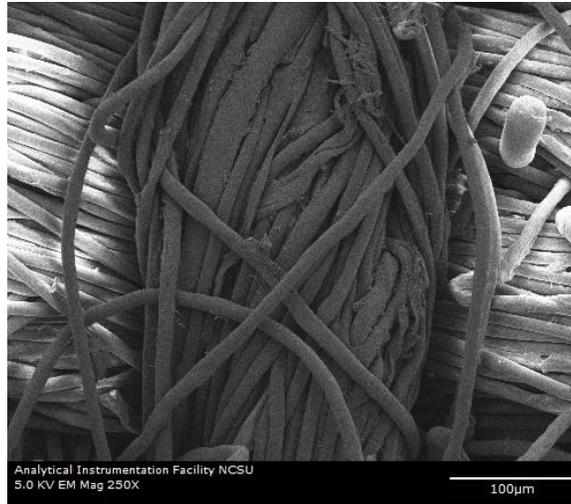


Figure 4.28: SEM Image of 25.0%THPC + 15.0% Urea + 0.5% TEOS + 3.0% TiO₂ Laundered Poly/Cotton Fabric



Figure 4.29: SEM Image of 25.0%THPC + 15.0% Urea + 0.5% TEOS + 9.0% TiO₂ Laundered Poly/Cotton Fabric

4.6 ICP Elemental Analysis of Finished Fabrics

To further address the concentrations of active ingredients (titanium and phosphorus) on both pre and post-laundered fabrics, ICP elemental analysis was conducted. Selected cotton and poly/cotton blended fabrics were finished with 25.0% THPC, 15.0% urea, 0.5%

TEOS cross-linker, varying percentages of TiO_2 , and the balance of H_2O owb. Sample fabrics were cut to weights of approximately 0.3 g and microwave digested under highly acidic conditions. These fabrics were then analyzed for elemental contents of active ingredients, titanium and phosphorus.

4.6.1 Un-Laundered Fabrics

Cotton and poly/cotton blended fabrics un-finished and finished with THPC and TiO_2 (0.5%, 3.0%, 6.0%, and 9.0% owb) were analyzed via ICP before laundering. Results of titanium analysis conducted on cotton fabrics are given in Figure 4.30.

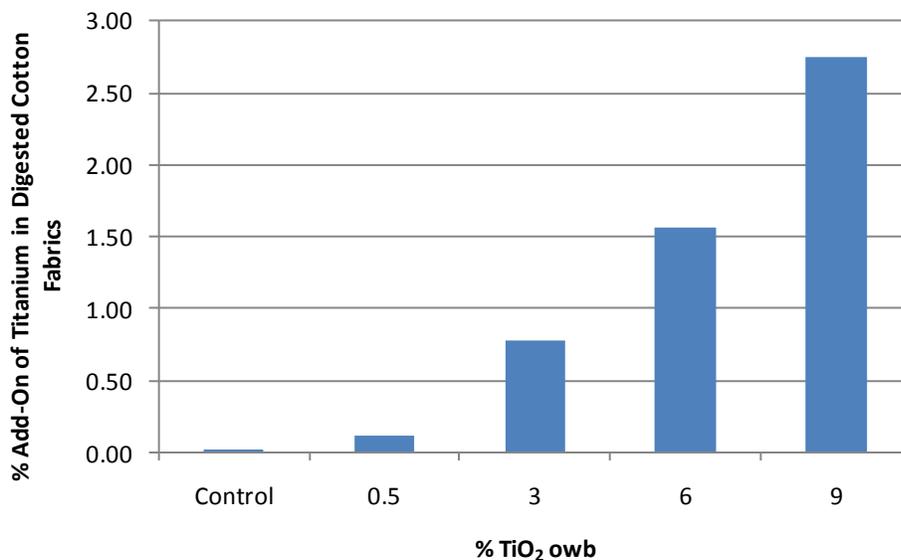


Figure 4.30: Titanium Add-On in Digested Cotton Fabrics

Titanium analysis conducted on cotton fabrics shows little to no titanium on the control sample. However, as percentage of TiO_2 owb increases, it is clear that the titanium concentration in finished fabrics increases by relatively the same amount. For example,

titanium concentration of the sample finished with 6.0% TiO₂ owb is approximately twice the titanium concentration of the sample finished with 3.0% TiO₂ owb. While this data does not disclose the actual TiO₂ add-on, it does clarify that the methodology used to mix sample chemistries yields evenly and uniformly dispersed TiO₂ nanoparticles. This data also discloses that TiO₂ is evenly distributed on all cotton fabrics, as ICP analysis fabrics were cut from random locations of finished fabric fabrics.

Similar results were obtained for poly/cotton fabrics, as depicted in Figure 4.31. The poly/cotton control sample shows slight titanium content (titanium is a common component in polyester fiber manufacturing). As a conclusion, it was also found that as percentage of TiO₂ owb increase, add-on increases by the same amount. Also, it can be concluded that TiO₂ is evenly distributed within all poly/cotton fabrics.

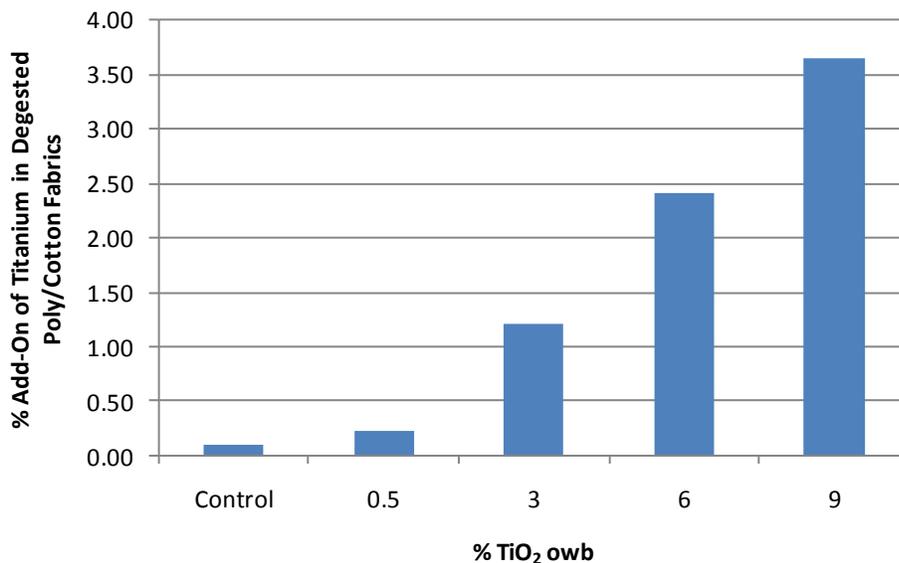


Figure 4.31: Titanium Add-On in Digested Poly/Cotton Fabrics

Although both fabrics were finished with identical percentages of THPC owb, Figure 4.32 concludes that the poly/cotton fabrics had a slightly higher total phosphorus concentration, which is to be expected considering poly/cotton's WPU of 95% compared to cotton's WPU of 73%. Results shown in Figure 4.32 consist of average phosphorus concentrations of all digested fabrics analyzed, including fabrics evaluated in the above titanium analyses of cotton and poly/cotton fabrics.

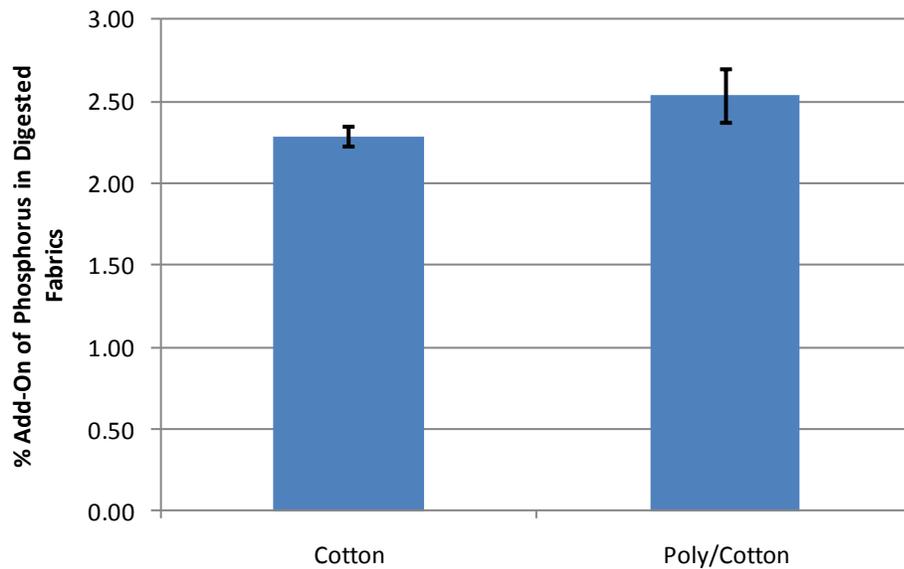


Figure 4.32: Phosphorus Add-On in Digested Fabrics

4.6.2 Laundered Fabrics

An evaluation was conducted of cotton and poly/cotton blend fabrics that had been exposed to 5 consecutive washing and drying cycles. These fabrics were finished with identical chemistries to un-laundered fabrics evaluated in the previous section. Although FR testing results clearly show that these fabrics suffer significant losses of flame retardant properties following laundering, it is particularly useful to quantify the effect of laundering

on attachment of TiO_2 . Figure 4.33 and Figure 4.34 are titanium analyses of laundered cotton and poly/cotton fabrics, respectively.

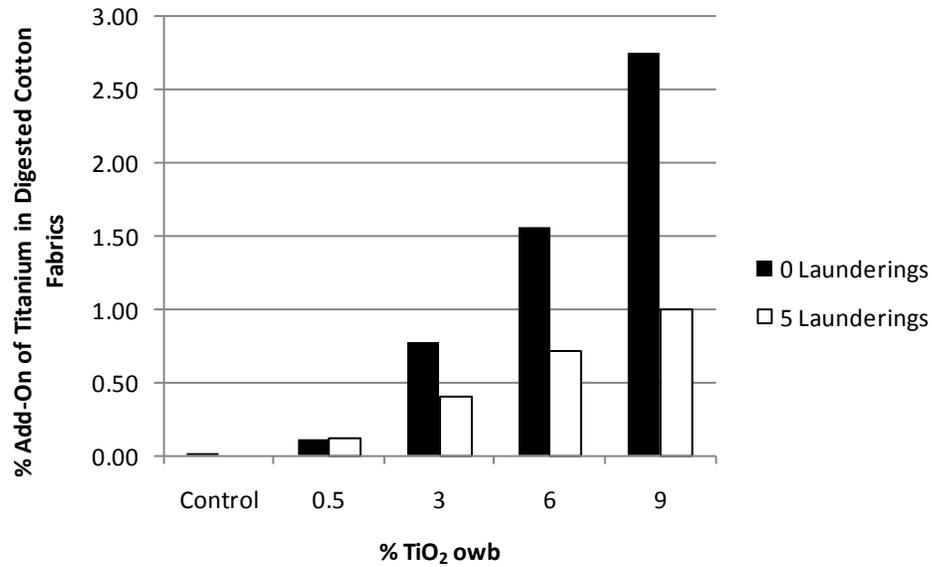


Figure 4.33: Comparison of Titanium Add-On in Digested Cotton Fabrics

From Figure 4.33, it is evident that titanium concentration decreases significantly on cotton fabrics after five launderings. Fabrics finished with 3.0% TiO_2 owb lost approximately 50% of TiO_2 following laundering. Fabrics finished with greater than 3.0% TiO_2 owb suffered even greater percentage losses of TiO_2 concentration. For example, titanium concentration decreased almost three-fold on the fabric finished with 9.0% TiO_2 owb after laundering.

Retention of titanium was slightly greater for poly/cotton fabrics, as shown in Figure 4.34.

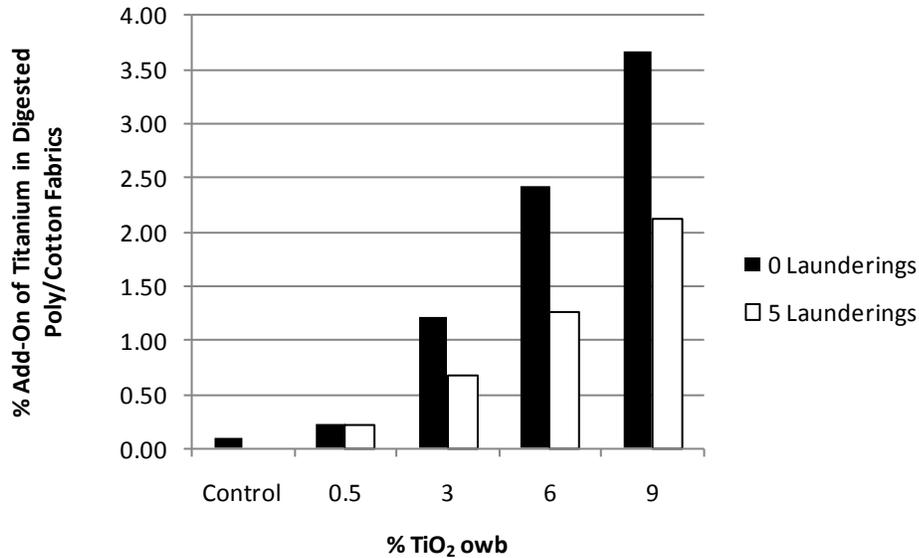


Figure 4.34: Comparison of Titanium % Add-On in Digested Poly/Cotton Fabrics

Poly/cotton fabrics retained more than half of the initial titanium concentration when subjected to five washing and drying cycles. Evidently, the silane cross-linker TEOS does a better job of durably attaching TiO₂ nanoparticles to the 80/20 poly/cotton blend fabric than to the 100% cotton fabrics.

Lastly, elemental phosphorus contents of laundered cotton and poly/cotton fabrics were also analyzed and compared to un-laundered fabrics in Figure 4.35.

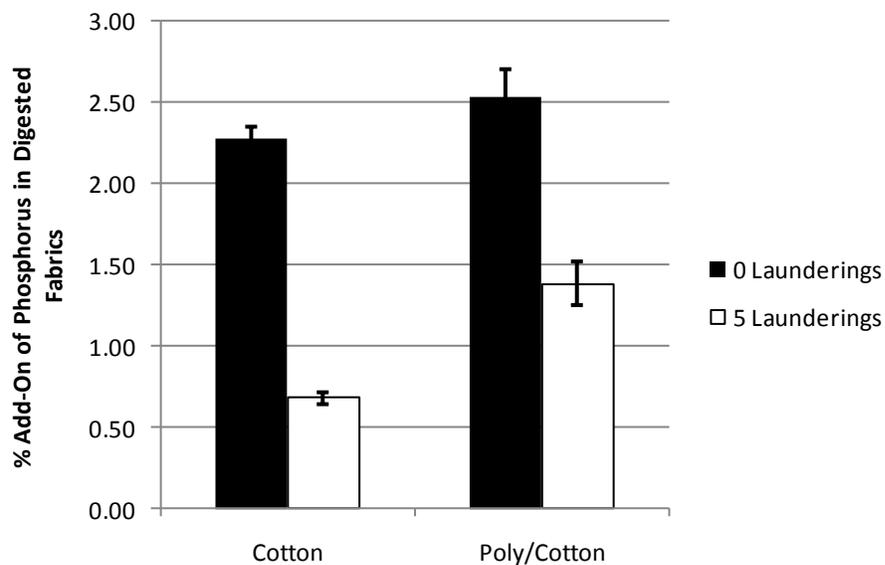


Figure 4.35: Comparison of Phosphorus % Add-On in Digested Fabrics

Control fabrics contained no phosphorus before or after laundering. However, not only is it clear that TEOS serves as a better cross-linker of TiO_2 to poly/cotton blended fabrics, but also as a better cross-linker of THPC to poly/cotton blended fabrics. Phosphorus content of laundered poly/cotton decreases by approximately two-fifths compared to the three-fourths decrease in phosphorus content of laundered cotton.

5 Conclusions

It was found that the addition of TiO₂ nanoparticles to FR finishes containing THPC, Urea, and multifunctional silanes not only improves flame retardant properties of cotton and poly/cotton blend fabrics, but also improves antimicrobial properties. However, the durability of the finishing needs to be improved.

5.1 Flame Retardant Properties

A significant portion of the scope of this work is to obtain flame retardant functional finishes on 100% cotton and 80/20 poly/cotton blended fabrics through the use of commercial flame retardants, multifunctional silane cross-linkers, and TiO₂ nanoparticles. Through experimentation, the effects of TiO₂ concentrations and silane types were evaluated on flame retardant properties. In addition, the effect of laundering on the durability of flame retardant finishes was investigated on cotton and poly/cotton blended fabrics.

- Flame retardant finishes can be employed on cotton fabrics and poly/cotton blended fabrics through the use of 25.0% THPC + 15.0% Urea + 0.5% silane cross-linker + TiO₂.
- Among all silanes, the silane cross-linker TEOS has the least negative effect on flame retardant properties of both cotton and poly/cotton fabrics.
- As %TiO₂ owb increases, percentage of self-extinguishing poly/cotton fabrics increases.
- As %TiO₂ owb increases, reduction of char length occurs on cotton and poly/cotton fabrics.

- Finished cotton fabrics self-extinguished after laundering; in addition, char length of cotton fabrics increased significantly, doubling the lengths of un-laundered fabrics.
- All finished poly/cotton fabrics underwent complete combustion, with no increase in afterflame time, compared with a laundered un-finished control.

5.2 Antimicrobial Properties

The second significant objective of this research is to establish the antimicrobial efficacy of experimental finishes against gram positive and gram negative bacteria under 3 lighting conditions: no light, visible light, ultraviolet (UV) light.

- Un-finished poly/cotton control fabrics showed no antimicrobial efficacy whatsoever.
 - Experienced growth of *S. aureus* and *K. pneumoniae* under all lighting conditions
- Fabrics finished with 25.0% THPC + 15.0% Urea + 0.0% TiO₂ + 0.5% TEOS showed positive antimicrobial efficacy against *S. aureus* under conditions of no light, visible light, and UV light.
 - All fabrics completely exterminated all *S. aureus* colonies under no light.
 - 4 out of 5 fabrics completely exterminated all *S. aureus* colonies under visible light. The fifth sample experienced colony growth, but at a slower rate than the unfinished control.
 - 2 out of 5 fabrics completely exterminated all *S. aureus* colonies under UV light. The remaining three fabrics experienced colony growth.

- Fabrics finished with 25.0% THPC + 15.0% Urea + 0.0% TiO₂ + 0.5% TEOS showed positive antimicrobial efficacy against *K. pneumoniae* under conditions of no light, visible light, and UV light.
 - All fabrics completely exterminated all *K. pneumoniae* colonies under all lighting conditions.
- Fabrics finished with 25.0% THPC + 15.0% Urea + 9.0% TiO₂ + 0.5% TEOS showed positive antimicrobial efficacy against *S. aureus* under conditions of no light, visible light, and UV light.
 - All fabrics completely exterminated all *S. aureus* colonies under no light.
 - 4 out of 5 fabrics completely exterminated all *S. aureus* colonies under visible light. The fifth sample experienced colony growth, but at a slower rate than the unfinished control.
 - All fabrics completely exterminated all *S. aureus* colonies under UV light. This experiment shows improved antimicrobial efficacy of TiO₂ compared to that of THPC + Urea.
- Fabrics finished with 25.0% THPC + 15.0% Urea + 9.0% TiO₂ + 0.5% TEOS showed positive antimicrobial efficacy against *K. pneumoniae* under conditions of no light, visible light, and UV light.
 - All fabrics completely exterminated all *K. pneumoniae* colonies under all lighting conditions.

5.3 Elemental Analysis

Although fabrics showed limited durability of flame retardant performance to 5 launderings, ICP elemental analysis was conducted on pre- and post-laundered fabrics to measure the durability of elemental attachment to cotton and poly/cotton substrates in order to further analyze the durability of finishes.

- Un-laundered cotton and poly/cotton fabrics received uniform distributions of well-dispersed TiO₂ nanoparticles and THPC flame retardant during the finishing process.
- All laundered fabrics suffered significant losses of elemental titanium and phosphorus.
 - Laundered cotton fabrics showed approximately 75% loss of phosphorus and titanium add-on.
 - Retention of phosphorus and titanium was the greatest for poly/cotton fabrics even though flame retardant performance was non-durable. Laundered poly/cotton retained greater than 50% of phosphorus and titanium add-on.

6 Recommendations for Future Work

As a result of this research, it is evident that new steps could be taken in numerous directions to develop more durable flame retardant and antimicrobial finishes incorporating TiO₂ nanoparticles.

6.1 Performance Improvements

First and foremost, further experimentation and testing should be conducted in regards to finishes generated in this work.

- Future work should investigate different silanes or cross-linking technologies to further improve the durability of flame retardant and TiO₂ attachment to fabrics.
- Antimicrobial efficacy should be evaluated on fabrics finished with %TiO₂ between 0.0% and 9.0% owb. An optimum initial bacterial count applied to fabrics finished with this range of TiO₂ should provide results showing trends in % reduction of colonies. While it is obvious that 9.0% TiO₂ owb effectively eliminates all colonies of *S. aureus* and *K. pneumoniae* under UV light, how low a %TiO₂ owb is required to maintain 100% bacterial reduction is still unknown.
- Antimicrobial efficacy should be evaluated using other bacteria types. Obviously certain bacteria are more difficult to kill than others. Efficacy tests against mildew or fungi, for example, would also prove valuable as a UV light-activated finish containing TiO₂ nanoparticles would be of particular benefit for outdoor fabrics, which are in optimum conditions to support the growth of fungi.
- Antimicrobial efficacy should be evaluated on laundered fabrics. While flame retardant performance may not be durable to launderings, antimicrobial properties

of TiO₂ remaining on fabrics after foregoing 5 laundering cycles have not been quantified.

- Another durability test that should be conducted on fabrics generated in this research. Testing should be conducted to validate durability of this finish to UV light. For example, outdoor fabrics are exposed to the sun's harmful rays (consisting of varying intensities of UV radiation). These rays are proven to be degenerative not only to fabrics and fibers, but also to dyes or finishes applied to them. The UV absorbing properties of TiO₂ could prolong the durability of such finishes (in this case, flame retardant) to weathering. These tests could be conducted in a Xenon Weather-O-Meter.
- TiO₂ is also known for its odor neutralizing properties. Volatile Organic Compound (VOC) reduction testing conducted could quantify its odor neutralizing effects, which also add value to today's antimicrobial apparel, etc.
- Dyed fabrics should have L*a*b color space measurements, numerical lightness/darkness, red/green, yellow/blue values, obtained prior to application of varying concentrations of TiO₂ owb applied. Following TiO₂ application, L*a*b color space measurements should be made again. Shade changes may then be quantified and correlated with add-on percentages of TiO₂.
- Perform a cost analysis to quantify financial benefits associated with additions or substitutions of TiO₂ nanoparticles to flame retardant and antimicrobial functional fabric finishes.

6.2 Introduction of TiO₂ Nanoparticles into Current Commercial Finishes

- Flame retardant performance of TiO₂ coupled with commercial FR chemistries should be evaluated as well. The current work evaluates only one FR: THPC + Urea, which performs in the condensed phase. However, other commercial FR technologies exist. TiO₂ should be applied with commercial FR's to analyze for further synergistic effects that can lead to improved performance of current commercial FR finishes.
- Antimicrobial performance of TiO₂ coupled with commercial antimicrobial finishing agents should also be evaluated. The addition of other elements could improve light absorption properties of TiO₂. TiO₂ may also be more effective against certain types of bacteria while antimicrobial agents may be more effective against other bacteria types, creating broader efficacy of the antimicrobial finish as a whole.

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Appendices

Appendix A: Raw Data Used to Make Graphs

Data from **Figure 4.1**

Percentage Self-Extinguishing Fabrics			
Sample	Curing Procedure		
	A	B	C
S/E %	33	100	100

Data from **Figure 4.2**

Char Lengths (in)			
Sample	Curing Procedure		
	A	B	C
1	4.75	5.25	4.88
2	BEL	3.50	4.88
3	BEL	5.38	4.25
Avg	4.75	4.71	4.67
StDev	0.00	1.05	0.36

Data from **Figure 4.3**

Afterflame Times (s)			
Sample	Curing Procedure		
	A	B	C
1	22.68	34.97	33.43
2	27.65	30.28	28.90
3	22.47	23.72	44.16
Avg	24.27	29.66	35.50
StDev	2.93	5.65	7.84

Data from **Figure 4.4**

Percentage of Self-Extinguishing Cotton Fabrics								
	% TiO ₂ owb							
	Control	0	0.5	1	1.5	3	6	9
S/E %	0	100	100	100	100	100	100	100

Data from **Figure 4.5** and **Figure 4.7**

Afterflame Times (s) of Cotton Fabrics									
Times Laundered	Sample	% TiO ₂ owb							
		Control	0	0.5	1	1.5	3	6	9
0	1	19.00	S/E						
0	2	20.42	S/E						
0	3	17.81	S/E						
5	1	3.31	S/E	3.59	S/E	S/E	2.44	3.78	0.90
5	2	1.69	S/E	0.71	1.05	S/E	S/E	4.87	0.50
5	3	3.03	1.97	2.22	4.12	1.79	1.37	3.00	2.78
	Avg (0)	19.08	S/E						
	StDev (0)	1.31	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Avg (5)	2.68	1.97	2.17	2.59	1.79	1.91	3.88	1.39
	StDev (5)	0.87	0.00	1.44	2.17	0.00	0.76	0.94	1.22

Data from **Figure 4.6** and **Figure 4.8**

Char Lengths (in) of Cotton Fabrics								
Sample		% TiO ₂ owb						
		Control	0	0.5	1	1.5	3	6
1	BEL	3.75	3.25	4.00	3.25	2.75	3.25	3.38
2	BEL	4.25	3.50	4.13	3.50	3.13	4.25	2.75
3	BEL	3.75	3.75	3.50	3.25	3.50	3.50	3.50
Avg	BEL	3.92	3.50	3.88	3.33	3.13	3.67	3.21
StDev	0	0.29	0.25	0.33	0.14	0.38	0.52	0.40
Laundered avg		12.00	12.00	12.00	12.00	12.00	12.00	12.00

Data from **Figure 4.9**

Percentage of Self-Extinguishing Poly/Cotton Fabrics							
	Silane Type						
	Control	TEOS	TMOS	BTESE	BTMSEB	BTMSE	BTMSH
S/E %	0	33	0	66	0	33	33

Data from **Figure 4.10**

Char Length (in) of Self-Extinguishing Poly/Cotton Fabrics							
Sample		Silane Type					
		Control	TEOS	TMOS	BTESE	BTMSEB	BTMSE
1	BEL	5.38	BEL	9.63	BEL	4.63	6.00
2	BEL	BEL	BEL	11.25	BEL	BEL	BEL
3	BEL	BEL	BEL	BEL	BEL	BEL	BEL
Avg	BEL	5.38	BEL	10.44	BEL	4.63	6.00
StDev	0.00	0.00	0.00	1.15	0.00	0.00	0.00

Data from **Figure 4.11**

Afterflame Times (s) of Poly/Cotton Fabrics							
Sample	Silane Type						
	Control	TEOS	TMOS	BTESE	BTMSEB	BTMSE	BTMSH
1	S/E	51.69	22.97	47.00	41.87	30.87	29.75
2	32.50	34.16	26.22	S/E	36.97	37.72	33.88
3	28.00	S/E	44.00	S/E	32.72	S/E	S/E
Avg	30.25	42.93	31.06	47.00	37.19	34.30	31.82
StDev	3.18	12.40	11.32	0.00	4.58	4.84	2.92

Data from **Figure 4.12**

Percentage of Self-Extinguishing Poly/Cotton Fabrics								
S/E %	% TiO ₂ owb							
	Control	0	0.5	1	1.5	3	6	9
	0	66	0	33	66	33	100	100

Data from **Figure 4.13**

Char Length (in) of Self-Extinguishing Poly/Cotton Fabrics								
Sample	% TiO ₂ owb							
	Control	0	0.5	1	1.5	3	6	9
1	BEL	6.25	BEL	6.75	7.00	5.38	4.88	5.63
2	BEL	6.75	BEL	BEL	8.25	BEL	4.88	5.25
3	BEL	BEL	BEL	BEL	BEL	BEL	4.25	4.13
Avg	BEL	6.50	BEL	6.75	7.63	5.38	4.67	5.00
StDev	0.00	0.35	0.00	0.00	0.88	0.00	0.36	0.78

Data from **Figure 4.14**

Afterflame Times (s) of Fully Combusting Poly/Cotton Fabrics								
Sample	% TiO ₂ owb							
	Control	0	0.5	1	1.5	3	6	9
1	S/E	28.93	36.78	27.37	38.56	51.69	S/E	S/E
2	32.50	S/E	27.60	30.00	S/E	34.16	S/E	S/E
3	28.00	S/E	50.06	S/E	S/E	S/E	S/E	S/E
Avg	30.25	28.93	38.15	28.69	38.56	42.93	S/E	S/E
StDev	3.18	0.00	11.29	1.86	0.00	12.40	0.00	0.00

Data from **Figure 4.15**

Afterflame Times (s) of Fully Combusted Poly/Cotton Fabrics									
Times Laundered	Sample	% TiO ₂ owb							
		Control	0	0.5	1	1.5	3	6	9
0	1	S/E	28.93	36.78	27.37	38.56	51.69	S/E	S/E
0	2	32.50	S/E	27.60	30.00	S/E	34.16	S/E	S/E
0	3	28.00	S/E	50.06	S/E	S/E	S/E	S/E	S/E
5	1	37.13	34.34	33.54	28.00	32.40	32.59	33.43	34.47
5	2	39.00	30.38	29.65	28.22	29.47	41.00	28.90	36.69
5	3	41.72	33.16	30.82	32.37	23.09	27.66	44.16	28.00
	Avg (0)	30.25	28.93	38.15	28.69	38.56	42.93	S/E	S/E
	StDev (0)	3.18	0.00	11.29	1.86	0.00	12.40	0.00	0.00
	Avg (5)	39.28	32.63	31.34	29.53	28.32	33.75	35.50	33.05
	StDev (0)	2.31	2.03	2.00	2.46	4.76	6.75	7.84	4.51

Data from **Figure 4.33**

Titanium % Add-On on Digested Cotton Fabrics					
Launderings	% TiO ₂ owb				
	Control	0.5	3	6	9
0	0.02	0.12	0.78	1.56	2.76
5		0.13	0.41	0.72	1.00

Data from **Figure 4.34**

Titanium % Add-On on Digested Poly/Cotton Fabrics					
Launderings	% TiO ₂ owb				
	Control	0.5	3	6	9
0	0.09	0.23	1.21	2.41	3.66
5		0.21	0.67	1.26	2.11

Data from **Figure 4.35**

Phosphorus % Add-On on Digested Fabrics		
Launderings	Cotton	Poly/Cotton
0	2.23	2.07
0	2.18	2.83
0	2.25	2.73
0	2.47	2.50
5	0.61	1.65
5	0.73	1.54
5	0.75	1.03
5	0.63	1.32
Avg (0)	2.28	2.53
Avg (5)	0.68	1.39
StDev (0)	0.13	0.34
StDev (5)	0.07	0.27