

## Abstract

WATSON JR., SAMUEL B. Improved Antistatic Properties of Polyester. (Under the direction of Dr. Stephen Michielsen.)

The accumulation of charge on textile materials can provide problems in manufacturing. Static electricity also is an inconvenience to the customer as both mild shocks and the clinging of clothing is not desired. Antistatic agents are often applied to polyester fabrics to reduce these effects by providing mobility of ions on the surface. Typically, excess chemicals are applied to help improve the durability. In this research, sulfonic esters and phosphate esters are covalently bonded to poly(acrylic acid) and applied to the surface of polyester fabrics to increase the durability. Sodium hydroxide is used to neutralize the acids for the mobility of ions. The sulfonic ester taurine was not found to provide any additional antistatic properties to the combination of poly(acrylic acid) and sodium hydroxide, however, o-phosphorylethanolamine did provide additional antistatic properties. Poly(ethylene glycol) was added to the combination of poly(acrylic acid), o-phosphorylethanolamine, and sodium hydroxide but was not found to provide any synergistic antistatic properties. Through use of poly(acrylic acid), o-phosphorylethanolamine, and sodium hydroxide, a pad/dry/cure application method was developed to obtain surface resistivity values of  $9.5 \text{ Log Ohms/Square}$  at 45 % relative humidity on polyester fabric with approximately one percent add on levels. The resistivity increased by less than a half an order of magnitude after three deionized water rinses. However, the resistivity increased by almost 3.5 orders of magnitude after one accelerated laundering equivalent to five home launderings. The finish was not

completely durable to an accelerated laundering, but the antistatic properties are still an improvement over untreated polyester fabric before and after subjection to the same accelerated laundering cycle. The use of poly(acrylic acid) and sodium hydroxide in conjunction with o-phosphorylethanolamine increased the antistatic properties over that of the phosphate ester o-phosphorylethanolamine. The durability was also improved.

Improved Antistatic Properties of Polyester

by  
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## **Biography**

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# 1. Introduction

Many antistatic finishes are used on textile products. Some are more durable than others, but all current antistatic finishes are limited in durability. To overcome this problem, often excess amounts of the antistatic finish are applied which can be cost prohibitive and harmful to the environment. The goal of this research is to determine if grafting chemical structures similar to traditional antistatic agents to the textile fabric will aid in durability and reduce consumption.

Upon successful completion, industry will be able to use less antistatic chemicals when applying antistatic finishes. A lower amount of chemical application will be less harmful to the environment and will reduce chemical purchases. There also will be less effluent to treat.

Chemical structures that were effective in antistatic finishes are determined. Combinations of the structures were formed that allow them to be mixed with a carrier polymer and grafted to the fabric. After application, the fabric was tested using AATCC antistatic test methods for effectiveness and durability.

In the following chapters a literature review is included which gives a technical background on the mechanisms of static electricity, generation, and dissipation. The literature review also reviews chemicals used in antistatic finishes on textile fabrics including their effectiveness and durability. The mechanisms of the chemicals are studied and used for the determination of a combination of structures to utilize in an antistatic finish that can be grafted to polyester fabric.

Static electricity has been studied for several years and the basics of static electricity have not changed. A reduction of static electricity can be approached in two ways, or a combination of both. One method to reduce static build up is to reduce the generation of the static electricity. Another method is to transport the charge through a conductive material. The focus of this review is on the transportation of the charge so it does not accumulate. Within the transportation mechanism through conduction, two methods are commonly used. Conductive materials can be incorporated into a polymer before spinning fibers or applied afterwards as a coating. The primary focus of this research and review is on the coating of textile materials with chemical finishes.

The understanding of static electricity is important because knowledge in how static is developed will aid in leading to methods of its dissipation. The antistatic finishes are studied and reviewed for an understanding of current consumption levels and costs. The durability of the finishes is also important. The mechanisms behind the antistatic properties are also studied to understand the phenomena. This research involves grafting of antistatic polymers to the surface of polyester fabric. Dr. Stephen Michielsen has conducted research grafting antimicrobial finishes to nylon surfaces using poly(acrylic acid). A similar approach is taken in this research. Poly(acrylic acid) is used to graft antistatic polymers to polyester fabrics. The test methods for antistatic properties are reviewed to obtain the most efficient method to test antistatic treated fabrics. The effectiveness, durability, and cost of the antistatic treatments are of the utmost importance.

## **2. Literature Review**

### ***2.1 Static Electricity***

#### **2.1.1 Disadvantages of Static Electricity**

From the point a fiber is being processed in manufacturing to after a finished garment is worn by a consumer, static electricity can cause many problems. Manufacturing operations can experience problems with static electricity that can reduce process reliability and cause defective production. For the consumer, static can be hazardous when dealing with flammable substances such as gasoline. Annoyances can occur from the electrical shock and the clinging of garments. Both the consumer and the manufacturer experience negative aspects of static electricity.

##### **2.1.1.1 Consumer Disadvantages**

Static electricity can be irritating to the customer such as the unanticipated shock while exiting the car. The clinging of pants to socks, skirts to legs, and dresses to the body causes the wearer to be uncomfortable. The bunching and riding up of undergarments is also undesirable. Stockings and socks can become charged and pick up soil, lint, and dirt. (Hersh, 1975) Some static electricity problems can be more serious. There is the potential for a fire while filling your tank with gas if the energy is not discharged before handling the pump. Parachutes have been known to fail because of the static charges of opposite signs preventing the parachute from opening. (Morton, Hearle, & Textile Institute, 2008) Static electricity can also cause problems to electronic equipment such as computers. (Schindler & Hauser, 2004; Hersh, 1975)

### **2.1.1.2 Manufacturer Disadvantages**

Other problems with static electricity can be apparent to the manufacturer. Many problems can occur such as when filaments are repelled. This can cause several processing problems including ballooning and snagging as well as other material handling problems. (Schindler & Hauser, 2004) As mentioned earlier, static electricity can attract dirt and lint. This can cause contamination during processing. The clinging of the materials due to static electricity can also make cutting and sewing operations more difficult. (Ranney, 1976)

### **2.1.2 Advantages of Static Electricity**

Electricity has become a necessity in everyday life. Static electricity is advantageous with the use of plastic wrap in the aid of clinging to food containers. Static electricity is also used for separation of different items. Purification by electrostatic precipitation and electrostatic separation of minerals and ores are just a few methods of filtration. Other advantages include electrostatic painting, printing, coating and copying. (Hersh, 1975) Despite the fact that static electricity has such a disadvantage in most fiber processing operations, static does aid in some processing of fibers. Static electricity is used in fiber separation and cleaning. It is also used to aid in fiber transport in open-end spinning. With all of the advantages and disadvantages to static electricity, it is of importance to understand the phenomena.

### **2.1.3 Generation of Static Electricity**

Static electricity can be formed by rubbing two surfaces. The formation of electricity by rubbing is called triboelectrification. Around 600 B.C., Thales of Miletus, a Greek



philosopher, noticed that amber attracted light particles when rubbed with cloth. (Edelstein, 1953) Dufay discovered that there are two different types of charges of electricity and defined them as vitreous and resinous. (Slade, 1998) Items charged with vitreous electricity repelled each other but attracted items of resinous charge. These charges, vitreous and resinous, were renamed by Benjamin Franklin to positive and negative respectively. Franklin proposed what is known as the single-fluid theory. The single-fluid theory is that negative electricity is generated from an excess of negative charge or electrons, and positive electricity is from a deficiency in negative charge. (Slade, 1998) Different materials will have different charges based on what materials they come into contact with or are rubbed against. Because of this, a list of materials was developed that listed the order in charge. The first triboelectric series was published by Wilche in 1757. (Wilche, 1757) An item from the list will become positively charged when rubbed against an item listed further down the list. At the same time, the item further down the list will become negatively charged. (Hersh, 1975; Schindler & Hauser, 2004) The same material that becomes positively charged when rubbed against a material further down the list will become negatively charged when rubbed against a material that is listed before it. Many triboelectric series have been developed as more materials are being analyzed. A sample triboelectric series is shown below in Table 2.1.

**Table 2.1: Triboelectric series** (Schindler & Hauser, 2004)

Positive end of the series	1. Glass 2. Wool 3. Nylon 6 4. Nylon 6,6 5. Rayon 6. Cotton 7. Acetate 8. Hemp 9. Silk 10. Polyester 11. Acrylic, Modacrylic
Negative end of the series	12. Polyethylene, polypropylene 13. Polytetrafluoroethylene

As the separation between the materials within the triboelectric series increases, the charge of each material being rubbed together becomes more difficult to predict. There are many factors that come in to play, such as differences in the molecular surface structure, surface impurities, intensity of contact, etc. (Slade, 1998)

### **2.1.3.1 Static Generation during Contact**

Atoms consist of protons within a nucleus that are surrounded by electrons. These electrons are attracted to the nucleus but the attraction is not strong enough to stop all electrons from being removed from the electron cloud. When two materials come into contact, electrons transfer from one material to the other in both directions. This process happens continuously and is usually not in equilibrium. Once the materials are separated, one material will have excess electrons while the other will have a shortage. (Schindler & Hauser, 2004) Therefore, a charge can be generated without rubbing. Leakage or flow of

electrons from inside to the surface can cause electrically conductive materials to reestablish equilibrium. (Slade, 1998) Insulators hold the charge and exhibit what is known as static electricity. Two layers of charge,  $Q$ , are present when two materials are in contact. Upon separation, the capacitance,  $C$ , between the materials decreases and the voltage,  $V$ , increases. The relation is shown below in Equation 2.1. (Hersh, 1975)

$$V = \frac{Q}{C}$$

**Equation 2.1: Relation between voltage, charge, and capacitance**

In 1779, Volta hypothesized that frictional electrification is not from the friction but rather the contact of two bodies. The effects of friction such as heating and transfer of material does not have an impact. The friction does allow for more surface contact between the two bodies which does play a significant roll in charge transfer. (Hersh, 1975) In addition to the Volta-Helmholtz hypothesis, Henry believed that transfer also occurs because of the differences in temperature. (Hersh, 1975) This occurs when rubbing on areas of a material that have not been rubbed.

### **2.1.3.2 Dissipation during Separation**

Separation of two objects can cause an electric field that tries to push the charged particles back. Some of the charges return with an overall reduced amount of charge. This leakage takes place during and after the separation. (Slade, 1998) Hersh has found that quantum mechanical tunneling across small gaps occurring during the initial stages of separation, conduction through the atmosphere, conduction through the contacting bodies, and conduction along the surface of the contacting bodies are all ways that leakage can take

place. (Hersh, 1975) The charge can be released by electrical discharge when two items in the triboelectric series have a difference in charge of approximately  $3 \times 10^6 \text{ Vm}^{-1}$ , which is the ionization potential of air. (Schindler & Hauser, 2004) It has been calculated by Harper that tunneling stops after separation of  $25 \text{ \AA}$  for conductive materials. (Harper, 1951) These calculations have not been performed in as much detail for insulator to conductor or insulator to insulator. Leakage through the air is possible when two objects separate past the free path of the gas molecules in the air. (Slade, 1998) This only occurs if the electric field from separation is greater than the dielectric strength or ionization potential of the air. The radius of curvature for fibers is small and causes the charge to be large before ionization. As the separation is increased, the field strength reduces. (Slade, 1998) This results in a lower capability for the surface to ionize the air. There is a false belief that the relative humidity of the air has impact on the conduction of electricity to the atmosphere. This is false because air has relatively the same dielectric strength across the range of relative humidity according to Medley. (Slade, 1998) However, the relative humidity does have an effect on the moisture regain of fibers, and therefore can affect the conductivity of the fibers. Medley's experiments have also shown that gaseous discharge is easily produced by rubbing small objects. Discharge through the distance of a gap of one mm or greater is usually of built up charge rather than a continuous stream. The discharge stops when the charge becomes lower than the initiation charge.

Discharge through the air can be increased by the use of static eliminators. Static eliminators ionize the air in two ways; application of a strong electrostatic field to ionize the

air or by radiation. The electrostatic field is applied by a corona discharge eliminator which consists of inductive or high voltage eliminators. (Kirk, Othmer, Grayson, & Eckroth, 1978)

#### **2.1.4 Transportation of Charge through Conductive Materials**

Most static is dissipated along a filament to ground. This is done most easily through a conductive material. Conductive materials can be inserted into a polymer or applied as a coating. (Slade, 1998) Waxes can be applied but are not durable. The problem is that the wax will wash off the first time the material is laundered.

Organic polymers are considered to be insulators. Natural fibers usually absorb more water than synthetic fibers because of the strong hydrogen bonding groups found in the natural fibers. The water helps with the transport of the charge because of its low resistivity. Therefore, natural fibers such as cotton, wool, and silk have better antistatic properties than synthetic fibers like polyacrylonitrile, polyester, and polyamides. Ionic conduction is dependent on the number of ions' available along with their mobility. (Slade, 1998) The salt content of a fiber is also a factor in the electrical resistance of a fiber. The salt content aids in the transport of charge. A more important factor in the conduction of electricity is the ions ability to group into neutral ion pairs. Neutral ion pairs reduce the amount of charged ions present to aid with the conduction of electricity therefore, reducing the conductivity. (Slade, 1998) The dielectric constant of the material is a good way to determine the materials conductivity. Low values for the dielectric constant coincides with larger forces attracting oppositely charged particles in the material than those of a higher dielectric constant. Neutral ion pairs are related to the amount of force attracting opposite charged particles. Increases in

neutral ion pairs, increases the resistance. Therefore, lower dielectric constants result in increased static electricity.

COONa, SO<sub>3</sub>Na, and CH<sub>2</sub>CH<sub>2</sub>O are functional groups that are found in some polymers. These functional groups serve as natural antistats because of their ability to absorb water. Cl, CN, and COOCH<sub>3</sub> in a polymer contribute less to these antistatic properties. (Slade, 1998)

## ***2.2 Methods for assessing electrostatic behavior***

To assess electrostatic behavior, it is important to condition samples in a controlled environment. The most important factor is the relative humidity. (Schindler & Hauser, 2004) Relative humidity is the percentage of the maximum amount of moisture that can be in the air at that given temperature. Higher relative humidity values of the air lead to increased amounts of moisture absorption and therefore increase the electrical flow. Warfield and Petree have discovered that the bulk resistivity of polymers is also dependent on the temperature as shown in Figure 2.1. (Warfield & Petree, 1961)

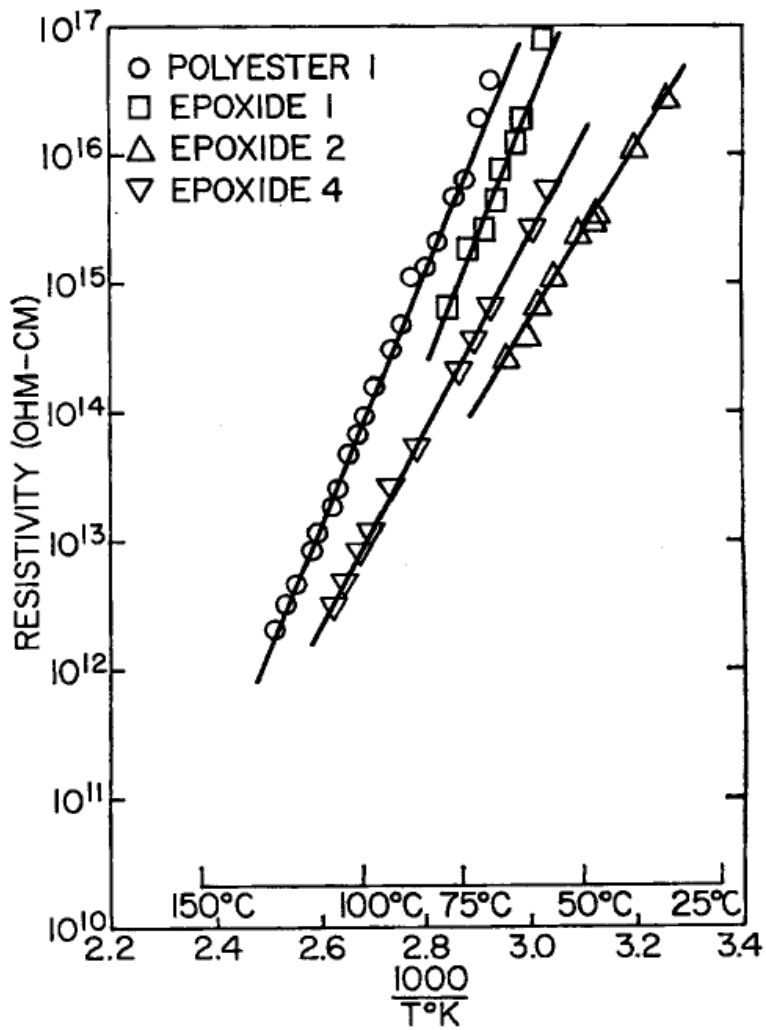


Figure 2.1: Volume resistivity dependence of polymers on temperature (Warfield & Petree, 1961)

As shown in Figure 2.1, only dramatic changes in temperature have an effect on antistatic behavior. Relative humidity has the biggest impact.

## **2.2.1 Cling tests**

Several test methods have been developed for assessing the static behavior of textile materials. These methods have been organized into three groups; measuring the cling time, the electrical resistance, and the electrostatic voltage or charge.

### **2.2.1.1 Ash Test**

The ash test is a simple test method for evaluation of static on textiles. (Schindler & Hauser, 2004) The method provides a rough estimate of static propensity. (Slade, 1998) Fabric is rubbed on a piece of plastic or rubber and then placed over a tray of ashes. A fabric with larger amounts of ashes clinging to the fabric has more static charge than a fabric with lesser amounts of ashes. This method is difficult to quantify and is generally used for qualitative results.

### **2.2.1.2 Fabric to Metal Cling Test**

The fabric to metal cling test was developed by AATCC. (American Association of Textile Chemists and Colorists, 2007) The fabric being tested is rubbed against a different material fabric to develop a static charge. The sample is then placed on a metal plate that is grounded and inclined. The amount of time it takes for the sample to begin to slide down the plate is measured. This method was developed primarily for lightweight tricot fabrics because the weight of heavier fabrics can cause them to slide down more easily. This method is not reliable. The amount of weight of the sample is a factor along with the user's technique. (Slade, 1998) The results can also be variable because of the rubbing on the



surface. Rubbing on the surface of the sample may alter the surface properties of the sample before being tested. (Slade, 1998) Overall, this test method is not reliable for quantitative results.

### **2.2.1.3 AATCC Test Method 115**

The AATCC Test Method 115 (American Association of Textile Chemists and Colorists, 2007): ‘Electrostatic clinging of fabrics’ is based on the same principle as the ash test but is slightly more quantitative. Electrically charged fabric is positioned beside a metal plate that is electrically grounded and inclined. The time required for the fabric to release from the metal plate is the measurement of the antistatic properties. The longer the amount of time to release, the more static charge there is on the fabric. Two common methods for measuring quantitatively the static electricity on textile materials are through the measurement of the electrical dissipation and the electrical resistivity.

## **2.2.2 Methods for measurement of static dissipation on textile materials**

The amount of dissipation of electricity is another method of testing the antistatic properties of a material. Several methods have been developed to measure the amount of dissipation as given below.

### **2.2.2.1 Hayek-Chromey Wheel**

The Hayek-Chromey is a method for measuring static dissipation. The test fabric is placed on a rotating wheel. The rotating wheel with the test fabric rubs against a selected material to create a static charge on the test fabric. The amount of charge is measured with

an electrometer. Once a constant charge is obtained, rubbing is stopped and the charge decay is measured. Results consist of the amount of time to obtain half the amount of charge or half life. This test method is objective but still has the potential for the results to be affected by the friction on the surface causing changes to the surface properties. (Slade, 1998)

### **2.2.2.2 The Static Honestometer**

The Static Honestometer was named after its ability to obtain reproducible results. This measurement method was found to be better than other static dissipation measurement systems of its time. (Slade, 1998) The Static Honestometer can be used on any construction fabric, yarn, or carpet. Corona discharge is used to electrically charge the sample. The sample is rotated on a turntable at 1750 revolutions per minute with a 10 kV discharge applied from a needle electrode. An oscilloscope is used to detect the amount of charge. The data can be analyzed by photographs of the oscilloscope face for comparisons of voltage versus time, the initial peak to peak charge, half life, or the percentage of the initial charge present after 44 seconds. Out of all of these analytical methods, photographs of the oscilloscope face for comparisons of voltage versus time is the best. (Slade, 1998)

### **2.2.2.3 The Rothschild Static Voltmeter**

The Rothschild Static Voltmeter is used to test static build up on fibers, yarns, and fabrics. Electrostatic charge is converted into a proportional voltage with a vibrator-condenser. One condenser plate is excited by an electromagnetic driving circuit. The voltage is picked up by the condenser electrode and amplified for display on a galvanometer.

A number of electrodes can be utilized. The electrodes include: The field measuring electrode, roller electrodes, contact electrode, resistance electrode, cup electrode, and carpet electrode. Each electrode has its own purpose whether it is for measurement on different types of samples or different measurement methods. Multiple methods are utilized with the Rothschild Static Voltmeter.

One method is to measure the electric field generated by the charge. For this method, the electrode must not come into contact with the sample. The distance of the electrode to the sample must remain constant for comparison of results. Another method is to put the electrode in contact with the sample. The sample is pulled across the electrode during measurements.

### **2.2.3 Methods for Measurement of Resistivity on Textile Materials**

Electrical resistivity is a measure of resistance of electrical current flow. Electricity can flow across the surface or through the volume. Most static electricity only involves the surface resistivity (Slade, 1998), so bulk or volume resistivity will not be discussed.

#### **2.2.3.2 AATCC Test Method 76**

The AATCC Test Method 76 (American Association of Textile Chemists and Colorists, 2007): 'Electrical resistivity of fabrics' is a method for measuring the surface resistivity of fabrics. The difference in voltage across a distance on the fabric is used to calculate the surface resistivity in the units of Ohms/Square. Typically, a value of less than  $10^{11}$  ohms/square is desirable. (Schindler & Hauser, 2004) Some resistivity values and how they relate to the textile industry are given below in Table 2.2.

**Table 2.2: Resistivity values of textiles (Schindler & Hauser, 2004)**

Surface resistivity range ( $\Omega/\text{sq.}$ ) at 65% r.h.	Assessment
$1 \times 10^6 - 1 \times 10^8$	Very good
$1 \times 10^8 - 1 \times 10^9$	Good
$1 \times 10^9 - 1 \times 10^{10}$	Satisfactory
$1 \times 10^{10} - 5 \times 10^{10}$	Limit of sufficiency
$> 5 \times 10^{10}$	Insufficient

## **2.3 Antistatic Textiles**

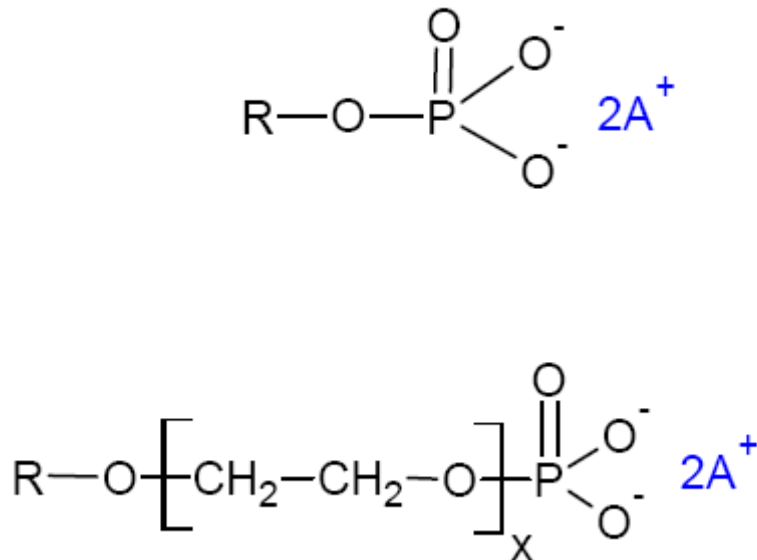
### **2.3.1 Non-Durable Finishes**

Non-durable finishes are typically preferred in fiber and yarn manufacturing because of their ease of removal. (Schindler & Hauser, 2004) Non-durable chemicals usually include surfactants, organic salts, glycols, polyethylene glycols, polyelectrolytes, quaternary ammonium salts, polyethylene oxide compounds, and esters of salts of alkylphosphonium acids. (Schindler & Hauser, 2004) Three general classifications of antistatic finishes include phosphate esters, quaternary ammonium amines, and non-ionic antistats.

#### **2.3.1.1 Phosphate Esters**

The largest group of non-durable antistatic finishes are esters of phosphoric acid. (Brown, Lemay, Bursten, & Burdge, 2003; Schindler & Hauser, 2004) Phosphated esters are classified as anionic. An ester is an organic compound that has an OR group attached to a carbon oxygen double bond or carbonyl. (Brown et al., 2003) Alkyl groups are groups formed by removing a hydrogen atom from an alkane. Alkanes are compounds of hydrogen

and carbon which only have carbon carbon single bonds. (Brown et al., 2003) A typical structure of a phosphoric ester is shown below in Figure 2.2 where R is an alkyl group.



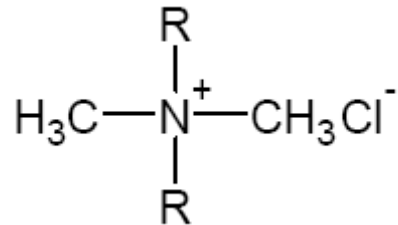
**Figure 2.2: Phosphoric ester antistat structure** (Schindler & Hauser, 2004)

Larger structures of phosphoric esters lead to increased durability once applied to a fabric. (Schindler & Hauser, 2004)

### 2.3.1.2 Quaternary Ammonium Amines

Quaternary amines are commonly used cationic antistats. (Grossman, 1993)  
Quaternary amines typically consist of tetra-substituted ammonium compounds (Slade, 1998) which make up the second largest group of non-durable antistatic finishes. (Schindler

& Hauser, 2004) The R-alkyl groups can be one of many different substituents. (Slade, 1998) Quaternary amines are also referred to as quaternary ammonium salts. The quaternary amine is produced through a reaction. Different reactions can create different final compounds. One of the easiest reactions is through the quaternization of a tertiary amine. (Slade, 1998) Quaternization is the synthesis of the cation from ammonia and tertiary refers to the overall shape. (Brown et al., 2003) The typical structure of a quaternary ammonium antistat is shown below in Figure 2.3.

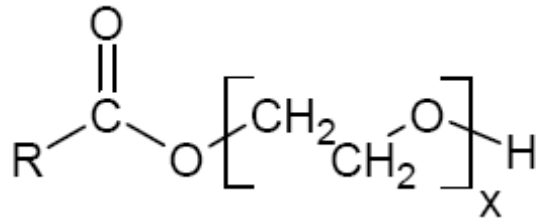


**Figure 2.3: Quaternary ammonium antistat structure** (Schindler & Hauser, 2004)

The structure of these antistats allow for a high affinity to textile fabrics. (Schindler & Hauser, 2004) Because of their high affinity, they can easily be applied through exhaustion which is a common process for applying chemicals and dyes to fabrics.

### **2.3.1.3 Non-Ionic Antistats**

Non-ionic antistats are composed of non-ionic compounds. These compounds could include ethoxylated fatty esters, alcohols, and alkylamines. (Schindler & Hauser, 2004) The typical structure of a non-ionic antistat is shown below in Figure 2.4.



**Figure 2.4: Non-ionic antistat structure** (Schindler & Hauser, 2004)

These structures are advantageous because of their ability to absorb water. As mentioned earlier, one mechanism for reducing static charge is by dissipation through a conductive material. Non-ionic and cationic antistats can be used together for combined antistatic properties. (Schindler & Hauser, 2004) Some commonly used non-ionic antistats are polyethylene oxide and polyethylene glycol.

### **2.3.2 Durable Finishes**

A common method for forming a durable antistat is by the reaction of polyamines with polyglycols to form a hydrophilic network like that shown in Figure 2.5. (Schindler & Hauser, 2004)

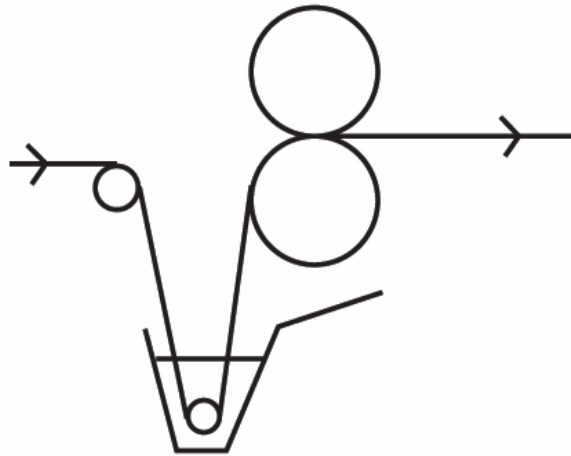




Kroschwitz, 1985) Conductive fibers can be manufactured by incorporating carbon particles in polymer melts before the extrusion process. Hydrophilic comonomers can also be utilized. (Schindler & Hauser, 2004) Metals such as stainless steel, aluminum, and other metals have been used in fiber production. Durable antistatic fabrics are obtained by spinning, knitting or weaving these conductive fibers. The problem with the conductive fibers is all of them are black. The fabrics with black conductive fibers will look off shade after being dyed a light color. This is undesirable for most of the apparel market but is tolerable in industrial fabrics. This technology is also sometimes found in specialized apparel and carpeting. (Schindler & Hauser, 2004)

#### **2.3.4 Application of Chemicals to Fabrics**

Chemical finishing typically takes place after the coloration step of wet processing. (Schindler & Hauser, 2004) Chemical finishing can also take place after the textile fabric has been made into a garment. The chemical finish can be applied in a few different methods. If the chemical has a high affinity for the textile material, the finish can be applied through exhaustion in a dye machine such as a dye beck or dye jet. (Schindler & Hauser, 2004) Finishes that do not have such an affinity for the textile material are applied by immersing the fabric into a bath of the chemical solution or mechanically applied. (Schindler & Hauser, 2004) One of the most common methods of applying chemical finishes is the pad-dry-cure process. The padding process is shown in Figure 2.6 below.



**Figure 2.6: Pad application** (Horrocks, Anand, & NetLibrary, 2000)

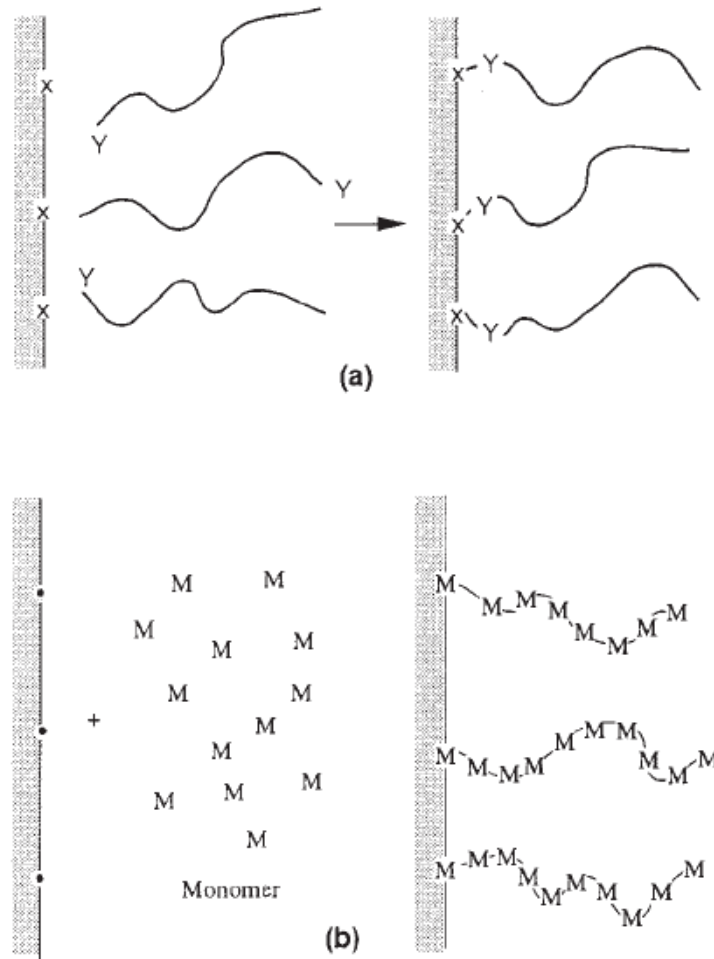
As displayed in Figure 2.6, the pad application consists of rollers to route the fabric through the solution and then between two rollers that are pressed against each other to reduce the amount of solution on the fabric. Removing the excess solution aids in reducing the cost of drying the fabric by decreasing the amount of time it takes for it to dry and also reducing the water consumption. The concentration of the solution can be adjusted so that the same percentage of chemical ends up on the fabric. The pad dry cure process is continuous as the fabric is directly dried and cured. In most cases, an oven is used to dry and cure the fabric within one process.

## ***2.4 Modification of Textile Surfaces by Grafting***

Grafting is an economical surface treatment that can be used to impart many different properties to a material. Surface grafting of textiles is a relatively recent technology that allows several ways to alter the surface of textile materials. Two methods for grafting to

surfaces include direct coupling of polymers and graft polymerization of monomers.

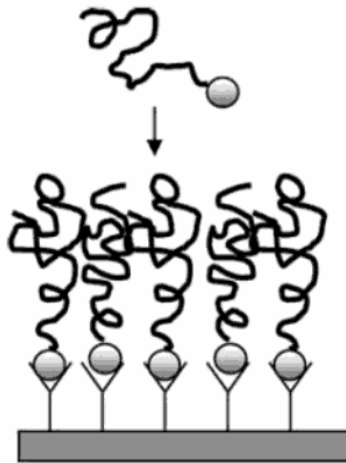
(Uyama, Kato, & Ikada, 1998) An illustration of each method is shown below in Figure 2.7.



**Figure 2.7: a) Direct coupling of polymers to the surface, b) Graft polymerization of monomers (Uyama et al., 1998)**

Chemical coupling reaction can take place if the surface to be modified has reactive groups to attach to. (Uyama et al., 1998)(Bhattacharya, Rawlins, & Ray, 2009) There are four overall methods to conduct surface grafting. The methods consist of 1) Plasma-induced

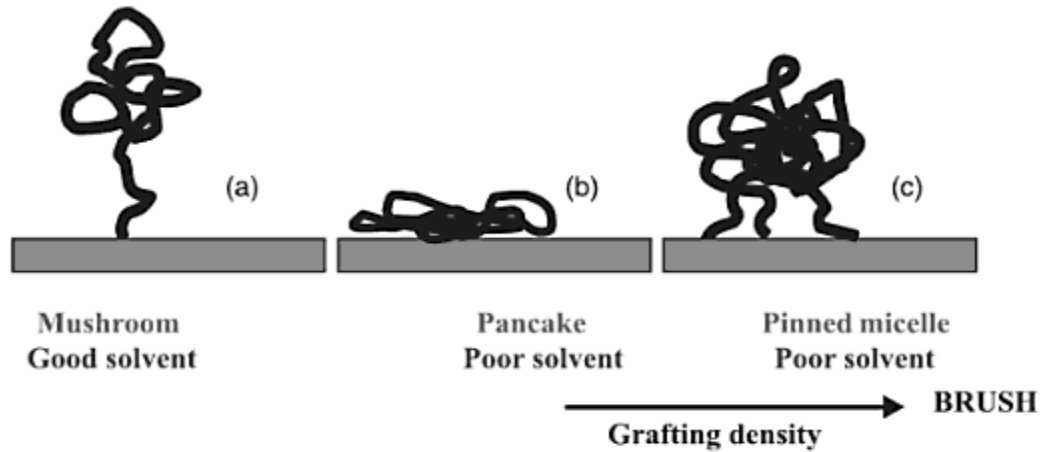
Grafting, 2) Radiation Induced Grafting, 3) Light-induced Grafting, and 4) Chemical Graft Polymerization. (Wei & Textile Institute, 2009) These methods are utilized to create free radical sites on the surface. Vinyl monomers in the grafting solution are subjected to copolymerization reactions with the free radical sites on the surface which serve as initiators. Grafts are bound to the structure making their properties durable. Some advantages of grafting include: 1) Capable of polymer chains with high density, 2) Localization of the polymer chain at the surface, 3) Durability of the layers, and 4) Capable of several different polymers. (Stamm, 2008) If high grafting density is reached, polymer brushes will be created. Figure 2.8 shows a representation of polymer chains forming brushes.



**Figure 2.8: Polymer chains creating brushes** (Stamm, 2008)

If diluted, polymer chains can appear in the mushroom form or pancake form depending on the solvent. If the interaction of the polymer chain is greater with the solvent than with the surface, the mushroom form is generated as shown in Figure 2.9a. If the

interaction of the polymer chain is greater with the surface than with the solvent, the pancake form is generated as shown in Figure 2.9b. If semi-diluted, polymer chains can interact with neighboring grafts by extending from the surface in a good solvent or by forming a pinned micelle in poor solvents as illustrated in Figure 2.9c. (Stamm, 2008)



**Figure 2.9:** a) Diluted good solvent, b) Diluted poor solvent, c) Semi-diluted poor solvent (Stamm, 2008)

As the grafting density increases, brushes are formed as previously represented in Figure 2.8. Grafting on surfaces can take place in two ways; “grafting to” and “grafting from” the surface. Both methods require reactive groups on the surface of the substrate. (Stamm, 2008)

“Grafting to” is when the polymer chains are grafted to the substrate. The polymer reacts with the functional groups on the surface to form chains on the surface. With this method, the amount of polymer that can be attached to the surface is limited. (Stamm, 2008) A major advantage of the “grafting to” method is the surface polymer can be characterized

before attaching it to the surface. (Tobiesen & Michielsen, 2002) This advantage alone makes it favorable in a continuous manufacturing operation where processing time is important.

“Grafting from” is when polymerization takes place from the surface. Unlike the “grafting to” method, monomers can easily penetrate through existing layers to form additional grafting. (Stamm, 2008) A major disadvantage to the “grafting from” method is polymerization times are often long. (Tobiesen & Michielsen, 2002) It also is almost impossible to determine the molecular weight of the polymer. (Tobiesen & Michielsen, 2002) The chemicals used for initiation or catalysts in the copolymerization of monomers can create hazardous waste. (Wei & Textile Institute, 2009) Another disadvantage is the modification of the substrate is usually not only on the surface. (Wei & Textile Institute, 2009)

#### **2.4.1 Plasma-Induced Grafting**

Plasma treatment is a clean, dry, and environmentally friendly technology. Activated species are used to create active sites on the surface. (Wei & Textile Institute, 2009) These active sites can then be used to initiate copolymerization with monomers. (Wei & Textile Institute, 2009) Plasma treatment is performed by applying a voltage across a space that is filled with a gas. The gas is then broken down and begins to conduct electricity. (Sarma, 2009) This broken down gas is considered to be the fourth state of matter after solid, liquid, and gas. (Shishoo & Textile Institute, 2007) Treatment with plasma can be used to impart dehydrogenation, unsaturated bond formation, trapped stable free radicals formation,

generation of polar groups, and increased surface roughness. (Liu, Xiong, & Lu, 2006) In experiments performed by Yan-Chun Liu et al., it was determined that surface roughness along with an increase in polar groups increased the surface wettability of acrylic fibers dramatically. (Liu et al., 2006) The antistatic properties were then aided by the increased surface wettability. Plasma treatment advantages include eliminating the use of water and low temperatures can be utilized. The low temperatures are possible because of the high concentrations of chemically active species. Some of the disadvantages of plasma treatment include the expense of costly gases and the high initial capital costs. The machinery available for use is limited. (Shishoo & Textile Institute, 2007) There are also doubts of its capability in a manufacturing setting. Plasma treatments can be complicated with various plasma processing types. This technology requires a higher level of knowledge and skilled labor. (Shishoo & Textile Institute, 2007)

## **2.4.2 Radiation-Induced Grafting**

High energy radiation is used for radiation-induced grafting. (Wei & Textile Institute, 2009) Some of the methods for radiation-induced grafting include: simultaneous irradiation and grafting through in-situ formed free radicals, grafting through peroxide groups introduced by pre-irradiation, and grafting initiated by trapped radicals formed by pre-irradiation. (Uyama et al., 1998) An advantage of radiation-induced grafting over chemical grafting is the amount of grafting can be controlled by the irradiation dosage and the irradiation time. (Wei & Textile Institute, 2009) Also, chemical initiators are not required. (Wei & Textile Institute, 2009)

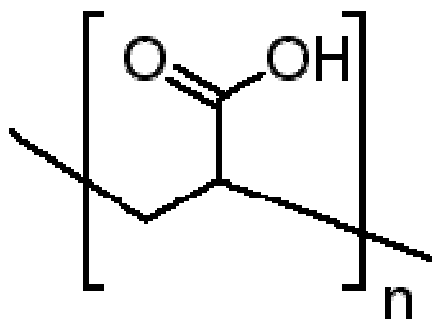
### **2.4.3 Light Induced Grafting**

Ultraviolet radiation-induced surface grafting is a simple method of grafting to surfaces. (Wei & Textile Institute, 2009) Radicals are created within the molecules on the surface via ultraviolet radiation ( $h\nu$ ). (Wei & Textile Institute, 2009) Similar to the other surface modification methods discussed, the radicals are used to initiate copolymerization reactions with the monomers. (Wei & Textile Institute, 2009) Grafting efficiency can be controlled by time, temperature, and concentration of the initiators. (Wei & Textile Institute, 2009) UV curing is becoming more popular because of its ease of use, energy efficiency, short curing times, and lack of water consumption. (Pionteck & Wypych, 2007)

### **2.4.4 Chemical Grafting**

In chemical grafting, radicals are created on the textile substrate. These radicals are used to initiate copolymerization with the monomers being attached. (Wei & Textile Institute, 2009) Fabrics such as polyester and nylon are limited in terms of reactive sites. Tobiesen and Michielsen have discovered that the use of poly(acrylic acid) on nylon 6,6 can increase the number of functional groups on the surface. (Tobiesen & Michielsen, 2002) In their research, poly(acrylic acid) was grafted using an amide linkage to the amine ends of nylon 6,6. 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) was used to activate the amidization. This research also showed that lower amounts of EDC could be used for the same amount of grafting if increased temperatures were also used. The chemical structure of poly(acrylic acid) is shown below in Figure 2.10.





**Figure 2.10: Chemical structure of poly(acrylic acid)** (Sigma-aldrich website, 2009)

Poly(acrylic acid) can be obtained in a variety of molecular weights because of the capability of varying the number of the repeat unit. Tobiesen and Michielsen's research found increasing the molecular weight of poly(acrylic acid) from 5 kD to 250 kD increased the surface coverage on nylon 6,6 by 50 percent. (Tobiesen & Michielsen, 2002) The grafting of poly(acrylic acid) turned each existing graft site on nylon into approximately 1000 graft sites. With successful grafting of poly(acrylic acid) to the surface as shown in Tobiesen and Michielsen's research, the poly(acrylic acid) can then serve as a scaffold for attaching other molecules that can modify the surface properties. (Tobiesen & Michielsen, 2002)

Sherill et al. used this technology to graft antimicrobials to the surface of nylon 6,6. Sherill et al. grafted protoporphyrin IX (PPIX) and zinc protoporphyrin IX to the surface of nylon 6,6 films using an ethylene diamine bridge and a poly(acrylic acid) scaffold. (Sherrill, Michielsen, & Stojiljkovic, 2003) The molecular weight of poly(acrylic acid) used was 450 kD. X-ray photoelectron spectroscopy was used to determine that 57 % of the nylon surface was covered by poly(acrylic acid). Approximately six percent of the carboxylic acid groups

in poly(acrylic acid) were converted to PPIX. (Sherrill et al., 2003) This research showed that antimicrobial chemicals could be permanently covalently bonded to the surface of nylon 6,6.

Chemical grafting presents several advantages such as its ease in application and low cost. Solutions can be created and then a pad/dry/cure process can be used to apply it to the fabric. This process is advantageous in a manufacturing environment because of the high rate at which this can take place.

## ***2.5 Environmental Impact of Antistats***

The potential release of antistatic chemicals to the environment is present during the manufacturing process, distribution, waste disposal, and during use of the product by the final customer. For this reason, it is important to understand their environmental impact. Unfortunately, there is not much information available on the environmental effects of the most used antistats. (Pionteck & Wypych, 2007) Antistats which are released into the environment are subject to physicochemical processes. (Pionteck & Wypych, 2007) These processes may occur in water, soil, and air. Solubility in water, vapor pressure, rate of degradation, and sorption by the environment are all properties of antistats that need to be measured to determine their effects on the environment. (Pionteck & Wypych, 2007)

### **2.5.1 Household Fabric Antistats**

Antistatic chemicals can have an impact on the environment. Antistats are found in household fabric softeners which are designed for improved fabric feel, freshness, and static reduction. (Levinson, 1999) The types of household applied softeners include rinse-added

softeners and dryer sheets. Another form of household application is in laundry detergent. (Ranney, 1976) This method began to become popular in the 1970's to eliminate the step of adding the fabric softener just before the rinse cycle. Rinse-added softeners are the fabric softeners in liquid form that are added in the household washing machine. Washing machines became more advanced and allowed for the fabric softeners to be poured into a tank and the washing machine automatically dispenses them onto the fabric during the rinse cycle. Dryer sheets are the fabric softening sheets that are placed in a tumble dryer. They are in solid form and are activated by the heat from the tumble dryer. Both methods are effective for decreasing static build up on the fabric. However, the chemicals are eventually released to the environment.

In 1983, dryer sheets made up 40 % of fabric softener sales by unit in the United States. (Levinson, 1999) Despite the unit sales of dryer sheets, rinse-added fabric softeners made up 80 % of the total fabric softener actives that were manufactured in the United States. (Levinson, 1999) The difference in the percentage of unit sales and percentage of softener actives is due to the different amounts of softener actives in rinse-added softeners and dryer sheets. Rinse-added softeners typically release five to seven grams of solid per load while dryer sheets only release one to three grams of solid per load. (Levinson, 1999)

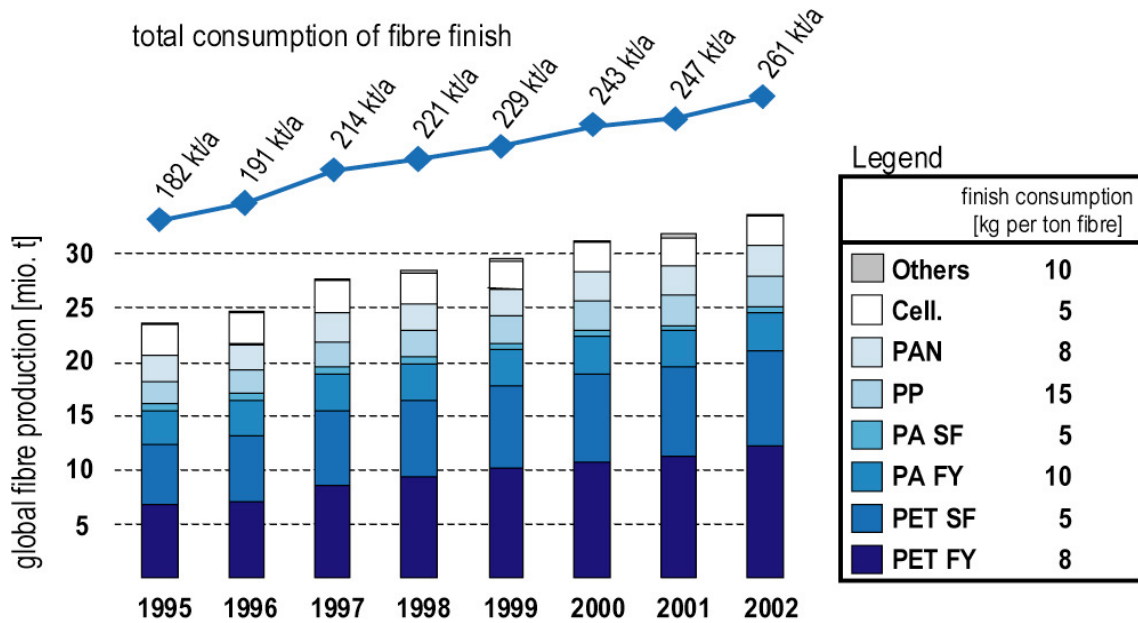
Quaternary ammonium compounds such as ditallowdimethylammonium chloride (DTDMAC) have been thought to be harmful to the environment. Because of this, fabric softeners with this ingredient were voluntarily banned in Europe in 1991. (Alder, Suter, Giger, & Fernandez, 1996) This led to an investigation of the soil in Switzerland by Pilar Fernandez, et al. to determine the presence of DTDMAC. Five different municipal sewage

treatment plants were chosen in Switzerland for samples of dry sludge. The results showed a decrease in mean concentrations of DTDMAC from 3.67 g/kg to 0.96, 0.47, and 0.21 in sludges from years 1991, to 1992, 1993, and 1994 respectively. (Alder et al., 1996) These results show a decrease of 94 % within three years of discontinuation. Smaller amounts of chemicals would find their way into the soil if they were durable on the fabric.

## **2.5.2 Manufacturer Applied Antistats**

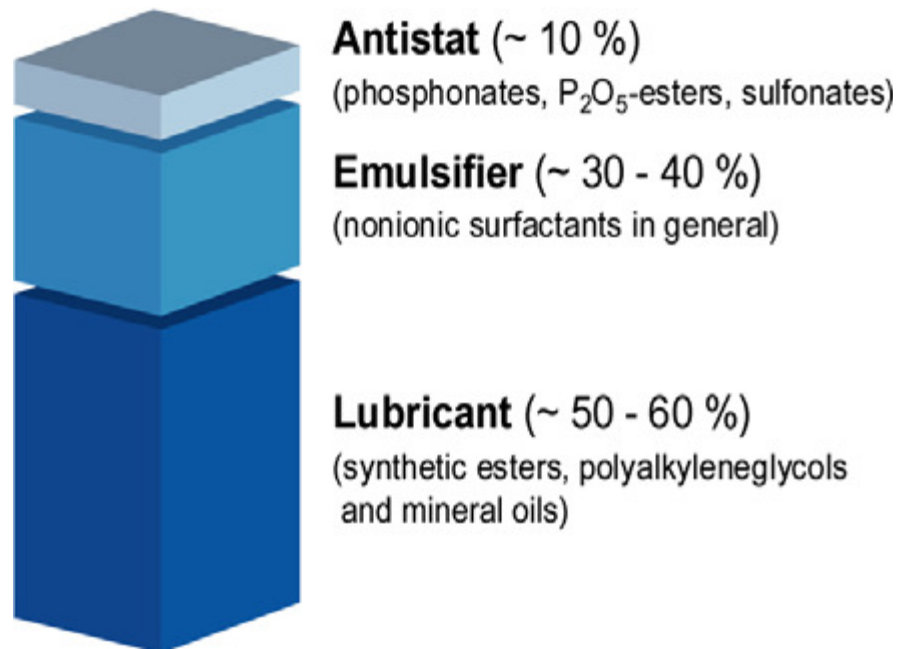
### **2.5.2.1 Antistats in Fiber Finishes**

Surfactants and emulsifiers are used to modify fabric properties for their end use but are also required to manufacture synthetic fibers. (Stock & GmbH, 2004) The manufacture of synthetic fibers has passed the manufacture of cotton fibers. In 2002, synthetic fiber production reached 36.5 million tons. (Stock & GmbH, 2004) Cotton production in 2002 was approximately 83 million bales. (Cotton Inc.) 480 lb. bales amount to approximately 19.9 million tons. Of the manufactured fibers, the fibers that required fiber finish are given in Figure 2.11 below.



**Figure 2.11: Estimated fiber production and consumption of spin finishes from 1995 to 2002** (Stock & GmbH, 2004) Fibers charted are only those that had spin finishes. The consumption values for fiber finish are based on calculations using the amount of fiber production. PET FY: Polyester filament yarn, PET SF: Polyester staple fiber, PA FY: Polyamide filament yarn, PA SF: Polyamide staple fiber, PP: Polypropylene filament, fibers and tapes, PAN: Polyacrylonitrile fiber and filament, Cell: Cellulosic fibers and filament.

Fiber finish consumption reached approximately 260,000 tons in 2002. (Stock & GmbH, 2004) The fiber finish serves to give lubrication to the fibers, fiber/fiber cohesion, and antistatic properties. Synthetic fibers require the use of spin finishes. A typical spin finish consists of antistats, emulsifiers, and lubricants as shown in Figure 2.12 below.



**Figure 2.12: Breakdown of weight fraction of common spin finish systems including antistatic agents, emulsifiers and lubricants.** (Stock & GmbH, 2004) Functional additives were neglected.

## **2.6 Conclusion**

Phosphate esters are the most commonly used antistats. They are also less harmful to the environment than quaternary ammonium compounds. The primary function of these types of antistats is to transfer ions, increasing the conductivity and dissipating the static charge. Nonionic antistats are used to absorb moisture from the air using the moisture to conduct electricity. In this research, polyester fabric is treated with a phosphate ester that is mixed with a carrier polymer. The chemical structures of the carrier polymer and the phosphate ester were selected so that covalent bonding takes place. This approach should allow for permanent attachment. Sulfonic esters were also used in place of the phosphate esters utilizing the same attachment methods. Nonionic antistats were added to determine if synergistic properties were achieved. This research is important to the textile industry

because of the potential for imparting durable antistat properties to polyester fabrics. There is also a potential for using less chemicals, resulting in lower costs and a lower environmental impact.

## **3. Experimental Methods and Procedures**

### ***3.1 Approach of this research***

The approach of this research was to treat 100 % polyester fabrics with phosphate esters and sulfonic esters and also graft these chemicals to the fabrics using poly(acrylic acid). A comparison is made between the effectiveness and durability of these treated fabrics. Poly(acrylic acid) modifies the surface by creating additional reactive sites for the antistatic chemical to covalently bond to. The antistatic chemicals were selected based on their chemical structure. The phosphate ester selected was o-phosphorylethanolamine and the sulfonic ester was taurine. Both of these chemicals contain NH<sub>2</sub> groups or amines, which covalently bond to the CO<sub>2</sub>H groups or carboxylic acids in poly(acrylic acid). The aim was to create a finish for polyester fabrics with advantages of

1. Excellent antistatic properties
2. Excellent durability
3. Easy processing
4. Low cost

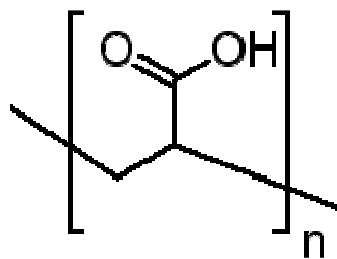
### ***3.2 Experimental Materials***

#### **3.2.1 Poly(acrylic acid)**

The poly(acrylic acid) selected has a molecular weight of 450,000. Poly(acrylic acid) is available in different molecular weights. The molecular weight of 450,000 was used



because some of the most recent research by Tobiesen and Michielsen was with the use of this molecular weight. It was obtained from Sigma-Aldrich® in solid form. (*Sigma-aldrich website*, 2009) The glass transition temperature is 106 °C. Each repeat unit has a molecular weight of 72. The molecular weight of poly(acrylic acid) divided by the molecular weight of the repeat unit (450,000/72) gives 6,250. This value represents the number of reactive sites available. Even though some of the reactive sites may be used for attachment to the fabric, the poly(acrylic acid) allows for increased sites on the surface of the fabric. The chemical structure of poly(acrylic acid) is shown below in Figure 3.1.



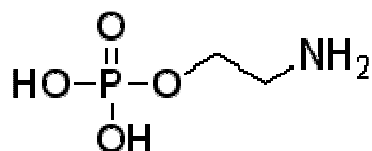
**Figure 3.1: Chemical structure of poly(acrylic acid)**

Poly(acrylic acid) is ideal for grafting because it is a highly functional polymer. It is fairly inexpensive and is water soluble.

### **3.2.2 O-Phosphorylethanolamine**

O-phosphorylethanolamine was obtained from Sigma-Aldrich. (*Sigma-aldrich website*, 2009) O-phosphorylethanolamine was selected because of its basic structure and its amine end. The NH<sub>2</sub> or amine covalently bonds with the carboxylic acid in poly(acrylic acid) to form permanent attachment. Antistats often have structures that are more complex in an

attempt to give the surface of the substrate additional properties. In this research, only the antistatic properties were of interest so the most basic composition was desired. O-phosphorylethanolamine is a phosphate ester with molecular weight of 141.06. The chemical structure is shown below in Figure 3.2.

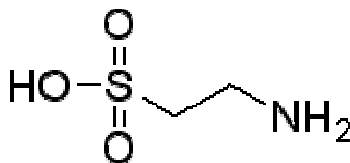


**Figure 3.2: Chemical structure of o-phosphorylethanolamine**

Figure 3.2 represents the structure of the phosphate ester used. The left portion of the structure in Figure 3.2 is the phosphate which aids in ion transfer on the surface. The amine is used for attachment to the poly(acrylic acid) or the surface of the substrate. O-phosphorylethanolamine is somewhat inexpensive and is water soluble.

### **3.2.3 Taurine**

Taurine was obtained from Sigma-Aldrich. (*Sigma-aldrich website*, 2009) Taurine was also selected because of its basic structure and amine end. The taurine covalently bonds with the poly(acrylic acid) similarly to the o-phosphorylethanolamine through the NH<sub>2</sub>. Taurine was selected to compare with the results of the o-phosphorylethanolamine because of its low cost. The structure of taurine is shown below in Figure 3.3.



**Figure 3.3: Chemical structure of taurine**

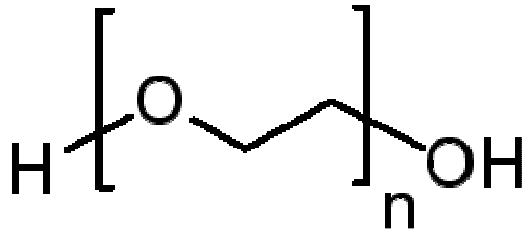
Figure 3.3 represents the structure of the sulfonic ester used. The amine is used for attachment to the poly(acrylic acid) or the surface of the substrate. Taurine is inexpensive and water soluble. It has a molecular weight of 125.15.

### **3.2.4 Sodium Hydroxide**

Sodium hydroxide was obtained from the pilot lab at North Carolina State University. The sodium hydroxide was a 50 % solution. Sodium hydroxide has a molecular weight of 40. It is a base and was used to neutralize the acids in the poly(acrylic acid), o-phosphorylethanolamine, and taurine. The chemical structure is NaOH. Sodium hydroxide is a commonly used chemical and was selected because of its low cost and its availability.

### **3.2.5 Poly(ethylene glycol)**

Poly(ethylene glycol) was obtained from Sigma-Aldrich. (*Sigma-aldrich website*, 2009) Poly(ethylene glycol) is a nonionic antistat. It is available in several molecular weights. A molecular weight of 35,000 was used for this research. The molecular structure of poly(ethylene glycol) is shown below in Figure 3.4.



**Figure 3.4: Chemical structure of poly(ethylene glycol)**

Poly(ethylene glycol) was selected because of its low cost and availability.

### **3.2.6 Fabrics Used**

Style 777 and style 493 were obtained from Testfabrics, Inc. (*Test fabrics, inc.*) The primary fabric used for experimental treatments was style 777. Style 777 is a 100 % spun polyester plain weave construction. The polyester fabric consists of 44 ends per inch in the warp direction and 54 ends per inch in the weft direction, which forms a fabric weight of 126 grams per square meter. Style 493 is a 100 % cotton plain weave construction that was used for comparison. The cotton fabric consists of 60 ends per inch in the warp direction and 60 ends per inch in the weft direction, which forms a fabric weight of 151 grams per square meter. The aim of this research was to match the antistatic properties of 100 % cotton. These fabrics were selected based on their similarity in end count and weight.

### ***3.3 Experimental Procedures***

#### **3.3.2 Fabric Preparation**

##### **3.3.2.1 As Received**

Polyester and cotton were not subjected to any cleaning or treatments.

##### **3.3.2.2 Cleaned with Methanol**

Methanol was used to clean the samples before treatment and testing. Other methods of cleaning could be used. 400 mL jars were filled with approximately 300 mL of methanol. Polyester and cotton fabrics were cut into 15 X 15 cm squares and placed into the jars. Each jar contained no more than six square samples to avoid overcrowding in the methanol solution. The lids were placed on the jars to avoid contamination. The jars were placed in an ultrasonic bath for 30 minutes at room temperature. The methanol was drained from the jars followed by one rinse with deionized water. After the water rinse, the jars were filled with approximately 300 mL of deionized water, lids were replaced, and jars placed in the ultrasonic for an additional 30 minutes. The samples were then rinsed with deionized water one last time before hung to air dry overnight.

##### **3.3.3 Control Samples**

Control samples consisted of 100 % polyester and 100 % cotton samples that were cleaned using methanol as described in 3.3.2.2.

### 3.3.4 Concentration Calculations

#### 3.3.4.1 Weight of Poly(acrylic acid) and Poly(ethylene glycol)

The amount of poly(acrylic acid) and polyethylene glycol was calculated based on the weight of the fabric. For example: to achieve one percent add on with a 100 gram piece of fabric, one gram of chemical would be applied. The chemicals were padded onto the fabrics. In order to determine the amount of chemical that ends up on the fabric, the wet pick-up (WPU) had to be determined. WPU is the percentage increase in weight of the sample after being padded and can be calculated as shown in Equation 3.1 below.

$$WPU = \frac{WetWeight - DryWeight}{DryWeight}$$

**Equation 3.1: Calculating wet pick-up from weight of the fabric wet and dry**

Where:

WPU = Wet pick-up

WetWeight = Weight of wet fabric (grams)

DryWeight = Weight of dry fabric (grams)

Style 777 100 % polyester fabric had a WPU of 86.6 %. This value remained constant throughout experimentation and was used for all concentration calculations for style 777 100 % polyester fabric treatments.

After padding on the solution, the water will dry leaving the chemical on the fabric. The percent concentration of the chemical can then be calculated as shown in Equation 3.2.

$$\%Concentration = (100) \frac{\%AddOn}{WPU}$$

**Equation 3.2: Calculating concentration from add on and wet pick-up**

Where:

$\%Concentration$  = Percent concentration of chemical being applied (%)

$\%AddOn$  = Percent add on to the fabric (%)

WPU = Wet pick-up

The value obtained from this equation is the weight of solid chemical needed for every 100 grams of solution to be padded on. All solutions were created so that the weight of the chemical in the solution was included in the total weight of the solution. For example, one gram of chemical in a 100 milliliter solution would contain 99 grams of water and one gram of chemicals.

### **3.3.4.2 Weight of O-phosphorylethanolamine, Taurine, and Sodium**

#### **Hydroxide**

Any other chemicals that were used in the experiments were based on the weight of poly(acrylic acid) used. These chemicals include o-phosphorylethanolamine, taurine, and sodium hydroxide. Each repeat unit of poly(acrylic acid) has a molecular weight of 72. The number of moles of the repeat unit of poly(acrylic acid) can be calculated using Equation 3.3 below.

$$N = \frac{Wt.PAA}{72}$$

**Equation 3.3: Calculating moles of repeat unit of poly(acrylic acid) from the weight**

Where:

N = Moles of repeat unit poly(acrylic acid)

Wt.PAA = Weight of poly(acrylic acid) (grams)

The weight of additional chemical is then calculated using the Equation 3.4 below.

$$Wt.Chem = MW.Chem \times N$$

**Equation 3.4: Calculating the weight of a chemical from its molecular weight and number of moles poly(acrylic acid)**

Where:

Wt.Chem = Weight of the additional chemical (grams)

MW.Chem = Molecular weight of the additional chemical

N = Moles of repeat unit poly(acrylic acid)

In the case of sodium hydroxide, 50 % solution was used. The value obtained from Equation 3.4 is doubled. These equations are valid for obtaining a 1:1 molar ratio. The amount of chemical required for other molar ratios can be determined by multiplying the molar ratio by the value obtained from Equation 3.4. If a molar ratio of 2:1 of o-phosphorylethanolamine to repeat unit poly(acrylic acid) is desired, multiply by the value by two and so on.



### 3.3.5 Treatment Process

#### 3.3.5.1 Pad/Dry/Cure

100 % polyester samples of style 777 that were previously cleaned with methanol as described in 3.3.2.2 were soaked in the chemical solution for 30 minutes. The samples were then padded using a laboratory scale pad made by H.W. Butterworth & Sons Co. as shown in Figure 3.5 below.



**Figure 3.5: H.W. Butterworth & Sons Co. laboratory scale pad**

The samples were directly dried and cured in a Werner Mathis AG LTF #134489 oven for one minute at 175 °C. The oven used is shown below in Figure 3.6.



**Figure 3.6: Werner Mathis AG LTF #134489 laboratory scale oven**

### **3.3.5.2 Pad/Dry**

Some samples were padded with chemicals after the initial pad/dry/cure process in section 3.3.5.1. For these samples, the same process was followed as the pad/dry/cure process except the samples were hung to dry overnight after padding rather than dried and cured in an oven.

### **3.3.6 Durability**

#### **3.3.6.1 Deionized water rinses**

For initial assessment of the durability of finishes, the samples were subjected to deionized water rinses. A 1000 mL beaker was filled with approximately 700 mL of

deionized water. The three treated samples for the trial being rinsed were placed into the beaker and allowed to soak in water for approximately five seconds. The samples were then all removed simultaneously from the beaker rotating the samples approximately two revolutions before fully exiting the beaker of water. The samples were held above the beaker long enough for the excess water to run off. The samples were dipped back into the water while being rotated two revolutions before removed again. This was repeated two additional times for a total of four submersions into the water. After this process the samples were hung to dry overnight. This series of steps is referred to as one deionized water rinse. In most cases, the samples received a total of three deionized water rinses. The preceding procedure was followed a total of three times allowing the samples to dry between each deionized water rinse.

### **3.3.6.2 Accelerated Laundering**

For the final assessment of the finish, the durability was tested by subjecting samples to accelerated launderings. The procedures of AATCC test method 61-2007 was followed using Test No. 2A. The test method calls for samples with measurements of 50 X 150 mm. The resistivity testing being performed after the launderings requires samples of at least 150 X 150 mm. Because of this, 150 X 150 mm samples were utilized instead. This was the only change made to the procedures of the test method. The test method is designed for evaluating colorfastness so the evaluation portion of the test method was not followed. The evaluation method of AATCC test method 76-2005 was followed to test resistivity of the

samples. A LEF Launder-Ometer® by Atlas Textile Test Instruments was used to perform the launderings.

The launder-ometer was preheated to 49 °C. A 150 mL solution of deionized water and 0.15 % 1993 AATCC standard referenced detergent WOB was poured into 90 X 200 mm canisters. 50 balls were placed in the solution within each canister. The canisters were then sealed using a sheet of teflon between the rubber gasket and the canister to prevent contamination of the fabric. The canisters were then clamped. To preheat the solutions within the canisters, the canisters were placed in the previously preheated launder-ometer and ran for two minutes. After the solution was preheated, the canister was opened and one crumpled sample was placed in each canister. The canisters were sealed and the launder-ometer was run at 40 revolutions per minute with the temperature maintained at 49 °C for 45 minutes. After the 40 minute cycle, the samples were rinsed. The rinsing was performed in 1000 mL beakers filled with approximately 700 mL of deionized water that was previously heated to 40 °C on a hot plate. The sample was placed in the beaker with occasional stirring for one minute. After a minute the water was poured out and replaced with another 700 mL of deionized water at 40 °C. This was repeated for a total of three rinses. The samples were then hung to air dry.

### **3.3.7 Conditioning Samples**

The samples were hung in a Scienceware® economy glove box with dimensions of 91W X 51D X 66H cm. The box was sealed for conditioning as shown below in Figure 3.7.



**Figure 3.7: Scienceware® economy glove box**

The relative humidity was controlled using different salt solutions and also by using compressed air. A list of the salts that were used is given below in Table 3.1.

**Table 3.1: Salts used for conditioning**

<b>Type of Salt</b>	<b>Approximate Relative Humidity Obtained (%)</b>
Sodium Chloride	76
Magnesium Nitrate	58
Potassium Carbonate	46
Magnesium Chloride	37
Calcium Bromide Hydrate	25

The salt solution was placed in a small 300 mL dish with approximately 50 grams of salt and enough deionized water to create a slushy mixture. Salts used for increased relative humidity values required additional amounts of water. The salt solution was placed on a hot plate with a magnetic stirrer. The stirring speed was approximately 600 rpm with no heat. A small fan was used to circulate the air within the glove box. For relative humidity values lower than that achievable from the salts used, a small amount of compressed air was blown through the environmental box to obtain a relative humidity of approximately 12 %.

### ***3.4 Experimental Testing Methods***

#### **3.4.1 Resistivity Testing**

##### **3.4.1.1 Resistivity Meter and Set Up**

The analysis of antistatic properties of fabrics was based on the resistivity of the fabrics. TRek model 152 resistivity meter and probe 152-CR were obtained from TRek Inc through their website: <http://www.trekinc.com>. A pictures of the probe used is shown below in Figure 3.8.



**Figure 3.8: TRek model 152-CR probe**

This meter conforms to ANSI/EOS/ESD S.11.11 standard for testing materials. The probe consists of two electrodes that electricity flows between. The outer ring has an inner diameter of  $57.15 \pm 0.64$  mm with a thickness of  $3.18 \pm 0.13$  mm. The inner disc has a diameter of  $30.48 \pm 0.64$  mm. The probe weighs 2.27 kilograms. The meter measures the amount of resistance between the disc and ring in Ohms and automatically calculates and displays the resistivity in Ohms/Square based on the size of the rings. The resistivity is calculated using Equation 3.5 below.

$$\rho_s = \frac{2\pi R_s}{\ln \frac{D_2}{D_1}}$$

**Equation 3.5: Calculating surface resistivity from measured resistance and ring diameters**

Where:

$\rho_s$  = Surface resistivity in (ohms/square)

$R_s$  = Measured resistance (ohms)

$D_2$  = Diameter of disc in (cm)

$D_1$  = Diameter of ring in (cm)

The meter has two voltages to choose between. The 10V setting allows for testing resistivity between  $10^4$  and  $10^{11}$  Ohms/Sq. while the 100V setting allows for testing resistivity between  $10^6$  and  $10^{14}$  Ohms/Sq. The set up of the measurement assembly consisted of a sheet of teflon that served as an insulator placed on top of a sheet of aluminum foil that served as a conductor. The fabric sample was placed on top of the insulating sheet of teflon with the probe set on top of the fabric sample. A ground wire was attached to the conductive sheet of aluminum foil and then connected to the meter. The meter set up is shown below in Figure 3.9.





**Figure 3.93.7: TRek model 152 resistivity meter and TRek model 152-CR probe set up**

The probe, teflon surface, and gloves were cleaned with isopropyl alcohol before the glove box was sealed for conditioning. Often times several trials were conditioned at the same time. This did not allow for cleaning of the probe between testing of each trial as the glove box would have to be opened. Opening the glove box would alter the conditions within the box. However, the surfaces were cleaned with isopropyl alcohol when the glove box had to be opened for changing out the salt solutions and samples.

### **3.4.1.2 Resistivity Testing Procedures**

AATCC test method 76-2005 was used for resistivity testing. The resistivity values measured in the experiments performed were greater than  $10^6$  Ohms/Sq. Therefore, the 100V setting was used on the TRek model 152 resistivity meter. As mentioned previously,

the 100V setting allows for resistivity measurements between  $10^6$  and  $10^{14}$  Ohms/Sq. The probe was placed on the fabric sample so that each edge was at least one inch from the outer diameter of the probe. This was done to eliminate any edge effects and/or contamination that could have occurred during curing or hanging the samples. The probe was allowed to remain on the sample for one minute and then the resistivity value was recorded. All three samples of each trial were tested two times on each side. It would have been sufficient to measure the same side of each sample every time but it is possible that marking the samples could contaminate them during water rinses. The three samples within a trial were distinguished by the number of corners cut off of the samples. Each trial was distinguished by labeling where the samples were hung.

### **3.4.2 pH Testing**

The pH testing of fabrics was based on the pH of the extract from the fabric. AATCC test method 81-2006 was followed. 250 mL of deionized water was measured into a 400 mL beaker. The water was brought to a moderate boil on a hot plate. The water was allowed to boil for 10 minutes. After 10 minutes of boiling, 10 grams of the fabric sample was submerged into the water and covered with a watch glass. The covered solution was allowed to boil for 10 minutes. After 10 minutes the covered sample and solution was allowed to cool to room temperature. Once cooled, the samples were removed from the solution allowing the excess water to run into the solution. The pH of the extract was measured using an accumet® BASIC AB15 pH Meter by Fisher Scientific.

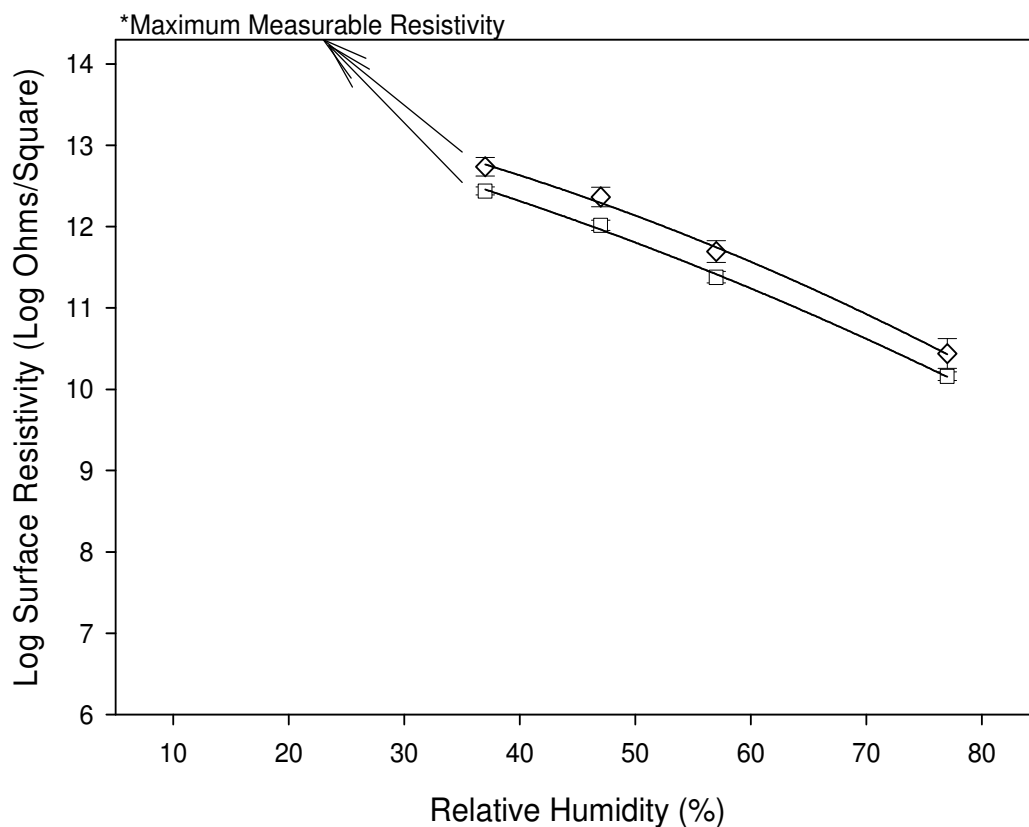
## **4. Results and Discussion**

### ***4.1 Cotton and Polyester Fabrics***

With the continuous increase in production of synthetic fibers, it is important to improve the problem with static electricity that is found in these fibers. Polyester was selected for this research because of its poor antistatic properties and high production. The aim was to treat polyester fabric to obtain the equivalent of the natural antistatic properties of cotton.

In order to have a base line for the resistivity of fabrics, cotton and polyester fabrics were tested as received and cleaned with methanol. The resistivity values at six relative humidity values are given in Figure 4.1 below.

## Cotton Fabric



**Figure 4.1: Log surface resistivity of cotton in relation to RH** ◇ 100% Cotton fabric cleaned with methanol, □ Cotton fabric as received. Polyester samples were out of range at every humidity value tested. Error bars are the standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.

It can be determined from Figure 4.1 that cotton fabrics have better antistatic properties than polyester fabrics. The cotton sample cleaned with methanol yielded a higher resistivity than the cotton samples as received. The cotton as received may contain some oils or waxes still present from previous manufacturing processes. All of the cotton samples follow the same trend as the relative humidity decreases. The polyester samples as received

and after being cleaned with methanol exceeded the maximum measurable resistivity of the resistivity meter ( $2 \times 10^{14}$  Ohms/Square) throughout the entire range of relative humidity values tested. Because of the poor antistatic properties of polyester, several experiments were performed with antistatic finishes on polyester fabrics.

## 4.2 Chemical Selection

Based on the literature review in Chapter two, it was decided to begin with concentrations of one percent OWF poly(acrylic acid) and one percent OWF poly(ethylene glycol). O-phosphorylethanolamine, taurine, and sodium hydroxide were used with a 1:1 molar ratio based on the repeat unit of poly(acrylic acid). The amounts of each chemical based on the weight of the fabric and the grams per liter of solution are given in Table 4.1 below.

**Table 4.1: Amounts of chemicals used in chemical selection**

Chemical	% OWF	grams/liter
1% Poly(acrylic acid)	1.00	11.55
1% Poly(ethylene glycol)	1.00	11.55
1:1 Sodium Hydroxide	0.55	6.40
1:1 Taurine	1.74	20.09
1:1 O-phosphorylethanolamine	1.96	22.63

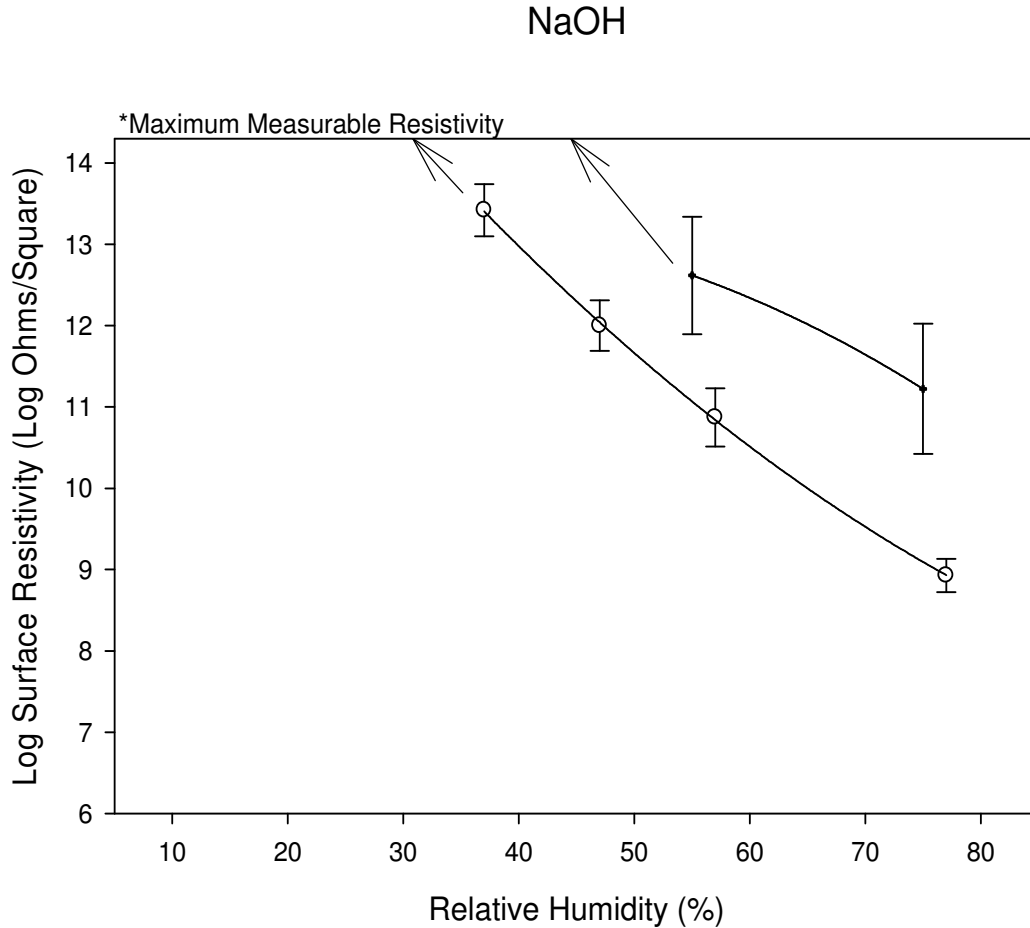
Within this section, the amounts of each chemical as listed in Table 4.1, were kept constant throughout each experiment. A list of the chemical combinations is listed below in Table 4.2.

**Table 4.2: Combinations of chemicals used for antistatic treatment in chemical selection Poly(acrylic acid) (PAA), sodium hydroxide (NaOH), taurine, o-phosphorylethanolamine (PEA), and poly(ethylene glycol) (PEG).**

Sample	PAA	NaOH	Taurine	PEA	PEG
1		X			
2	X				
3	X	X			
4			X		
5		X	X		
6	X		X		
7	X	X	X		
8				X	
9		X		X	
10	X			X	
11	X	X		X	
12	X	X		X	X

### **4.2.1 Sodium Hydroxide**

Sodium hydroxide is a base used throughout the research to neutralize the acids of the chemicals applied. It was important to determine the effects of sodium hydroxide applied to polyester fabrics without any other chemicals. Sodium hydroxide was pad applied to 100 % polyester fabric. The fabric was then dried/cured at 175 °C for one minute. To determine the durability to rinsing, the samples were tested after treatment and after each of three deionized water rinses. The resistivity values are given below in Figure 4.2.



**Figure 4.2: Log surface resistivity of polyester fabric treated with NaOH in relation to RH after rinsing with deionized water** ○ zero times, ● one time, ▼ two times, and ■ three times. 6.40 g/L sodium hydroxide (NaOH) padded on polyester fabric and cured at 175 °C for one minute. Error bars are +/- one standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.

From analysis of the data given in Figure 4.2, it can be determined that sodium hydroxide applied to the fabric alone is not sufficient as an antistat. Testing of the fabrics before any deionized water rinses only yielded satisfactory resistivity values above 50 % relative humidity. The testing of samples after deionized water rinses proved that the

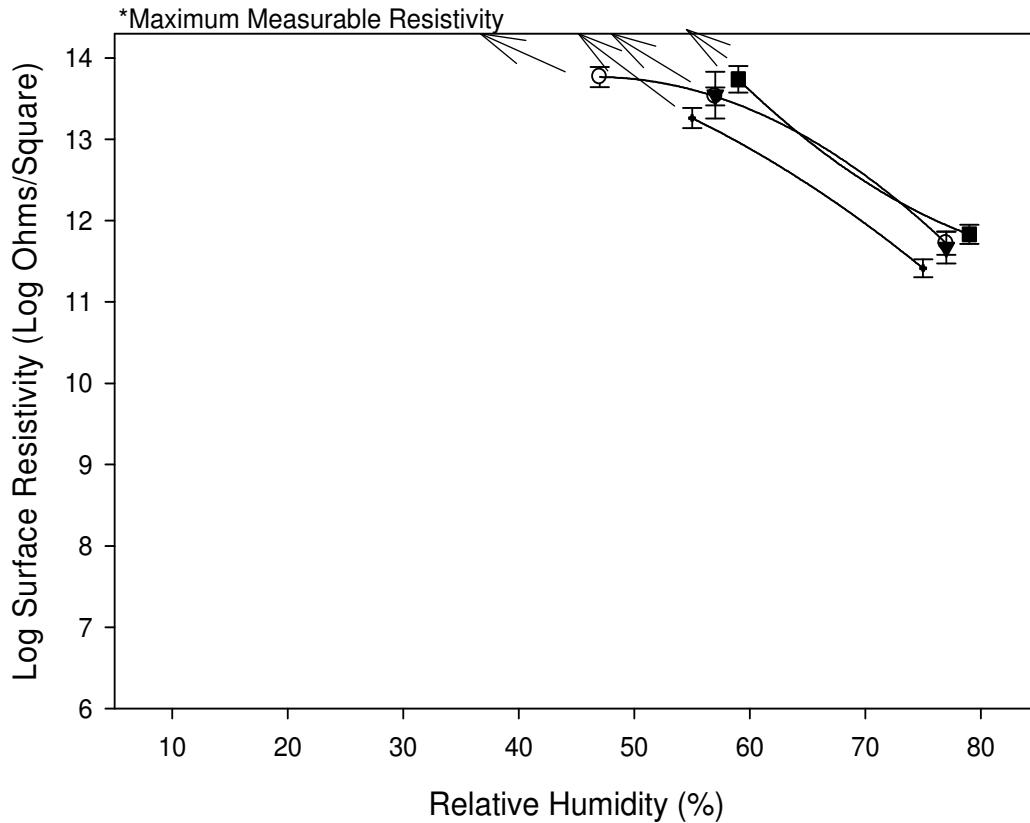


treatment was not durable. Even after the first deionized water rinse, the resistivity values increased by up to two orders of magnitude. By the second deionized water rinse, the resistivity values for the highest humidity tested was beyond the maximum measurable value of the resistivity meter. Sodium hydroxide can be irritating to the skin and therefore would require at least one water rinse before finding its way to the customer, and therefore sodium hydroxide alone is not a sufficient treatment as an antistat.

#### **4.2.2 Poly(acrylic acid)**

Based on the literature review in Chapter two, poly(acrylic acid) has successfully been used to graft antimicrobials to the surface of fabrics. Within this research, poly(acrylic acid) is used to graft antistatic chemicals to fabric. It was important to determine how poly(acrylic acid) would perform as an antistat by itself. Poly(acrylic acid) was applied to polyester fabric followed by drying and curing at 175 °C for one minute. Durability testing was performed by subjecting the samples to deionized water rinses and testing surface resistivity after each rinse. The results of the resistivity testing are given below in Figure 4.3.

## PAA



**Figure 4.3: Log surface resistivity of polyester fabric treated with PAA in relation to RH after rinsing with deionized water** ○ zero times, ● one time, ▼ two times, and ■ three times. 11.55 g/L poly(acrylic acid) (PAA) padded on polyester fabric and cured at 175 °C for one minute. Error bars are +/- one standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.

The data displayed in Figure 4.3 shows that poly(acrylic acid) gives some antistatic properties when applied to the fabric by itself. The use of poly(acrylic acid) alone does not provide sufficient antistatic properties. The durability testing did prove that poly(acrylic acid) is a durable to deionized water rinses. Testing of the samples after the first deionized

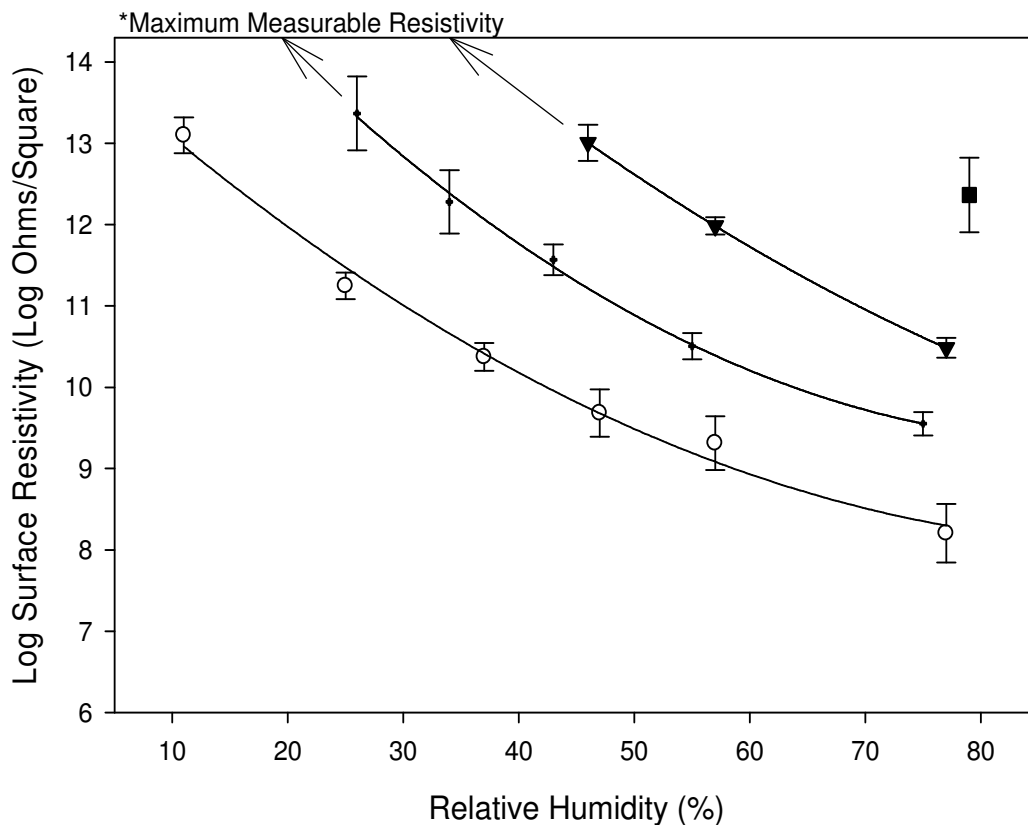
water rinse gave lower resistivity values than that of the treated fabric without any water rinses. Improvement of antistatic properties after deionized water rinses is not anticipated with any treatments as the rinses are expected to remove any excess chemical or chemicals that are not attached to the surface. This could be due to experimental error. Another possible reason for these results is related to how the poly(acrylic acid) is attaching to the fabric. The attachment of the poly(acrylic acid) to polyester is not fully understood. There are no functional groups on the polyester that would allow the poly(acrylic acid) to attach. The attachment could be mechanical. In this case, the poly(acrylic acid) is embedded into the fabric and mechanically held in place. The first deionized water rinse could have brought the poly(acrylic acid) closer to the surface and therefore gave better surface resistivity values. Another potential reason is moisture hysteresis. Moisture hysteresis is a phenomenon that has to do with the equilibrium of conditioning samples. Samples that were soaked in water and left to air dry would have more moisture content after conditioning than samples that were dried in an oven and then conditioned. This is the same difference in the samples being tested. The samples tested after treatment were dried and cured in an oven and conditioned in the glove box. This process completely dried out the samples before conditioning and therefore less moisture is absorbed in the samples after conditioning. The deionized water rinsed samples were saturated in water and air dried before conditioning in the glove box. Air drying only dried the samples to a level of moisture just above the level in the air. Conditioning the samples at the same relative humidity yields an increased amount of moisture content in the sample. Another potential reason for improving resistivity after a deionized rinse has to do with the stiffness of the fabric. Add on levels of one percent OWF

provided a stiff fabric. The stiff fabric could have some unevenness that allows charge to dissipate more easily. During handling of these samples, the pathways can be obstructed. The deionized water rinse could serve to level out the finish evenly and therefore correct some of the broken passageways. Testing of the samples after the second deionized water rinse gave resistivity values similar to that of the values before any rinses. The third deionized water rinse caused a slight increase in resistivity. The results prove that poly(acrylic acid) is durable to deionized water rinses and provides some antistatic properties. The antistatic properties of poly(acrylic acid) alone are not sufficient but are durable.

#### **4.2.3 Poly(acrylic acid) and Sodium Hydroxide**

As mentioned previously, sodium hydroxide is used to neutralize the acids within the chemicals applied to aid in the mobility of ions on the surface of the fabric. Results for resistivity of both sodium hydroxide and poly(acrylic acid) were both previously analyzed as separate finishes. In order to test the effects of sodium hydroxide used with poly(acrylic acid), the same amounts of poly(acrylic acid) and sodium hydroxide previously applied to polyester fabric were pad applied as a homogeneous solution to polyester fabric. The samples were then dried and cured at 175 °C for one minute. Testing of the samples for resistivity was performed at six relative humidity values. The testing was performed after the treatment and after each of three deionized water rinses to determine the durability. The resistivity values are given below in Figure 4.4.

## PAA and NaOH



**Figure 4.4: Log surface resistivity of polyester fabric treated with PAA and NaOH in relation to RH after rinsing with deionized water** ○ zero times, ● one time, ▼ two times, and ■ three times. 11.55 g/L poly(acrylic acid) (PAA) and 6.40 g/L sodium hydroxide (NaOH) padded on polyester fabric and cured at 175 °C for one minute. Error bars are +/- one standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.

From the resistivity values given in Figure 4.4, it can be determined that poly(acrylic acid) and sodium hydroxide used as a treatment for polyester fabric provides significant antistatic properties before any deionized water rinses. The deionized water rinses proved the finish lacks the desired durability. Each deionized water rinse increased the resistivity by over one order of magnitude. By the third deionized water rinse, most of the antistatic

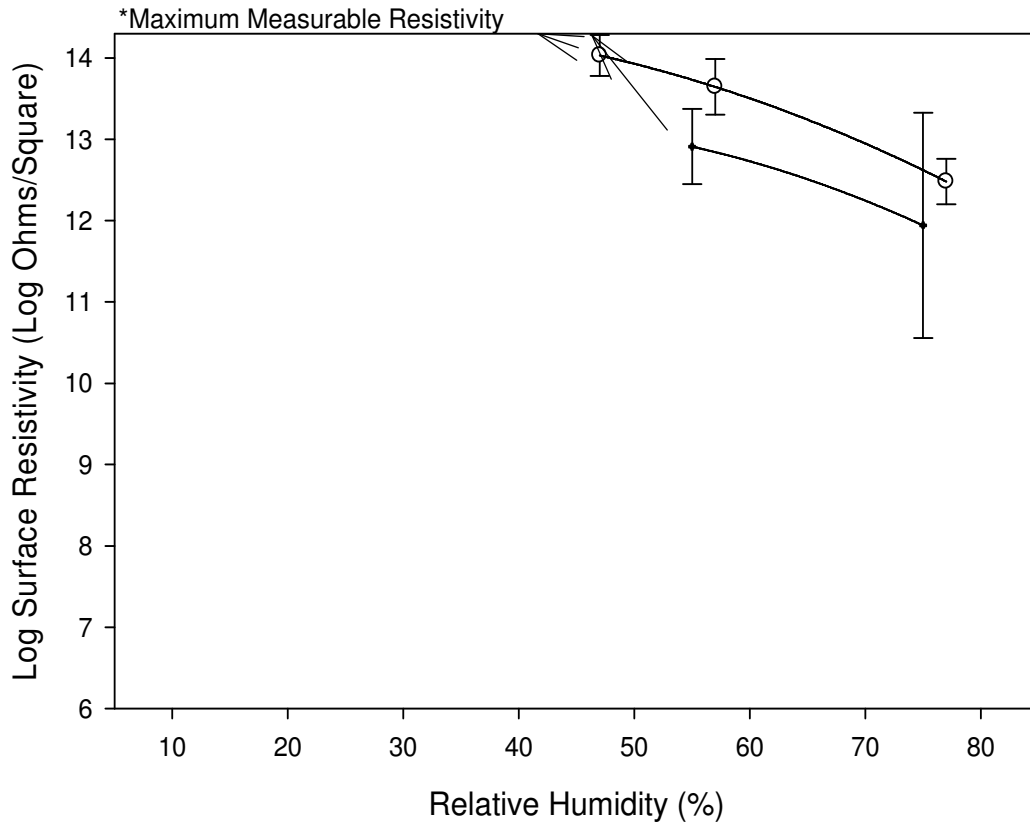
properties were diminished. After the third deionized water rinse, the only measurement of resistivity within the range of the resistivity meter was that measured at the highest relative humidity tested.

#### **4.2.4 Sulfonic Ester**

##### **4.2.4.1 Taurine**

It is well known that phosphate esters provide antistatic properties. To determine if inexpensive sulfonic esters can also provide antistatic properties, polyester fabrics were treated with taurine. Taurine was pad applied to polyester fabric followed by a dry and cure process at 175 °C for one minute. The resistivity values after the treatment and after each of three deionized water rinses are given in Figure 4.5 below.

## Taurine



**Figure 4.5: Log surface resistivity of polyester fabric treated with taurine in relation to RH after rinsing with deionized water** ○ zero times, ● one time, ▼ two times, and ■ three times. 20.09 g/L taurine padded on polyester fabric and cured at 175 °C for one minute. Error bars are +/- one standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.

From the data given in Figure 4.5, it can be determined that taurine provides some antistatic properties at humidity values above 45 %. The sample with one deionized water rinse has improved antistatic properties over the sample without any rinses. This is similar to the results from testing of fabric treated with poly(acrylic acid) in section 4.2.2. The reasons for this are the same as explained within section 4.2.2. In short, the potential reasons

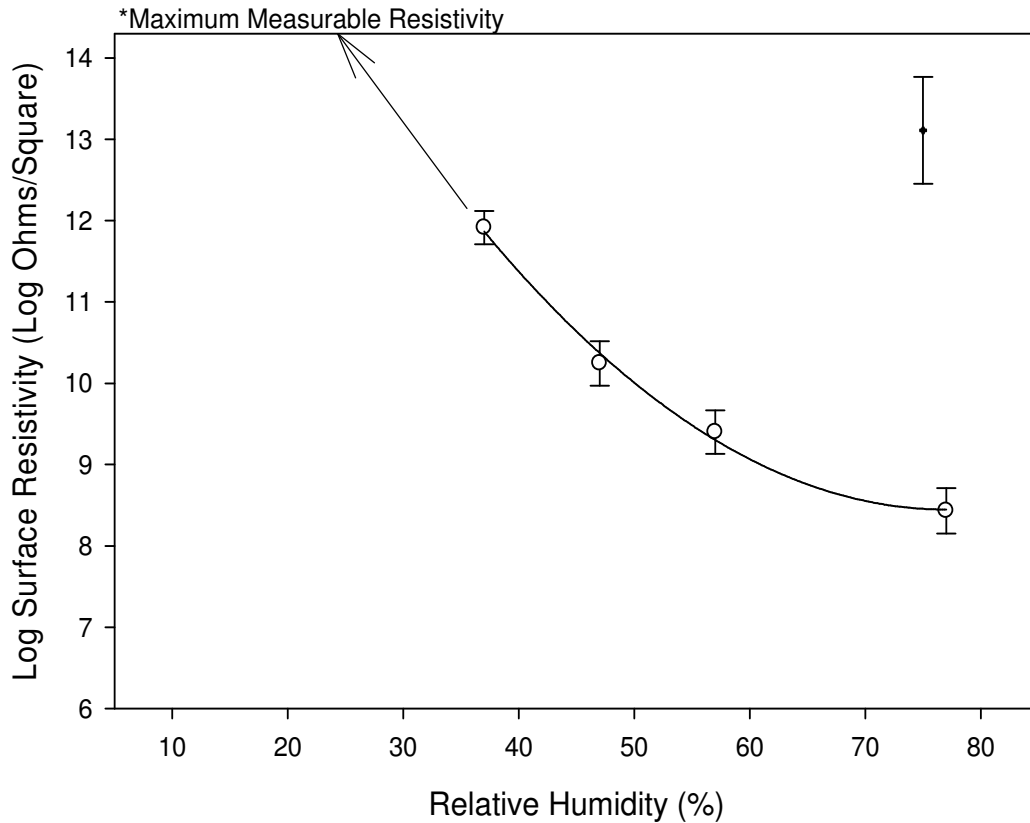
explained were 1) experimental error, 2) moisture hysteresis, 3) mechanical attachment, and/or 4) uneven treatment. Measurements of resistivity after the second and third deionized water rinses were greater than the maximum measurable value of the meter ( $2 \times 10^{14}$  Ohms/Square). This shows that taurine alone is not a durable antistatic treatment.

#### **4.2.4.2 Taurine and Sodium Hydroxide**

With results showing that taurine by itself has some antistatic properties, it was important to see what effects the addition of sodium hydroxide would have. A solution of taurine and sodium hydroxide was pad applied to polyester fabric followed by drying and curing at 175 °C for one minute. The amounts of taurine and sodium hydroxide applied were the same as previously applied in their individual treatments. The resistivity was tested at six different humidity values after treatment and after each of three deionized water rinses. The results are given in Figure 4.6 below.



## Taurine and NaOH



**Figure 4.6: Log surface resistivity of polyester fabric treated with taurine and NaOH in relation to RH** after rinsing with deionized water ○ zero times, • one time, ▼ two times, and ■ three times. 20.09 g/L taurine and 6.40 g/L sodium hydroxide (NaOH) padded on polyester fabric and cured at 175 °C for one minute. Error bars are +/- one standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.

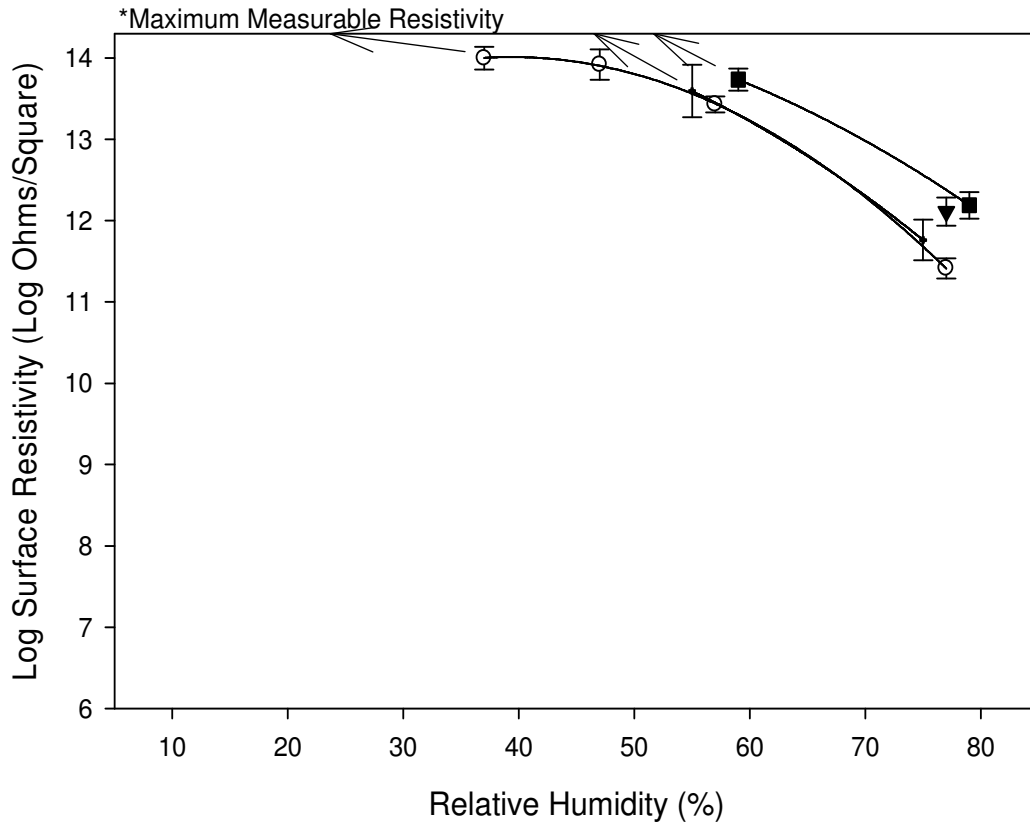
From analysis of the results in Figure 4.6, it can be determined that the addition of sodium hydroxide improved the antistatic treatments by several orders of magnitude over treatment with just taurine. However, after being subjected to one deionized water rinse, the only point within the maximum measurable value of the meter was that measured at a

relative humidity over 75 %. By the second deionized water rinse, the resistivity was greater than the measurable value of the meter ( $2 \times 10^{14}$  Ohms/Square) for all relative humidity values tested. The finish provides excellent antistatic properties above 40 % humidity before being subjected to any deionized water rinses but fails to exhibit any durability.

#### **4.2.4.3 Grafting Taurine with Poly(acrylic acid)**

Polyester fabric was previously treated with poly(acrylic acid) and taurine individually. Each treatment showed some antistatic properties but only the polyester treated with poly(acrylic acid) had durability to deionized water rinses. To determine if poly(acrylic acid) would provide increased durability when covalently bonded with taurine, polyester fabrics were treated with both taurine and poly(acrylic acid). Curing the polyester fabric after applying poly(acrylic acid) and taurine allows the amine end of taurine to covalently bond with the carboxylic acids in poly(acrylic acid). Taurine and poly(acrylic acid) were pad applied to polyester fabric as a homogeneous solution followed by drying and curing at 175 °C for one minute. The results for resistivity testing at six different humidity values after treatment and after each of three deionized water rinses are presented in Figure 4.7 below.

## PAA and Taurine



**Figure 4.7: Log surface resistivity of polyester fabric treated with PAA and taurine in relation to RH** after rinsing with deionized water  $\circ$  zero times,  $\bullet$  one time,  $\blacktriangledown$  two times, and  $\blacksquare$  three times. 11.55 g/L poly(acrylic acid) (PAA) and 20.09 g/L taurine padded on polyester fabric and cured at 175 °C for one minute. Error bars are +/- one standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.

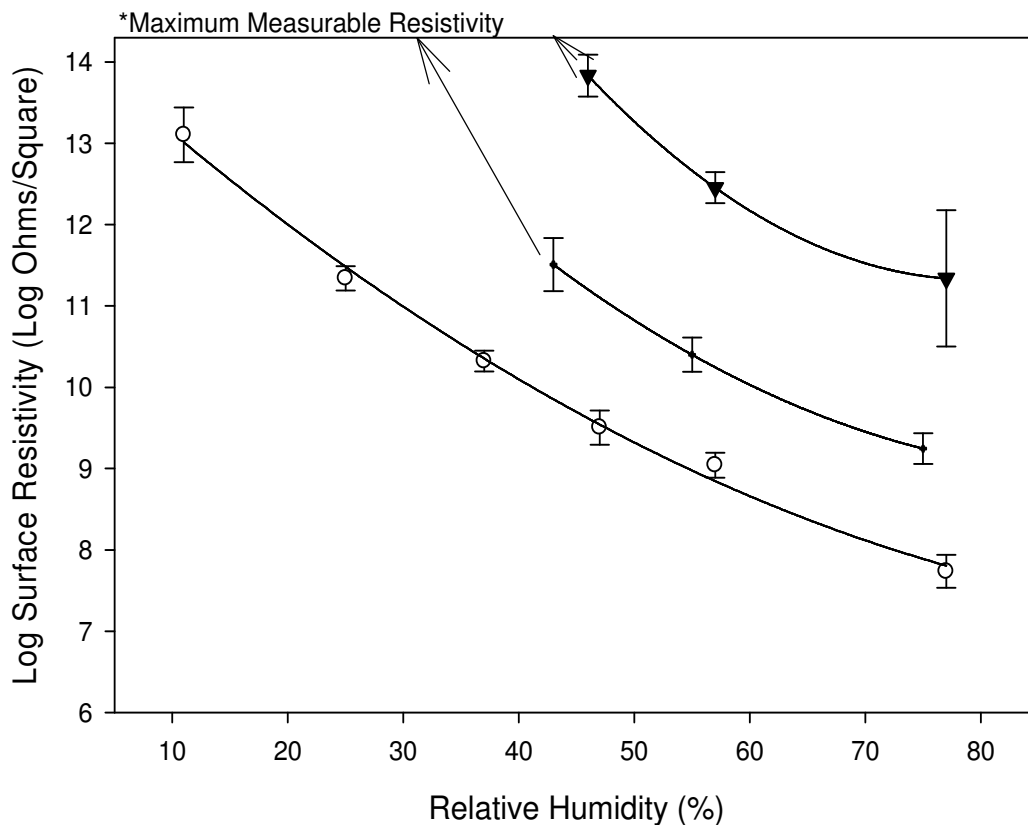
As displayed in Figure 4.7, antistatic properties are present but only at high humidity values. The finish seems to have durability to the deionized water rinses. The durability of poly(acrylic acid) seen in previous experiments is utilized in attaching the taurine and poly(acrylic acid) structures. However, the antistatic properties from utilizing both

poly(acrylic acid) and taurine in one treatment does not seem to provide any synergistic properties. This combination of chemicals does not appear to provide much better resistivity values than treating the fabric with poly(acrylic acid) or taurine individually.

#### **4.2.4.4 Grafting Taurine and Sodium Hydroxide with Poly(acrylic acid)**

Up to this point, poly(acrylic acid), taurine, and sodium hydroxide have each been tested individually as antistatic treatments on polyester fabric. Combinations of chemicals have also been tested such as poly(acrylic acid) with sodium hydroxide, taurine with sodium hydroxide, and poly(acrylic acid) with taurine. Both poly(acrylic acid) and taurine treatments were improved by several orders of magnitude when sodium hydroxide was included in the treatment. To determine if sodium hydroxide has the same effects when used in conjunction with the poly(acrylic acid) and taurine combination, a solution of poly(acrylic acid), taurine, and sodium hydroxide was pad applied to polyester fabric followed by drying and curing at 175 °C for one minute. The resistivity values were measured and recorded at six humidity values after treatment and after each of three deionized water rinses. The resistivity values are displayed in Figure 4.8 below.

## PAA, Taurine, and NaOH



**Figure 4.8: Log surface resistivity of polyester fabric treated with PAA, taurine, and NaOH in relation to RH after rinsing with deionized water** ○ zero times, ● one time, ▼ two times, and ■ three times. 11.55 g/L poly(acrylic acid) (PAA), 20.09 g/L taurine, and 6.40 g/L sodium hydroxide (NaOH) padded on polyester fabric and cured at 175 °C for one minute. Error bars are +/- one standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.

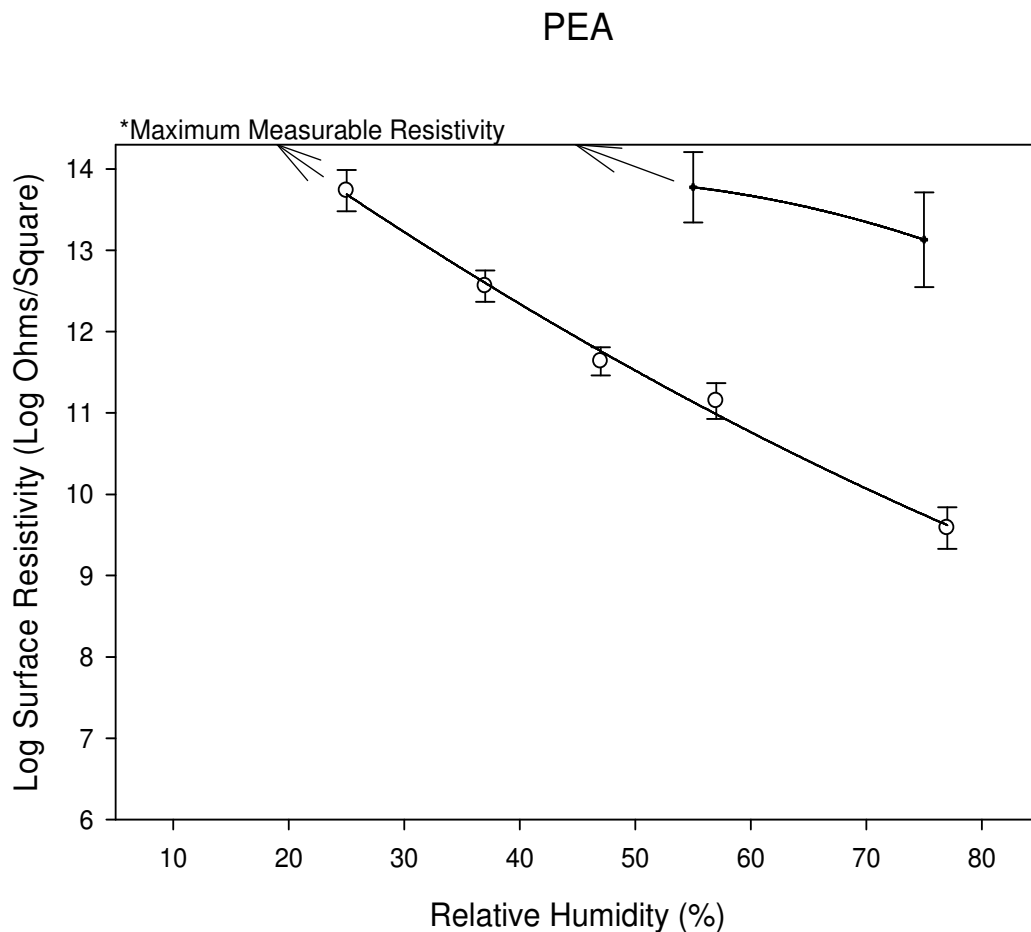
As seen in Figure 4.8, the combination of poly(acrylic acid), taurine, and sodium hydroxide provides excellent antistatic properties at relative humidity values above 30 % humidity before any deionized water rinses. The finish is not durable to the deionized water rinses. The first deionized water rinse reduced the antistatic properties by over one order of

magnitude. The second deionized water rinse increased the resistivity even further. By the third deionized water rinse, resistivity values exceeded the maximum measurable value of the meter ( $2 \times 10^{14}$  Ohms/Square) throughout the entire range of humidity values tested. The antistatic properties are almost identical to those of the combination of poly(acrylic acid) and sodium hydroxide treated fabrics in terms of resistivity before any rinses. The durability to deionized water rinses is similar in that either finish did not display durability. The similarity in results from polyester fabric treated with the chemical combination of poly(acrylic acid) and sodium hydroxide and the results of the same combination with the addition of taurine suggests the taurine provides no additional benefit to the antistatic finish. Sulfonic esters are not traditionally used as antistatic finishes for fabrics. However, phosphate esters are the most popular used antistats. The same series of experiments using sulfonic esters were duplicated but replacing the sulfonic ester with a phosphate ester.

## **4.2.5 Phosphate Ester**

### **4.2.5.1 O-phosphorylethanolamine**

The sulfonic ester taurine did not provide the desired antistatic properties. For comparison with a class of chemicals widely used as antistats, polyester fabric was treated with the phosphate ester o-phosphorylethanolamine. Phosphate esters are the most widely used class of antistatic chemicals. O-phosphorylethanolamine was pad applied to polyester fabric followed by drying and curing at 175 °C for one minute. The resistivity of the fabric was measured at six humidity values following treatment and after each of three deionized water rinses. The results are given in Figure 4.9 below.



**Figure 4.9: Log surface resistivity of polyester fabric treated with PEA in relation to RH after rinsing with deionized water ○ zero times, ● one time, ▼ two times, and ■ three times. 22.63 g/L o-phosphorylethanolamine (PEA) padded on polyester fabric and cured at 175 °C for one minute. Error bars are +/- one standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.**

It can be determined from Figure 4.9 that o-phosphorylethanolamine provides better antistatic properties than taurine before any deionized water rinses by comparing with the results in Figure 4.5. The first deionized water rinse decreased the antistatic properties by several orders of magnitude. The second and third deionized water rinse decreased the

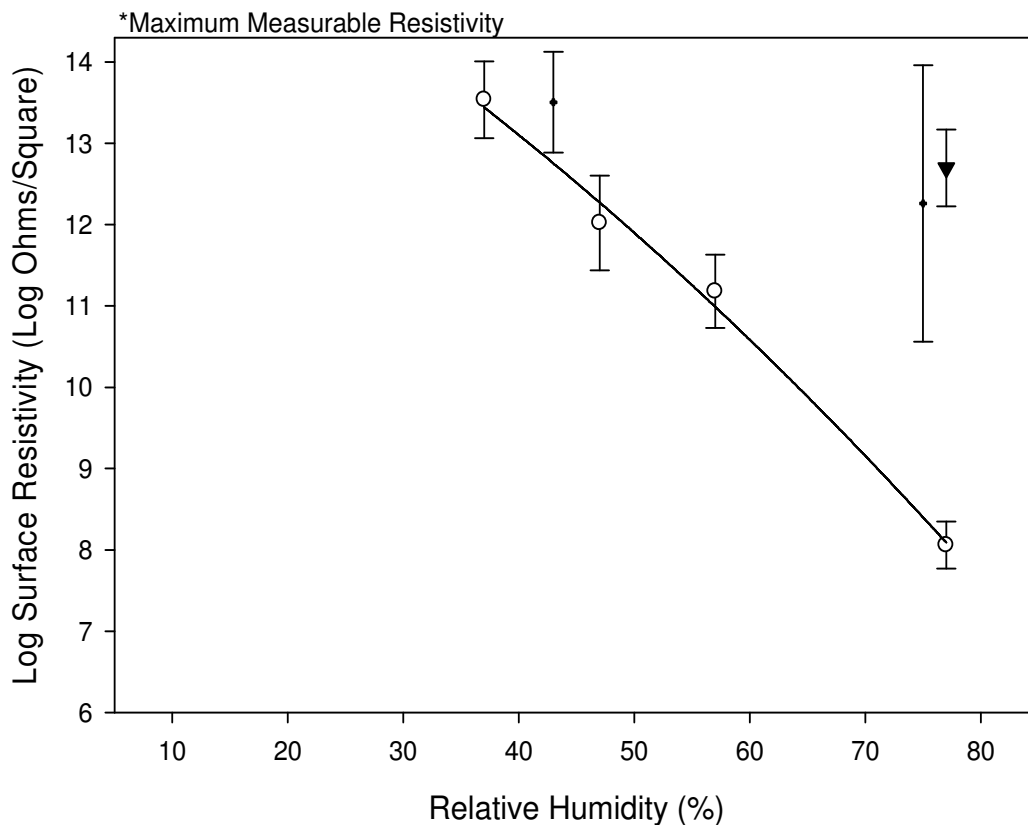
antistatic properties beyond the measurable value of the resistivity meter ( $2 \times 10^{14}$  Ohms/Square). It is determined that o-phosphorylethanolamine provides excellent antistatic properties but is not a durable finish when applied to the fabric alone.

#### **4.2.5.2 O-phosphorylethanolamine and Sodium Hydroxide**

In all previous experiments, the addition of sodium hydroxide to the finish provided better antistatic properties before any deionized water rinses. To determine if sodium hydroxide has the same influence on the phosphate ester; o-phosphorylethanolamine, a solution of o-phosphorylethanolamine and sodium hydroxide was pad applied to polyester fabric. After the pad application, the fabric was dried and cured at 175 °C for one minute. The resistivity was measured at six humidity values after treatment and after each of three deionized water rinses. The results are given in Figure 4.10 below.



## PEA and NaOH



**Figure 4.10: Log surface resistivity of polyester fabric treated with PEA and NaOH in relation to RH** after rinsing with deionized water ○ zero times, • one time, ▼ two times, and ■ three times. 22.63 g/L o-phosphorylethanolamine (PEA) and 6.40 g/L sodium hydroxide (NaOH) padded on polyester fabric and cured at 175 °C for one minute. Error bars are +/- one standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.

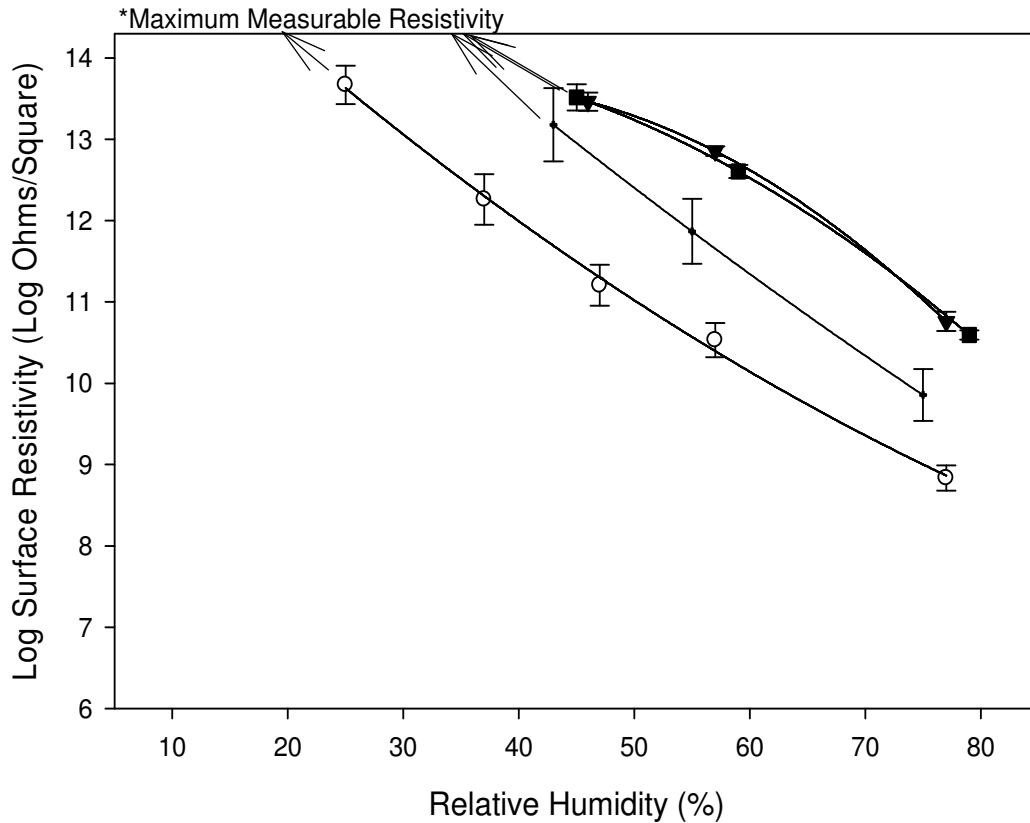
From the results displayed in Figure 4.10, it can be determined that sodium hydroxide did not improve the antistatic properties over that of polyester fabric treated with o-phosphorylethanolamine alone. If anything, the sodium hydroxide made the treatment more dependent on the humidity. As the humidity value is decreased, the resistivity increases at a

higher rate than fabric treated with just o-phosphorylethanolamine. From Figure 4.10, it can also be determined that the finish is not durable to deionized water rinses. By the third deionized water rinse, all the previous antistatic properties were beyond the maximum measurable value of the resistivity meter ( $2 \times 10^{14}$  Ohms/Square).

#### **4.2.5.3 Grafting O-phosphorylethanolamine with Poly(acrylic acid)**

Previous experiments have shown that poly(acrylic acid) can provide antistatic properties and make finishes more durable. The durability is due to the chemical reactions taking place between the chemicals and the fabric. O-phosphorylethanolamine has an amine end similarly to taurine. The attachment of o-phosphorylethanolamine to poly(acrylic acid) happens in the same manner. The amine end of o-phosphorylethanolamine covalently bonds with the carboxylic acid in poly(acrylic acid). To determine the effects of grafting o-phosphorylethanolamine to polyester with poly(acrylic acid), a solution of poly(acrylic acid) and o-phosphorylethanolamine was pad applied to the fabric. The fabric was then dried and cured at 175 °C for one minute. The resistivity was measured at six humidity values after treatment and after each of three deionized water rinses. The data is displayed in Figure 4.11 below.

## PAA and PEA



**Figure 4.11: Log surface resistivity of polyester fabric treated with PAA and PEA in relation to RH after rinsing with deionized water** ○ zero times, ● one time, ▼ two times, and ■ three times. 11.55 g/L poly(acrylic acid) (PAA) and 22.63 g/L o-phosphorylethanolamine (PEA) padded on polyester fabric and cured at 175 °C for one minute. Error bars are +/- one standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.

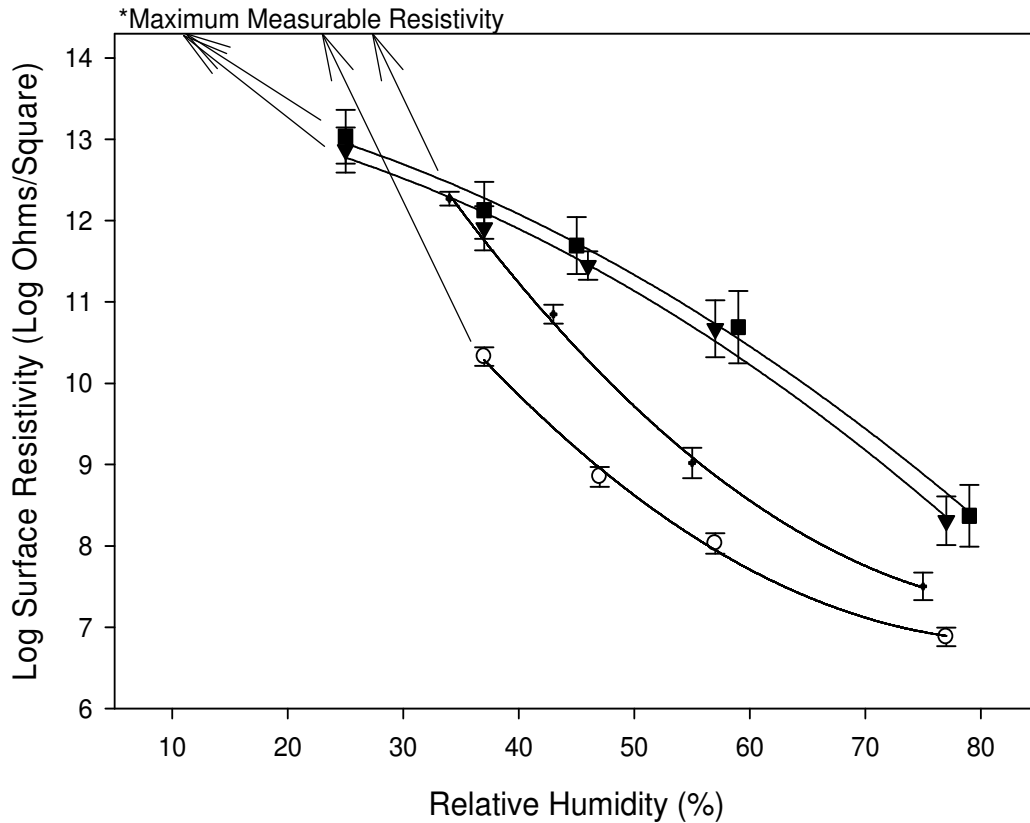
As can be seen in Figure 4.11, o-phosphorylethanolamine grafted to polyester with poly(acrylic acid) provides excellent antistatic properties down to 45 % humidity before any deionized water rinses. The antistatic properties are improved over using o-phosphorylethanolamine alone by over a half an order of magnitude. The durability to deionized water rinses has improved over using o-phosphorylethanolamine alone. The first

deionized water rinse increases the resistivity measurements by approximately one order of magnitude at each humidity. The second deionized water rinse increases the resistivity by another order of magnitude. The measurements after the third deionized water rinse are relatively the same as after the second deionized water rinse. This could be because all excess, unattached chemicals have been removed by the first two deionized water rinse. The finish only seems to be somewhat durable.

#### **4.2.5.4 Grafting O-phosphorylethanolamine and Sodium Hydroxide with Poly(acrylic acid)**

The addition of sodium hydroxide to chemicals applied to polyester fabric has shown improvements in the antistatic properties. The sodium hydroxide neutralizes the acids and provides mobility of ions. To determine the effect of the addition of sodium hydroxide to poly(acrylic acid) and o-phosphorylethanolamine, a solution of poly(acrylic acid), o-phosphorylethanolamine, and sodium hydroxide was pad applied to polyester fabric. The fabric was then dried and cured at 175 °C for one minute. The resistivity of the fabric was measured at six relative humidity values after treatment and after each of three deionized water rinses. The data is displayed in Figure 4.12 below.

## PAA, PEA, and NaOH



**Figure 4.12: Log surface resistivity of polyester fabric treated with PAA, PEA, and NaOH in relation to RH after rinsing with deionized water** ○ zero times, ● one time, ▼ two times, and ■ three times. 11.55 g/L poly(acrylic acid) (PAA), 22.63 g/L o-phosphorylethanolamine (PEA), and 6.40 g/L sodium hydroxide (NaOH) padded on polyester fabric and cured at 175 °C for one minute. Error bars are +/- one standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.

As seen in Figure 4.12, resistivity values are excellent until 35 % humidity before any deionized water rinses. The antistatic properties are better than any other chemical combinations at humidity values over 35 % tested up to this point. After the first deionized water rinse, the resistivity increases by slightly under an order of magnitude. The second

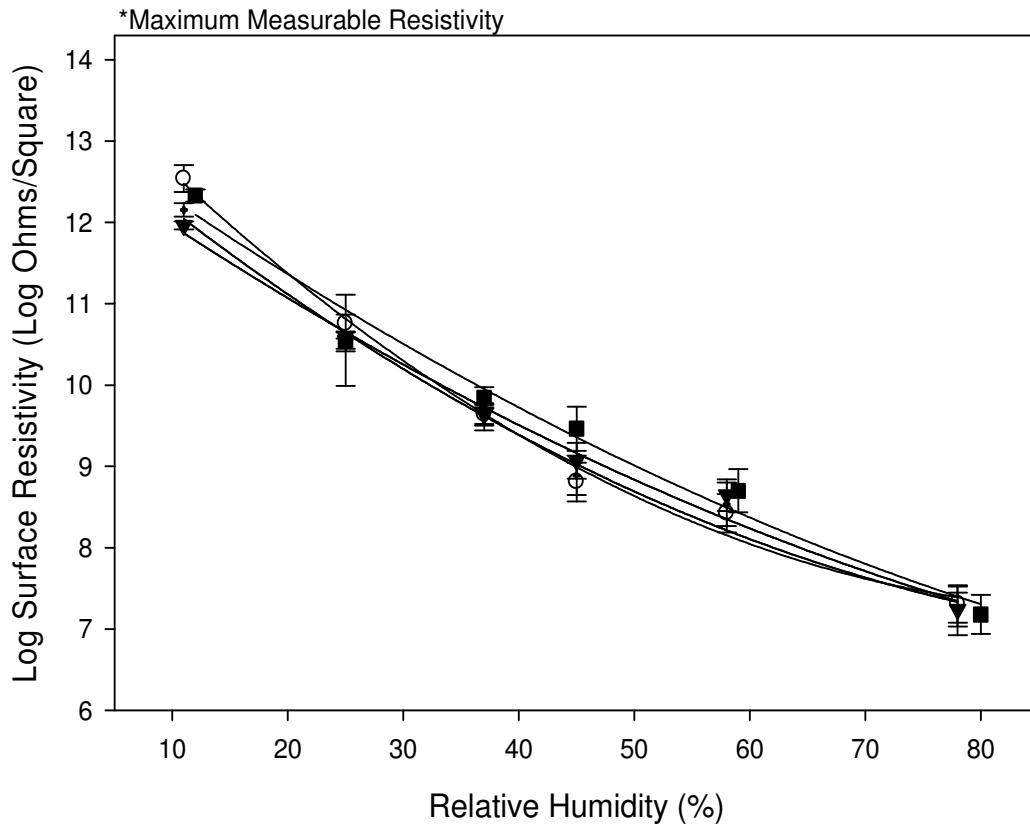
deionized water rinse further increases the resistivity of the fabric. The resistivity after the third deionized water rinse stays approximately the same as after the second deionized water rinse. The excess chemicals that have not been fully attached to the fabric have been removed from the surface by the first two deionized water rinses. This trend is similar to that found previously with the same chemical treatment excluding the sodium hydroxide. The overall antistatic properties including the sodium hydroxide are improved over that when the sodium hydroxide is not present.

#### **4.2.5.5 Grafting O-phosphorylethanolamine with Poly(acrylic acid) and pad applying Sodium Hydroxide**

The use of sodium hydroxide has proved to be advantageous when used with all the chemicals tested. The previous application method has been through the application of homogeneous solutions of chemicals pad applied and then dried and cured at 175 °C for one minute. With the application method used so far, the sodium hydroxide is in the original solution and subjected to the heat in the drying and curing process. It was hypothesized that the sodium hydroxide could be interfering with the reactions taking place between the chemicals and the fabric and therefore causing the finish to not be as durable. To test this theory, a new application method was tested. From the previous experiments, the chemical combination of poly(acrylic acid), o-phosphorylethanolamine, and sodium hydroxide has shown the best antistatic properties. Because of this, this chemical selection was chosen for the trial. A solution of poly(acrylic acid) and o-phosphorylethanolamine was pad applied to polyester fabric. The samples were then dried and cured at 175 °C for one minute. Sodium

hydroxide was pad applied after the fabric was cured and allowed to air dry. The resistivity of the fabric was measured at six humidity values after treatment and after each of three deionized water rinses. The results are given below in Figure 4.13.

### PAA and PEA - Pad apply NaOH after Curing



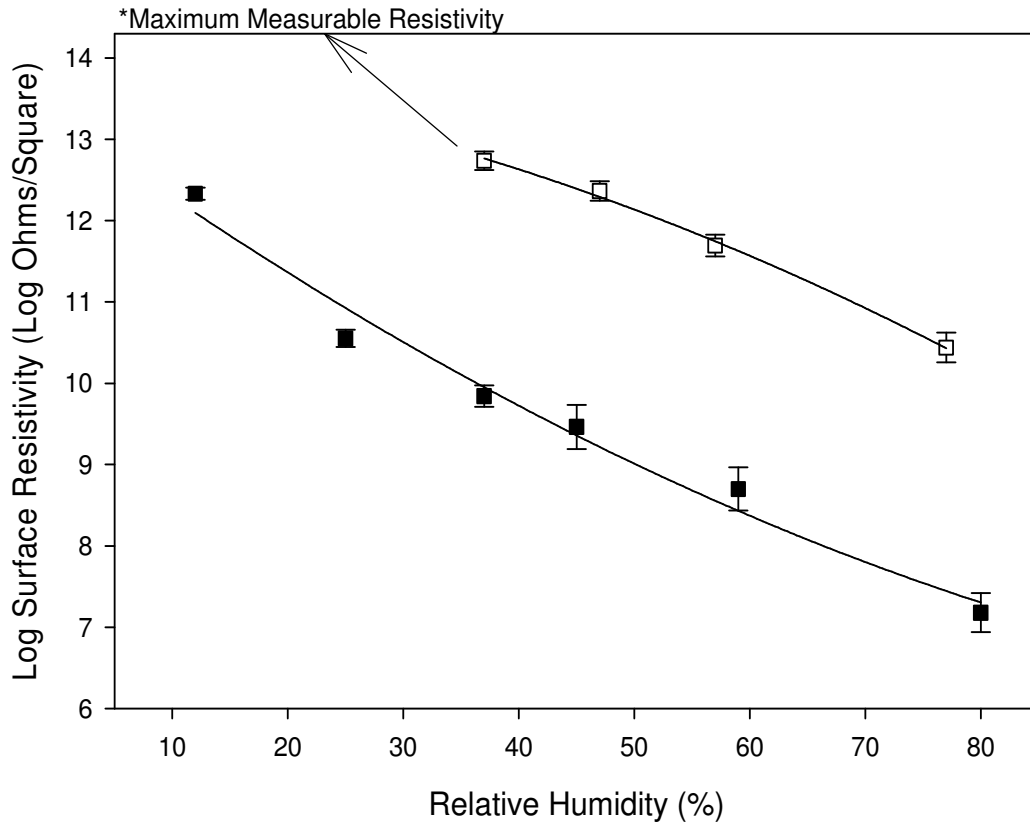
**Figure 4.13: Log surface resistivity of polyester fabric treated with PAA and PEA with NaOH applied after curing in relation to RH after rinsing with deionized water** ○ zero times, ● one time, ▼ two times, and ■ three times. 11.55 g/L poly(acrylic acid) (PAA) and 22.63 g/L o-phosphorylethanolamine (PEA) padded on polyester fabric and cured at 175 °C for one minute. 6.40 g/L sodium hydroxide (NaOH) pad applied after curing and then air dried. Error bars are +/- one standard deviation of the Log surface resistivity.

From the results given in Figure 4.13, it is determined that pad applying the sodium hydroxide after curing dramatically improves the antistatic properties. The difference in the treatments is the sodium hydroxide is not present during the chemical reactions that take place during the curing of the fabric. The sodium hydroxide is not subjected to any heat. The finish shows excellent antistatic properties down to 25 % humidity. The finish provides better durability to the deionized water rinses than any treatments tested. After three deionized water rinses, the resistivity is within a half an order of magnitude of the treatment without any deionized rinses. The antistatic properties of this finish both before and after the deionized water rinses prove to be better than any of the previous trials.

The aim of this research was to match the antistatic properties of cotton. A comparison of the resistivity values of cotton fabric with that of polyester fabric treated with poly(acrylic acid), o-phosphorylethanolamine, and sodium hydroxide with the sodium hydroxide applied after curing and after three deionized water rinses is shown in Figure 4.14 below.



## PAA and PEA-Pad NaOH vs. Cotton



**Figure 4.14: Log surface resistivity of polyester fabric treated with PAA and PEA with NaOH applied after curing vs. cotton in relation to RH** ■ Treated polyester fabric after rinsing with deionized water three times and □ cotton fabric cleaned with methanol. 11.55 g/L poly(acrylic acid) (PAA) and 22.63 g/L o-phosphorylethanolamine (PEA) padded on polyester fabric and cured at 175 °C for one minute. 6.40 g/L sodium hydroxide (NaOH) pad applied after curing and then air dried. Error bars are +/- one standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.

As shown in Figure 4.14, the treated polyester fabric has better antistatic properties than cotton throughout the entire range of humidity values tested. The antistatic properties of treated polyester at 12 % relative humidity is better than cotton below 45 % relative humidity. The aim was to match the values of cotton at 45 % relative humidity with

polyester at 20 % relative humidity. With these concentrations of chemicals, that goal was easily met even after three deionized water rinses.

#### **4.2.6 Polyethylene Glycol Antistat**

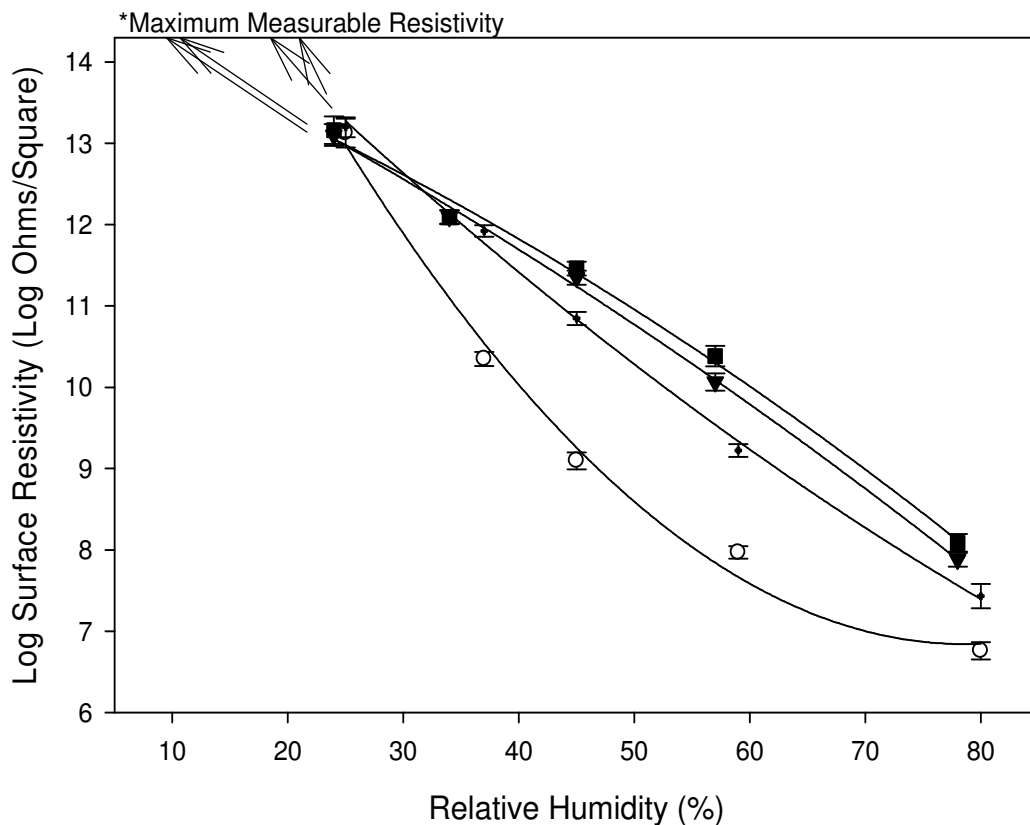
The water absorption of cotton provides natural antistatic properties. Humectants are often used to provide moisture absorptions to other materials. To determine the effects of a common humectant, experiments were performed with poly(ethylene glycol). Poly(ethylene glycol) is a commonly used non-ionic antistat often used with charge carrying antistats for synergistic properties. In previous experiments it was determined that the best combination of chemicals used was poly(acrylic acid), o-phosphorylethanolamine, and sodium hydroxide. It was also found that this combination works best if the sodium hydroxide is applied after the heat treatment. These chemicals were used in experimentation with poly(ethylene glycol). It was not know if the poly(ethylene oxide) could withstand the heat used during curing so three different application methods were used.

- 1) Apply poly(acrylic acid), o-phosphorylethanolamine, sodium hydroxide, and poly(ethylene glycol) as a homogeneous solution before curing
- 2) Apply poly(acrylic acid), o-phosphorylethanolamine, and sodium hydroxide before curing. Apply poly(ethylene glycol) after curing
- 3) Apply poly(acrylic acid) and o-phosphorylethanolamine before curing. Apply sodium hydroxide and poly(ethylene glycol) after curing

#### **4.2.6.1 Grafting O-phosphorylethanolamine, Sodium Hydroxide, and Poly(ethylene glycol) with Poly(acrylic acid)**

To determine if poly(ethylene glycol) provides any additional antistatic properties when applied before the curing process, a homogeneous solution of poly(acrylic acid), o-phosphorylethanolamine, sodium hydroxide, and poly(ethylene glycol) was pad applied to polyester fabric. The samples were dried and cured at 175 °C for one minute. The resistivity was measured at six different humidity values after treatment and after each of three deionized water rinses. The data is displayed in Figure 4.15 below.

## PAA, PEA, NaOH, PEG



**Figure 4.15: Log surface resistivity of polyester fabric treated with PAA, PEA, NaOH, and PEG in relation to RH after rinsing with deionized water** ○ zero times, ● one time, ▼ two times, and ■ three times. 11.55 g/L poly(acrylic acid) (PAA), 22.63 g/L o-phosphorylethanolamine (PEA), 6.40 g/L sodium hydroxide (NaOH), and 11.55 g/L poly(ethylene glycol) (PEG) padded on polyester fabric and cured at 175 °C for one minute. Error bars are +/- one standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.

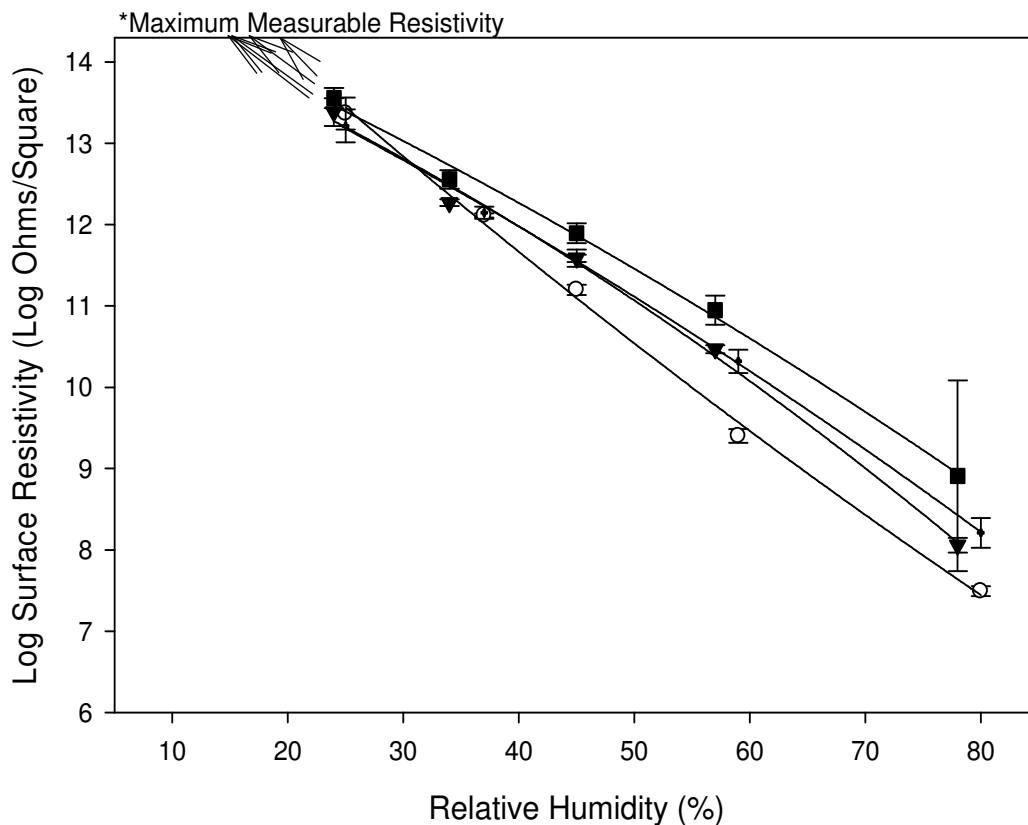
From Figure 4.15, it can be determined that the combination of poly(acrylic acid), o-phosphorylethanolamine, sodium hydroxide, and poly(ethylene glycol) provides excellent antistatic properties to 35 % humidity before any deionized water rinses. The question that is trying to be answered by doing this trial is whether or not the poly(ethylene glycol) provides any synergistic properties by adding it to the combination of poly(acrylic acid), o-

phosphorylethanolamine, and sodium hydroxide. By comparing the results of chemical combinations of poly(acrylic acid), o-phosphorylethanolamine, and sodium hydroxide with and without polyethylene glycol, the effects of poly(ethylene glycol) can be analyzed. From comparisons of Figures 4.15 and 4.12, it can be determined that the results are similar. Before any rinses, both trials display an almost identical trend. The first deionized water rinse shows a slight difference between the trials. This could be due to a slight variation in the intensity of the deionized water rinses. The second and third deionized water rinses again show an almost identical trend with or without the poly(ethylene glycol). The resistivity after the second deionized water is relatively the same as the resistivity after the third deionized water rinse in both trials. The reason for the resistivity to remain the same between these two deionized rinses is the same as described previously. The excess chemicals are removed by the second deionized water rinse. From a comparison of these chemical combinations, it can be determined that the addition of poly(ethylene glycol) to the solution of poly(acrylic acid), o-phosphorylethanolamine, and sodium hydroxide before curing provides no additional benefit. These results were not anticipated. To test if the poly(ethylene glycol) is being degraded by the heat in the curing process, additional samples were run padding the poly(ethylene glycol) on to the fabric after the curing process in the trials to follow.

#### **4.2.6.2 Grafting O-phosphorylethanolamine and Sodium Hydroxide with Poly(acrylic acid) and pad applying Poly(ethylene glycol)**

To test the effects of the padding on poly(ethylene glycol) after curing polyester fabric treated with poly(acrylic acid), o-phosphorylethanolamine, and sodium hydroxide, a solution of poly(acrylic acid), o-phosphorylethanolamine, and sodium hydroxide was pad applied to polyester fabric. The samples were then dried and cured at 175 °C for one minute. Poly(ethylene glycol) was pad applied afterwards and air dried. The samples were tested for resistivity after the treatments and after each of three deionized water rinses. The data is displayed in Figure 4.16 below.

## PAA, PEA, and NaOH - Pad apply PEG after Curing



**Figure 4.16: Log surface resistivity of polyester fabric treated with PAA, PEA, and NaOH with PEG applied after curing in relation to RH after rinsing with deionized water** ○ zero times, ● one time, ▼ two times, and ■ three times. 11.55 g/L poly(acrylic acid) (PAA), 22.63 g/L o-phosphorylethanolamine (PEA), and 6.40 g/L sodium hydroxide (NaOH) padded on polyester fabric and cured at 175 °C for one minute. 11.55 g/L poly(ethylene glycol) (PEG) pad applied after curing and then air dried. Error bars are +/- one standard deviation of the Log surface resistivity. Arrows indicate trend is off scale.

A comparison of the results between a treatment with poly(ethylene glycol) in the solution that is cured at 175 °C for one minute and a treatment with poly(ethylene glycol) pad applied after curing and air dried can be made by analyzing Figures 4.15 and 4.16

respectively. The results after rinses are similar between these trials. The deionized water rinsed samples show the same trends between each trial. Before any rinses, the poly(ethylene glycol) padded on after curing in Figure 4.16 shows a slight difference than that of the same chemicals all applied before curing in Figure 4.15 without any rinses. Pad applying the poly(ethylene glycol) after the curing process subjects the dry samples to a solution of deionized water and poly(ethylene glycol). The submersion of the samples into a solution in the padding process rinses some of the excess chemicals that have been previously applied. Therefore, samples with poly(ethylene glycol) pad applied after curing have a similar trend of samples without any rinses as that of those with one deionized water rinse for the same treatment but without poly(ethylene glycol) as shown in Figure 4.12. Within previous trials, it has been demonstrated that sodium hydroxide pad applied after curing improves the antistatic properties of the finish and its durability. To test the effect of including poly(ethylene glycol) in the solution of sodium hydroxide applied after curing, another trial was performed.

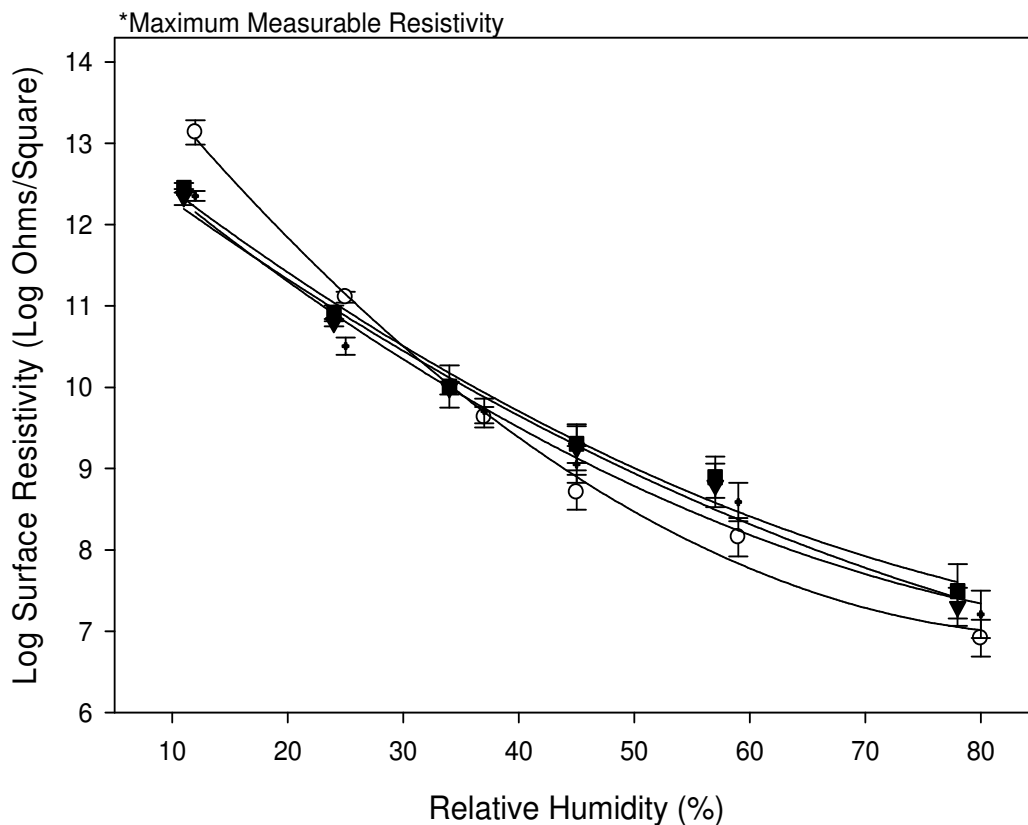
#### **4.2.6.3 Grafting O-phosphorylethanolamine with Poly(acrylic acid) and pad applying Sodium Hydroxide and Poly(ethylene glycol)**

To this point, poly(ethylene glycol) has not shown any benefit in the antistatic treatments. The best treatment process has been pad applying sodium hydroxide to fabric after curing a padded solution of poly(acrylic acid) and o-phosphorylethanolamine for one minute at 175 °C. To test the effects of poly(ethylene glycol) in the padded solution of sodium hydroxide after curing, a solution of poly(acrylic acid) and o-



phosphorylethanolamine were pad applied to polyester fabric. The samples were then cured at 175 °C for one minute before a solution of sodium hydroxide and poly(ethylene glycol) was also pad applied. The samples were then air dried. Testing of the resistivity was done at six different humidity values after treatment and after each of three deionized water rinses. The results are displayed in Figure 4.17 below.

## PAA and PEA - Pad apply NaOH and PEG after Curing



**Figure 4.17: Log surface resistivity of polyester fabric treated with PAA and PEA with NaOH and PEG applied after curing in relation to RH after rinsing with deionized water** ○ zero times, ● one time, ▼ two times, and ■ three times. 11.55 g/L poly(acrylic acid) (PAA) and 22.63 g/L o-phosphorylethanolamine (PEA) padded on polyester fabric and cured at 175 °C for one minute. 6.40 g/L sodium hydroxide (NaOH) and 11.55 g/L poly(ethylene glycol) (PEG) pad applied after curing and then air dried. Error bars are +/- one standard deviation of the Log surface resistivity.

The only difference between the trial being performed and a previous trial of curing a solution of poly(acrylic acid) and o-phosphorylethanolamine followed by pad applying sodium hydroxide in section 4.2.5.5 is the addition of poly(ethylene glycol) to the solution that is padded on after curing. From a comparison between the results of each trial in Figures

4.17 and 4.13, it can be seen that the resistivity values are similar and almost identical. The trends before any rinses and after the deionized rinses are similar. From the data, it can be determined that the poly(ethylene glycol) has no additional benefit when pad applied after curing with sodium hydroxide.

From the series of trials with poly(ethylene glycol), it is apparent that poly(ethylene glycol) does not provide any value to the antistatic treatment. Three different application methods were tested. Poly(ethylene glycol) was applied with the initial solution and cured afterwards. A comparison was made between the results of the same experiment excluding the poly(ethylene glycol) and there was no significant difference between the two. Further experiments were performed to determine if the heat was causing the poly(ethylene glycol) to degrade and therefore not providing any synergistic properties. Two trials were performed including the poly(ethylene glycol) in a solution that was pad applied after curing with and without sodium hydroxide. All trials showed that poly(ethylene glycol) did not provide any benefit in antistatic properties whether applied before or after the curing process. Because of this, poly(ethylene glycol) is excluded from any further trials.

### ***4.3 Optimization***

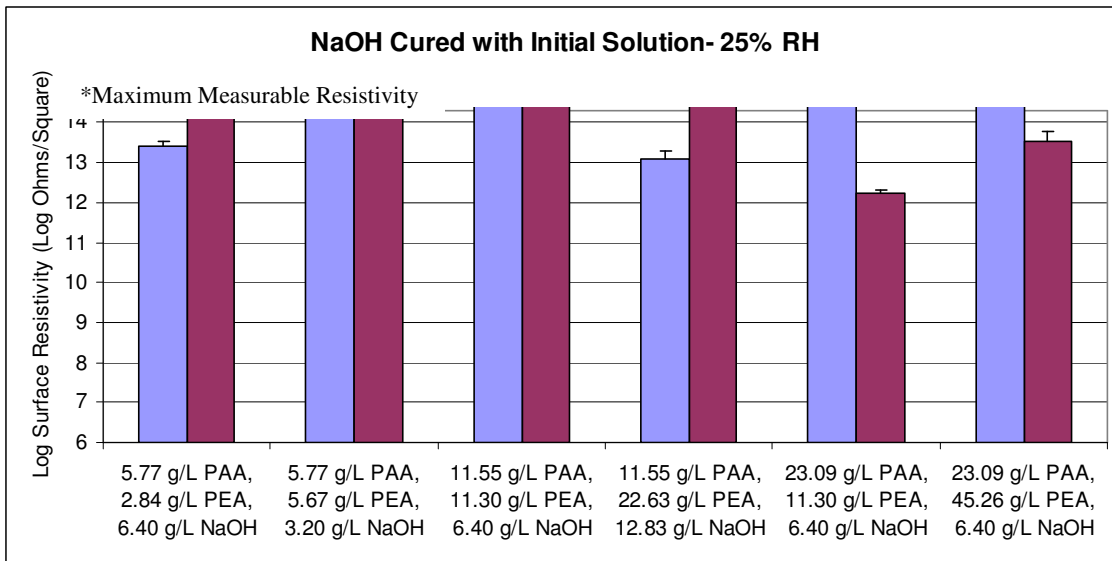
The best combination of chemicals was previously determined through experimentation. Curing treated fabrics with poly(acrylic acid) and o-phosphorylethanolamine followed by rinsing the samples with sodium hydroxide provided the best antistatic properties and durability to deionized water rinses. The same chemicals all applied in the initial solution before curing also provided good antistatic properties but were

not as good as those with the sodium hydroxide applied after the curing process. Applying the sodium hydroxide after curing is obviously the best method for the lowest resistivity values and most desirable durability. However, the additional steps involved with applying the sodium hydroxide as a separate treatment adds cost to the processing. It is not known how much of each chemical is needed in either treatment method. JMP 7 is a statistical package that was used to perform a design of experiments. Statistical software was used because it reduces the number of experiments needed when determining the impact of the concentration for each chemical. Twelve trials were performed based on the different concentrations of each of the three chemicals and the two application methods. The selected concentrations of poly(acrylic acid) were based on the percentage OWF. The concentrations of both o-phosphorylethanolamine and sodium hydroxide were based on the molar ratio between the repeat unit of poly(acrylic acid) and the chemical being applied. The twelve different chemical concentrations are listed below in Table 4.3 in the percentage on weight of fiber and in grams per liter.

**Table 4.3: Chemical concentrations and application methods for optimization trials Poly(acrylic acid) (PAA), o-phosphorylethanolamine (PEA), and sodium hydroxide (NaOH).**

Chemical Concentrations	PAA	PEA		NaOH		Application Method
	g/L	% OWF	g/L	% OWF	g/L	
2% OWF PAA, 0.25:1 PEA:PAA, 1:1 NaOH:PAA	23.09	0.98	11.30	1.11	12.83	Pad on after curing
1% OWF PAA, 1:1 PEA:PAA, 2:1 NaOH:PAA	11.55	1.96	22.63	1.11	12.83	Pad on after curing
2% OWF PAA, 0.5:1 PEA:PAA, 2:1 NaOH:PAA	23.09	1.96	22.63	2.22	25.67	Pad on after curing
0.5% OWF PAA, 0.5:1 PEA:PAA, 0.5:1 NaOH:PAA	5.77	0.49	5.67	0.14	1.60	Pad on after curing
1% OWF PAA, 0.25:1 PEA:PAA, 0.5:1 NaOH:PAA	11.55	0.49	5.67	0.28	3.20	Pad on after curing
0.5% OWF PAA, 1:1 PEA:PAA, 1:1 NaOH:PAA	5.77	0.98	11.30	0.28	3.20	Pad on after curing
2% OWF PAA, 0.25:1 PEA:PAA, 0.5:1 NaOH:PAA	23.09	0.98	11.30	0.55	6.40	Padded on before curing
0.5% OWF PAA, 0.25:1 PEA:PAA, 2:1 NaOH:PAA	5.77	0.25	2.84	0.55	6.40	Padded on before curing
1% OWF PAA, 0.5:1 PEA:PAA, 1:1 NaOH:PAA	11.55	0.98	11.30	0.55	6.40	Padded on before curing
2% OWF PAA, 1:1 PEA:PAA, 0.5:1 NaOH:PAA	23.09	3.92	45.26	0.55	6.40	Padded on before curing
1% OWF PAA, 1:1 PEA:PAA, 2:1 NaOH:PAA	11.55	1.96	22.63	1.11	12.83	Padded on before curing
0.5% OWF PAA, 0.5:1 PEA:PAA, 1:1 NaOH:PAA	5.77	0.49	5.67	0.28	3.20	Padded on before curing

The samples were tested at 25 % humidity after treatment and after the third deionized water rinse. The data is broken up into two figures based on the application method. Resistivity for samples treated with poly(acrylic acid), o-phosphorylethanolamine, and sodium hydroxide pad applied in the initial solution and then cured at 175 °C for one minute are displayed in Figure 4.18 below.

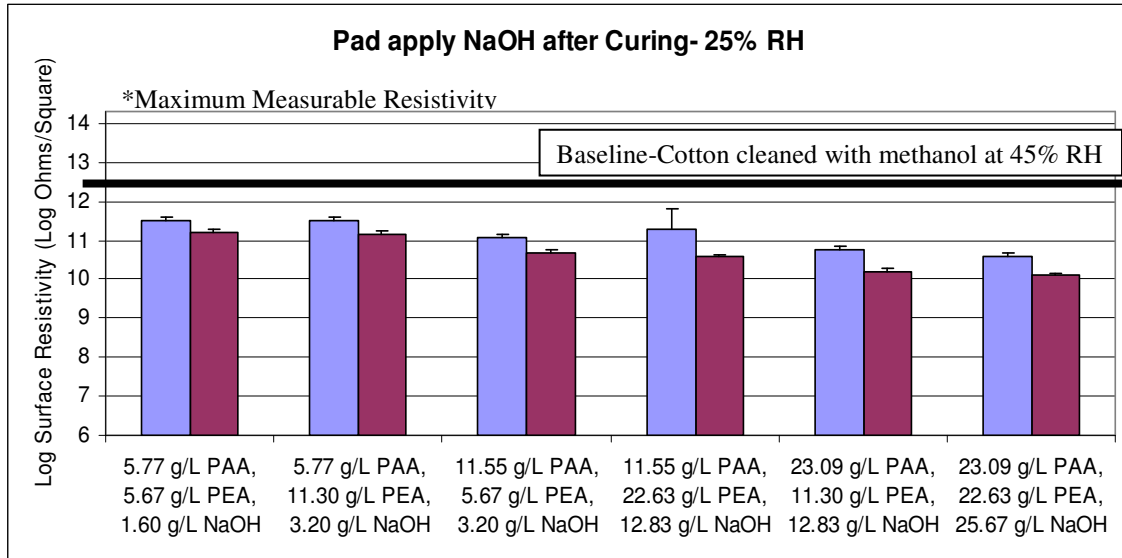


**Figure 4.18: Log surface resistivity of polyester fabric treated with PAA, PEA, and NaOH with different concentrations at 25% RH after rinsing with deionized water (bar on left) zero times and (bar on right) three times. Poly(acrylic acid) (PAA), o-phosphorylethanolamine (PEA), and sodium hydroxide (NaOH) padded on polyester fabric and cured at 175 °C for one minute. Error bars are + one standard deviation of the Log surface resistivity.**

As shown in Figure 4.18, only two of the six samples measured before any rinses are within the maximum range of the resistivity meter ( $2 \times 10^{14}$  Ohms/Square). After the three deionized water rinses, two of the samples are within the range of the resistivity meter but are not the same samples that were previously within range before the three deionized water rinses. Previous trials within the chemical combination section with the same chemical

combination had similar results with samples showing lower resistivity after the deionized rinses at low relative humidity values. The reason as explained before is attributed to moisture hysteresis or an uneven finish before the deionized water rinses. These same samples were also tested at 12 % relative humidity and none of the samples were within range of the resistivity meter ( $2 \times 10^{14}$  Ohms/Square) before any deionized water rinses or after the three deionized water rinses. From the experimental data of the samples treated with sodium hydroxide before curing, it is determined that the finish does not provide sufficient antistatic properties at relative humidity values of 25 % and lower. The increased concentrations of any of the chemicals applied did not provide enough additional antistatic properties to warrant this application method feasible.

The samples with the same chemicals applied in different concentrations with the sodium hydroxide applied after curing were also tested at 25 % relative humidity. Figure 4.19 includes the samples treated with poly(acrylic acid) and o-phosphorylethanolamine pad applied and cured at 175 °C for one minute followed by the pad application of sodium hydroxide.



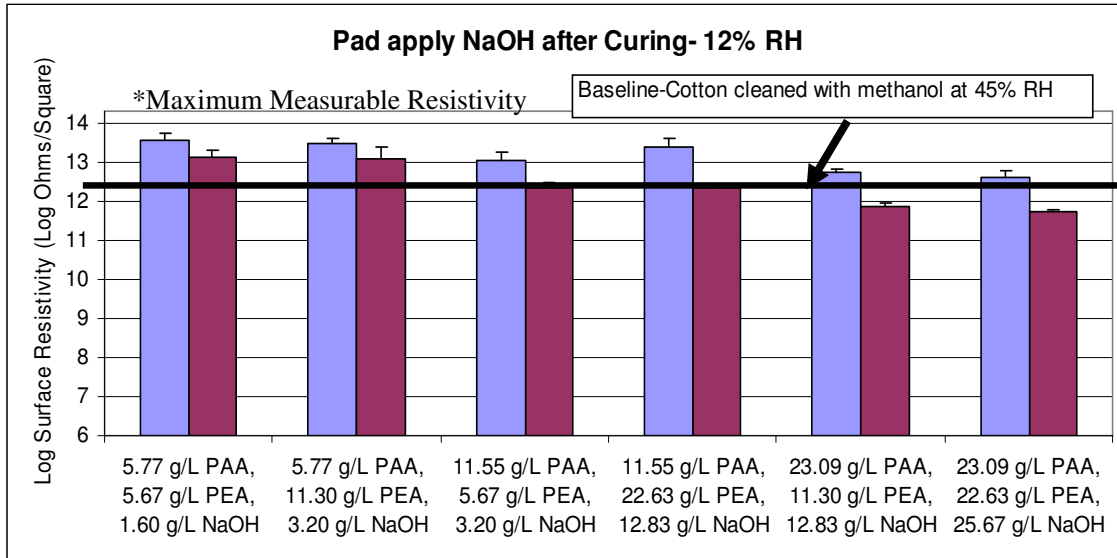
**Figure 4.19: Log surface resistivity of polyester fabric treated with PAA, PEA, and NaOH with different concentrations at 25% RH after rinsing with deionized water (bar on left) zero times and (bar on right) three times. Poly(acrylic acid) (PAA) and o-phosphorylethanolamine (PEA) padded on polyester fabric and cured at 175 °C for one minute. Sodium hydroxide (NaOH) pad applied after curing and then air dried. Error bars are +/- one standard deviation of the Log surface resistivity.**

The results for applying sodium hydroxide to cured polyester samples with poly(acrylic acid) and o-phosphorylethanolamine as displayed in Figure 4.19 shows improvement over including the sodium hydroxide in the curing process. All six samples tested are within the range of the resistivity meter before and after the three deionized water rinses. After three deionized water rinses, each trial showed improved antistatic properties. This can be attributed to moisture hysteresis and/or uneven application before the rinses. The results are arranged from left to right firstly based on the amount of poly(acrylic acid) and then by the amount of o-phosphorylethanolamine.

The two trials treated with 5.77 g/L poly(acrylic acid) showed similar results for resistivity before any deionized water rinses. They also had similar results after the



deionized water rinses. Doubling both the o-phosphorylethanolamine and sodium hydroxide from 5.67 to 11.30 g/L and 1.60 to 3.20 g/L respectively did not have much effect on the resistivity measurements. By doubling the amount of poly(acrylic acid) to 11.55 g/L, the resistivity decreases slightly. Between the two samples with 11.55 g/L poly(acrylic acid), the increases in concentrations of o-phosphorylethanolamine and sodium hydroxide again did not have a big impact. If anything, the antistatic properties before any rinses were decreased and improved between the two trials after the three deionized water rinses. Doubling the amount of poly(acrylic acid) from 11.55 to 23.09 g/L again showed a slight improvement in resistivity values. The two trials with 23.09 g/L poly(acrylic acid) showed similar antistatic properties even though the amounts of o-phosphorylethanolamine and sodium hydroxide were doubled between each trial. This is similar to the results seen with 5.77 g/L poly(acrylic acid). The samples were also tested at 12 % humidity after treatment and after three deionized water rinses. The data is displayed in Figure 4.20 below.



**Figure 4.20: Log surface resistivity of polyester fabric treated with PAA, PEA, and NaOH with different concentrations at 12% RH after rinsing with deionized water (bar on left) zero times and (bar on right) three times. Poly(acrylic acid) (PAA) and o-phosphorylethanolamine (PEA) padded on polyester fabric and cured at 175 °C for one minute. Sodium hydroxide (NaOH) pad applied after curing and then air dried. Error bars are +/- one standard deviation of the Log surface resistivity.**

As seen in Figure 4.20, all the trials were within range at 12 % relative humidity. Each trial has shown an increased in resistivity by approximately 1.5 orders of magnitude over that measure at 25 % relative humidity. All the results have a similar trend to that seen when measured at 25 % relative humidity. The resistivity is approximately the same between samples treated with the same amount of poly(acrylic acid). The concentrations of o-phosphorylethanolamine and sodium hydroxide did not have a big impact on the resistivity.

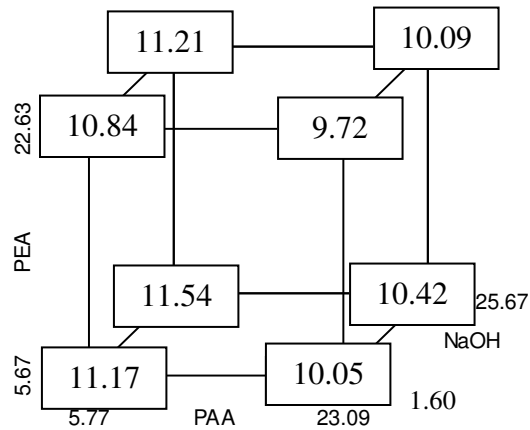
To further study the effects of the amounts of each chemical, the results for the resistivity measurements at 25 % relative humidity after the three deionized water rinses were entered into the statistical software; JMP 7. The results from applying the sodium

hydroxide before the curing process were excluded from analyses because most of the trials were out of range. An additional trial that was previously completed within the chemical combination was included in the analysis. The concentrations of the additional trial consisted of 11.55 g/L poly(acrylic acid), 22.63 g/L o-phosphorylethanolamine, and 6.40 g/L sodium hydroxide and resulted in a Log surface resistivity value of 10.55 Log Ohms/Square at 25 % relative humidity after three deionized water rinses. This made a total of seven trials at different concentrations to be analyzed. From the results of JMP 7, the t-values are displayed in Table 4.4 below.

**Table 4.4: Statistical analysis** Poly(acrylic acid) (PAA) and o-phosphorylethanolamine (PEA) padded on polyester fabric and cured at 175 °C for one minute. Sodium hydroxide (NaOH) pad applied after curing and then air dried.

<b>Term</b>	<b>Estimate</b>	<b>Std Error</b>	<b>t Ratio</b>	<b>Prob&gt; t </b>
Intercept	11.62317	0.155601	74.7	<.0001
PAA	-0.06456	0.01319	-4.89	0.0163
PEA	-0.01925	0.008915	-2.16	0.1197
NaOH	0.015385	0.013956	1.10	0.3508

From the t-values in Table 4.4, it is determined that the poly(acrylic acid) has the most significance. A t-value less than 0.05 means that with a 95 % confidence, there is a statistically significant difference in the amount of chemical used. Poly(acrylic acid) is the only chemical that showed a statistical difference. For further analysis, a cube plot was created within JMP 7. The cube plot is given below in Figure 4.21.



**Figure 4.21: Cube plot** Poly(acrylic acid) (PAA) and o-phosphorylethanolamine (PEA) padded on polyester fabric and cured at 175 °C for one minute. Sodium hydroxide (NaOH) pad applied after curing and then air dried. Values within box are estimated Log surface resistivity from statistical software JMP 7. Values outside of boxes are g/L of designated chemical.

The cube plot as shown in Figure 4.21 gives the values of the lowest and highest concentration of each chemical tested. The values inside the boxes are the estimated Log surface resistivity values at the given concentrations. The lowest estimate for Log surface resistivity is 9.72 Log Ohms/Square. The concentrations of each chemical at this value are 23.09 g/L poly(acrylic acid), 22.63 g/L o-phosphorylethanolamine, and 1.60 g/L sodium hydroxide. These are the highest concentrations tested for both poly(acrylic acid) and o-phosphorylethanolamine and the lowest concentration for sodium hydroxide. From the t-values previously given in Table 4.4, there was no statistically significant difference in the amount of sodium hydroxide with the range on concentrations tested and the amount of data. If anything, a lower amount of sodium hydroxide improves the antistatic properties. From the data, one may be led to believe that the sodium hydroxide should be left out of the

treatment. However, previous experiments within the chemical combinations section have shown that sodium hydroxide is a necessity. A comparison between Figures 4.11 and 4.13 shows the importance of using sodium hydroxide.

The t-values also showed that the amount of o-phosphorylethanolamine was not statistically significant with the concentrations tested and the limited amount of data. From looking at the difference between the different concentrations of o-phosphorylethanolamine, the Log surface resistivity only changes by less than a half an order of magnitude at every concentration of sodium hydroxide and poly(acrylic acid). In short, increasing the amount of o-phosphorylethanolamine by four times only improves the Log surface resistivity by less than an half an order of magnitude. From the data as presented in Table 4.4 and Figure 4.21, it is questionable whether or not the o-phosphorylethanolamine is necessary. Within the chemical selection section, trials were performed using poly(acrylic acid) and sodium hydroxide with and without o-phosphorylethanolamine. The trials showed that o-phosphorylethanolamine was beneficial to the antistatic properties before and after the deionized water rinses. These trials were completed with the sodium hydroxide cured within the initial solution. Up to this point, trials have not been performed to determine the effects of excluding o-phosphorylethanolamine with the sodium hydroxide applied after curing.

Increasing the amount of poly(acrylic acid) has the biggest impact. The Log surface resistivity improves by over one order of magnitude at every concentration of o-phosphorylethanolamine and sodium hydroxide when the amount of poly(acrylic acid) is increased by four times as much. The downfall with using high concentrations of poly(acrylic acid) is the feel of the fabric. Concentrations much higher than 5.77 g/L

poly(acrylic acid) provides a stiff fabric even after three deionized water rinses. This would not be desirable to the wearer. For this reason, the highest concentration of poly(acrylic acid) to be used is 5.77 g/L.

Through analysis of the effects of each chemical, it was determined what concentrations of each chemical should be used for testing the durability to launderings. The concentration of poly(acrylic acid) was selected to be 5.77 g/L. This concentration was selected because it provided sufficient antistatic properties without the fabric being too stiff. The concentration of o-phosphorylethanolamine was selected to be 5.67 g/L. This concentration was selected because the statistical data showed no significant difference amongst the concentration range tested with the amount of data given. 5.67 g/L was the lowest concentration of o-phosphorylethanolamine tested. The concentration of sodium hydroxide was selected as 1.60 g/L. This was the lowest concentration of sodium hydroxide tested. The lowest concentration of sodium hydroxide was selected because the amount of sodium hydroxide did not show significant differences in the amount used. If anything, lower amounts of sodium hydroxide provided better antistatic properties.

#### ***4.4 Durability to Accelerated Launderings***

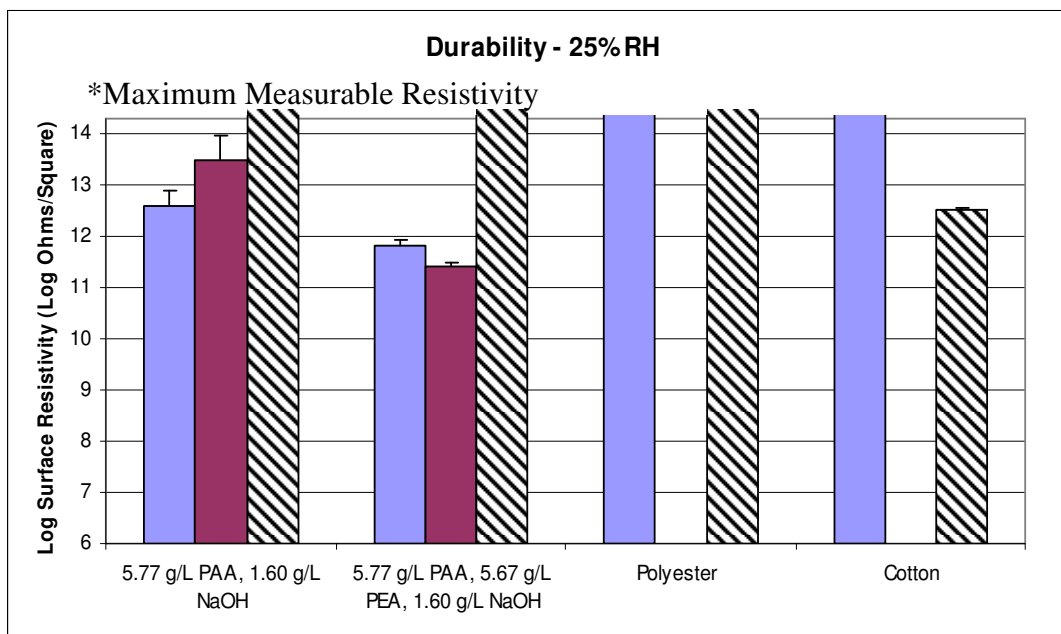
The concentrations of each chemical were determined in the optimization section to be 5.77 g/L poly(acrylic acid), 5.67 g/L o-phosphorylethanolamine, and 1.60 g/L sodium hydroxide. It was also questionable whether or not the o-phosphorylethanolamine is necessary. Trials were performed with these concentrations with and without the o-phosphorylethanolamine. The amounts of each chemical by molar ratio to the repeat unit of

poly(acrylic acid), grams per liter, and the percentage on weight of fiber are listed below in Table 4.5.

**Table 4.5: Concentrations for durability testing** Poly(acrylic acid) (PAA), o-phosphorylethanolamine (PEA), and sodium hydroxide (NaOH).

Chemicals	PAA	PEA		NaOH	
	g/L	% OWF	g/L	% OWF	g/L
0.5% OWF PAA, 0.0:1 PEA: PAA, 0.5:1 NaOH:PAA	5.77	0.00	0.00	0.14	1.60
0.5% OWF PAA, 0.25:1 PEA:PAA, 0.5:1 NaOH:PAA	5.77	0.49	5.67	0.14	1.60

Samples were made by padding the chemical solution of poly(acrylic acid) and o-phosphorylethanolamine for one trial and one trial without o-phosphorylethanolamine. The samples were cured at 175 °C for one minute. The samples were tested after treatment, after three deionized water rinses, and after one cycle using the accelerated launder-ometer. The launder-ometer was used following AATCC test method 61-2007. This test is equivalent to five home launderings. The detergent contains surfactants that provide some antistatic properties. To make sure the resistivity values measured after accelerated launderings are due to the finish applied and not because of the detergent used, polyester samples cleaned with methanol were also tested after one cycle in the launder-ometer. Cotton samples were cleaned with methanol and also subjected to one cycle in the launder-ometer for comparisons. The results for all of the samples described when tested at 25 % relative humidity are given in Figure 4.22 below.

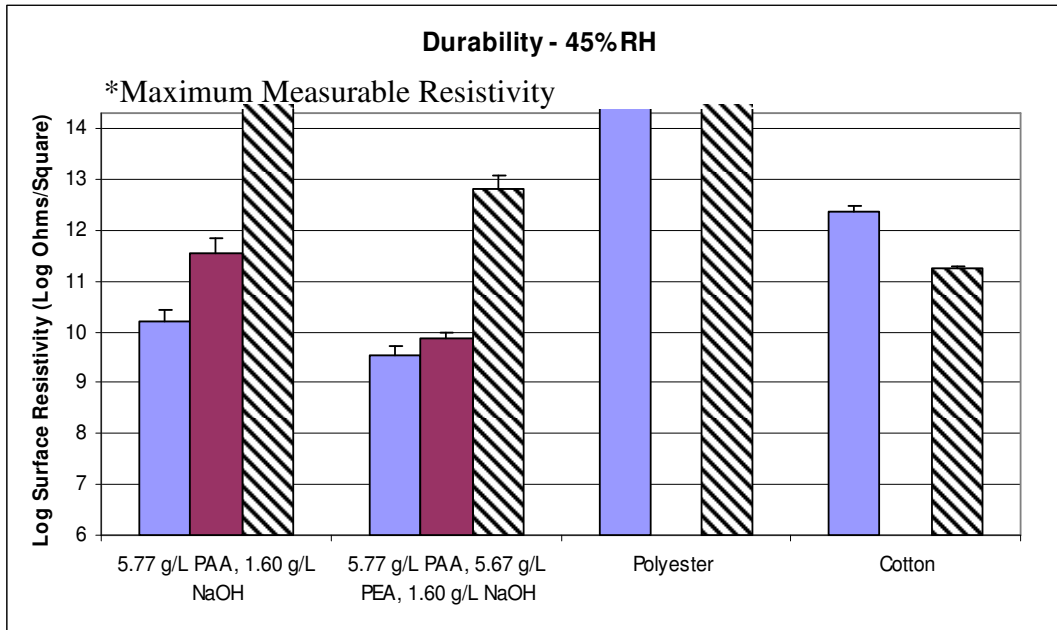


**Figure 4.22: Log surface resistivity of treated polyester fabric and cotton fabric at 25% RH** after rinsing with deionized water (bar on left) is zero times and (bar in center) three times. (bar on right) is one accelerated laundering equivalent to five home launderings. First series of data on left: Poly(acrylic acid) (PAA) padded on polyester fabric and cured at 175 °C for one minute. Sodium hydroxide (NaOH) pad applied after curing and then air dried. Second series of data from the left: PAA and o-phosphorylethanolamine (PEA) padded on polyester fabric and cured at 175 °C for one minute. NaOH pad applied after curing and then air dried. Third series of data from the left: 100% Polyester cleaned with methanol. Fourth series of data from the left: 100% cotton cleaned with methanol. Error bars are +/- one standard deviation of the Log surface resistivity.

As seen in Figure 4.22, samples treated with poly(acrylic acid), cured and then treated with sodium hydroxide afterwards without the use of o-phosphorylethanolamine did not provide sufficient antistatic properties before any deionized water rinses or after the three deionized water rinses. The resistivity increased after three deionized water rinses. When o-phosphorylethanolamine is used, the resistivity has gone down after the three deionized water rinses. One of the possible explanations has been moisture hysteresis. The data shown



supports this theory as the use of o-phosphorylethanolamine could be absorbing moisture from the air. The oxygen groups within the ethylene oxide of o-phosphorylethanolamine provide moisture absorption that aids in the antistatic properties. At the concentrations of 5.77 g/L poly(acrylic acid), 5.67 g/L o-phosphorylethanolamine, and 1.60 g/L sodium hydroxide, the sample that included o-phosphorylethanolamine provided good antistatic properties and durability to the three deionized water rinses. However, at 25 % relative humidity, none of the polyester samples provided antistatic properties after the accelerated launderings. This shows the finish is not durable to the equivalent of five home launderings at 25 % relative humidity. The only sample within range of the resistivity meter at 25 % relative humidity after one cycle of accelerated laundering is the cotton sample. The natural antistatic properties of cotton are enhanced by the accelerated laundering. This is due to the antistatic properties of the surfactant within the detergent. The resistivity values of cotton samples cleaned with methanol without any treatments are outside the range of the meter ( $2 \times 10^{14}$  Ohms/Square) at 25 % relative humidity. To determine if the antistatic finishes provided any antistatic properties after one accelerated laundering, the samples were also tested at 45 % relative humidity. The data is displayed in Figure 4.23 below.



**Figure 4.23: Log surface resistivity of treated polyester fabric and cotton fabric at 25% RH** after rinsing with deionized water (bar on left) is zero times and (bar in center) three times. (bar on right) is one accelerated laundering equivalent to five home laundings. First series of data from the left: Poly(acrylic acid) (PAA) padded on polyester fabric and cured at 175 °C for one minute. Sodium hydroxide (NaOH) pad applied after curing and then air dried. Second series of data from the left: PAA and o-phosphorylethanolamine (PEA) padded on polyester fabric and cured at 175 °C for one minute. NaOH pad applied after curing and then air dried. Third series of data from the left: 100% Polyester cleaned with methanol. Forth series of data from the left: 100% cotton cleaned with methanol. Error bars are +/- one standard deviation of the Log surface resistivity.

As shown in Figure 4.23, the polyester samples treated with 5.77 g/L poly(acrylic acid) and 5.67 g/L o-phosphorylethanolamine, cured at 175 °C for one minute, and treated with sodium hydroxide showed some antistatic properties after one accelerated laundering equivalent to five home laundings. Although the resistivity values were not as low as desired, it is apparent that not all of the finish was removed by the accelerated laundering. None of the other polyester samples were within range of the resistivity meter ( $2 \times 10^{14}$  Ohms/Square) including the sample treated with the same concentrations of chemicals

excluding o-phosphorylethanolamine. This confirms that the treatment of the samples treated with poly(acrylic acid), o-phosphorylethanolamine, and sodium hydroxide provides additional antistatic properties to that obtained from the surfactant in the detergent.

The accelerated laundering is abusive to the fabric. 50 metal balls are used in the bath that may be abrading the finish from the surface. The fabrics have undistinguishable hand between the polyester fabric as received and treated fabrics with 5.77 g/L poly(acrylic acid), 5.67 g/L o-phosphorylethanolamine, and 1.60 g/L sodium hydroxide after the accelerated launderings. The treated fabrics with three deionized water rinses have a slightly stiffer hand than that of the polyester fabrics as received. The rinsing process within the accelerated laundering test method is also more drastic than the deionized water rinses used for initial assessment of durability. Even though the finish does not provide the antistatic properties that were originally desired, a surface resistivity less than 13 Log Ohms/Square for polyester at 45 % relative humidity is not easily accomplished after the equivalent of five home launderings.

#### ***4.5 pH of the Extract***

The pH of the fabrics treated with poly(acrylic acid) and sodium hydroxide with and without o-phosphorylethanolamine were tested using AATCC test method 81-2006. pH of the extract was tested after one deionized water rinse and after one accelerated laundering equivalent to five home launderings. The data is displayed in Table 4.6 below.

**Table 4.6: pH of extract** after one deionized water rinse and after one accelerated laundering equivalent to five home launderings. First series of data: Poly(acrylic acid) (PAA) padded on polyester fabric and cured at 175 °C for one minute. Sodium hydroxide (NaOH) pad applied after curing and then air dried. Second series of data: PAA and o-phosphorylethanolamine (PEA) padded on polyester fabric and cured at 175 °C for one minute. NaOH pad applied after curing and then air dried.

Treatment	pH after one deionized water rinse	pH after one accelerated laundering
5.77 g/L PAA, 0.0 g/L PEA 1.60 g/L NaOH	8.36	8.95
5.77 g/L PAA, 5.67 g/L PEA, 1.60 g/L NaOH	8.87	9.36

As shown in Table 4.6, the pH levels were within the 8-9 range for all fabrics tested.

This test was performed as an initial assessment of the fabrics integrity. Fabrics with high pH levels have a tendency to degrade and yellow with relatively high pH values.

## **4.6 Cost**

### **4.6.1 Cost of Chemicals**

Poly(acrylic acid) and o-phosphorylethanolamine were obtained from Sigma-Aldrich® in low quantities. The largest quantity of poly(acrylic acid) listed at [www.sigmaaldrich.com](http://www.sigmaaldrich.com) is 250 grams at \$201.00 as item number 181285-250G. This

amounts to \$804.00 per kilogram. Poly(acrylic acid) can be obtained in larger quantities from Spectrum MFG Corp. with the name Carbomer 934. The largest quantity listed at [www.spectrumchemical.com](http://www.spectrumchemical.com) is 45 kilograms for \$2843.75 as item number CA251-45KGBL. This amounts to \$63.19 per kilogram. This is also with a molecular weight of 3,000,000 rather than the 450,000 that has been used in this research.

The largest quantity of o-phosphorylethanolamine listed at [www.sigmaaldrich.com](http://www.sigmaaldrich.com) is 500 grams at \$807.00 as item number P0503-500G. This chemical is also available through ScienceLab.com in larger quantities with the name Phosphoryl Colamine. The largest quantity listed at [www.sciencelab.com](http://www.sciencelab.com) is 50 kilograms at \$8,241.22 as item number SLP2470-50KG. This amounts to \$164.82 per kilogram.

Sodium hydroxide is inexpensive. It can be obtained from Sigma-Aldrich® in pellet form. The largest quantity listed at [www.sigmaaldrich.com](http://www.sigmaaldrich.com) is five kilograms at \$191.00 as item number S5881-5KG. This amounts to \$38.20 per kilogram. Sodium hydroxide is also available from Brenntag. Quantities over 40,000 pounds are available in 50 % solution at \$0.11 per pound to be pumped in to storage tanks. Smaller amounts can be obtained by barrel for approximately \$0.22 per pound in 50 % solution. This amounts to \$0.97 per kilogram as 100 % sodium hydroxide. The prices for each chemical are given in Table 4.7 below.

**Table 4.7: Cost of chemicals per kilogram Calculated as 100% solid form**

Chemical	Cost per kilogram (\$/kg)	Supplier
Poly(acrylic acid)	63.19	Spectrum Chemical MFG Corp.
O-phosphorylethanolamine	164.82	ScienceLab.com
Sodium hydroxide	0.97	Brenntag

All of the chemicals can be purchased at significantly lower costs if purchased in bulk. With add on levels used within the durability section, the cost of chemicals is calculated. The costs are based on the polyester fabrics used at 150.70 g/Yd.<sup>2</sup> and are listed in Table 4.8 below.

**Table 4.8: Cost of chemicals per square yard of fabric Polyester fabric used is 150.70 grams per square yard**

Chemical	% OWF	Cost per square yard (\$/Yd. <sup>2</sup> )
Poly(acrylic acid)	0.50	0.048
O-phosphorylethanolamine	0.49	0.1217
Sodium hydroxide	0.14	0.0002
<b>Total</b>	<b>1.13</b>	<b>0.1699</b>

As shown in Table 4.8, the cost of chemicals per square yard is calculated to be \$0.1699. This is an estimate based on the prices obtained from chemical suppliers. There is

potential to get each chemical at significantly lower prices through negotiation when purchasing in higher quantities.

#### **4.6.2 Cost of Processing**

The processing cost is subject to many factors within manufacturing that can play a role in the cost of processing. Some of the factors include the size and energy consumption of the tenter frame, width of the fabric, and labor costs. These costs can vary even between manufacturing facilities within the same company. Because of this, the processes necessary will be described. The total cost for processing can be calculated by summing the estimated processing of fabric in each step in dollars per square yard.

The first process includes the initial treatment of the fabric. A solution of both poly(acrylic acid) and o-phosphorylethanolamine is pad applied to the fabric with the add on levels listed in Table 4.8. Directly after padding on the chemicals, the fabric is cured in a traditional tenter frame for one minute at 175 °C. The speed of the fabric is dependent on the length of the tenter frame.

The second process includes the application of sodium hydroxide. The dry fabric sample previously cured in the oven is processed again. A solution of sodium hydroxide is pad applied at 0.14 % OWF. Directly after padding on the sodium hydroxide, a water rinse is necessary to remove excess sodium hydroxide before drying. The rinse could take place after drying but the fabric would have to be dried an additional time. This can be performed as a continuous process if two pads are utilized. The first pad is used to remove the excess liquid before the rinsing process. The second pad removes the excess liquid after the rinsing

process. The fabric enters a tenter frame directly afterwards to dry the fabric. The temperature and duration is dependent on the tenter frame. Enough heat and duration should be used to dry the fabric. Elevated temperatures are not required as the curing has already taken place in previous processes. For estimation purposes, the same cost to dry and cure the fabric at 175 °C for one minute is used for drying after the sodium hydroxide and water rinse.

The estimated cost for drying and curing fabric for one minute at 175 °C was obtained from the research findings of Wade Tyner. (Tyner, 2007) Wade Tyner obtained estimates from American Monforts for energy consumption as shown in Table 4.9 below.

**Table 4.9: Estimated energy usage for processing (Tyner, 2007)**

Machine	Montex-TwinAir Stenter, 10 zones
Actual Speed	24 yards/min
Heat Energy without Heat Recovery	1405861 BTU/hr
Heat Requirement per kg Evaporated H <sub>2</sub> O	3056 BTU/kg H <sub>2</sub> O
<b>Total Electrical Power</b>	<b>224 KW</b>

Using estimated costs of \$0.1265/KWh, \$7.85/MMBTU, and processing of 65 inch wide fabric, costs were calculated for a total energy cost of \$0.0187/Yd<sup>2</sup> to dry and cure fabric at 175 °C for one minute. (Tyner, 2007) A list of every process is given in Table 4.10 below. Costs associated with applying the chemicals and rinsing the fabric are considered to be negligible.



**Table 4.10: Cost of processing a square yard of fabric Poly(acrylic acid) (PAA), o-phosphorylethanolamine (PEA), and sodium hydroxide (NaOH).**

<b>Process</b>	<b>Cost per square yard (\$/Yd.<sup>2</sup>)</b>
Pad applying PAA and PEA	Negligible
Curing at 175 °C for one minute	0.0187
Pad applying NaOH	Negligible
Rinsing the fabric	Negligible
Drying the fabric	0.0187
<b>Total</b>	<b>0.0374</b>

As mentioned previously, these values are estimations and are dependent on several variables such as the type of tenter frame and current energy costs.

### 4.6.3 Total Cost

The total cost can be estimated by adding the calculated cost of chemicals from Table 4.8 to the estimated processing costs from Table 4.10. The costs are summed in Table 4.11 below.

**Table 4.11: Total cost of chemicals and processing**

Cost of chemicals (\$/Yd. <sup>2</sup> )	0.1699
Cost of processing (\$/Yd. <sup>2</sup> )	0.0374
<b>Total Cost (\$/Yd.<sup>2</sup>)</b>	<b>0.2073</b>

Antistatic treatment of polyester fabrics can be performed for under \$0.21 in a manufacturing environment. There is potential for this cost to be significantly lower. The cost of chemicals makes up the biggest cost. As mentioned previously, the cost of chemicals are initial estimates from suppliers in small quantities. These chemicals can be purchased at significantly lower prices when acquired in bulk. Even with the high chemical costs, the estimated cost of this antistatic treatment is reasonable. The antistatic treatment is found to be successful because of its improved durability over using phosphate esters alone, and its low cost.

## 5. Conclusions

Several combinations of chemicals were tested for surface resistivity on 100 % polyester fabric. The use of taurine was not found to provide any additional benefit when used with a solution of poly(acrylic acid) and sodium hydroxide. Good antistatic properties were obtained when o-phosphorylethanolamine was used in place of taurine. When poly(ethylene glycol) was added to the antistatic treatment, no additional antistatic properties were obtained.

Although none of the treatments were durable to accelerated launderings, the treatments can still be used in applications which do not require launderings. Some applications include nonwovens and carpets. Curing polyester fabric with poly(acrylic acid) and o-phosphorylethanolamine at 175 °C for one minute and then applying sodium hydroxide after the curing process was found to be an effective antistatic treatment. The treatments were found to be durable to deionized water rinses but not to an accelerated laundering equivalent to five home launderings.

The use of sodium hydroxide after the curing process was found to be the most effective application method. Both the resistivity before and after deionized water rinses was improved. This was most likely because the sodium hydroxide was interfering with the chemical reactions taking place between o-phosphorylethanolamine, poly(acrylic acid), and the polyester fabric. This is of importance because lower levels of resistivity can be reached that otherwise would not be possible using the same chemicals. Applying the sodium hydroxide after curing allows for significantly lower concentrations of each chemical.

The finish was not as durable to the accelerated laundering as desired but still provided some additional antistatic properties to polyester fabric. Untreated polyester fabric was outside the range of the resistivity meter throughout the entire range of relative humidity values tested. The antistatic treatment with poly(acrylic acid), o-phosphorylethanolamine, and sodium hydroxide provided antistatic properties to the polyester fabric with a surface resistivity value of 12.80 Log Ohms/Square after the equivalent of five home launderings. The grafting of o-phosphorylethanolamine to poly(acrylic acid) and polyester fabric followed by the application of sodium hydroxide improved the durability over using the phosphate ester alone. Improvement upon the use of a phosphate ester as an antistat is beneficial as phosphate esters are the largest class of antistats used. An improvement upon the antistatic properties was made by the use of poly(acrylic acid) and sodium hydroxide. The addition of poly(acrylic acid) and sodium hydroxide to o-phosphorylethanolamine provides a greater increase in antistatic properties than by increasing the amount of o-phosphorylethanolamine by the same amount. This improvement can benefit by the use of lower amounts of antistatic chemicals and therefore reducing the amount of chemicals in the effluent stream.

The cost of chemicals to treat one square yard of fabric was estimated to be \$0.2073. There is potential to purchase these chemicals in higher quantities with significantly lower prices. The costs are also based on concentrations required to achieve resistivity values of less than 11.50 Log Ohms/Square at 25 % relative humidity on 100 % polyester fabric. At 25 % relative humidity, antistatic properties at this level are difficult to obtain.

Even the natural antistatic properties of 100 % cotton cannot provide resistivity values of 11.50 Log Ohms/Square at 25 % humidity without any treatments. The

concentrations of each chemical on polyester could be reduced significantly if the resistivity values needed to be within the same range but at higher relative humidity values. The concentration potentially could be reduced further if applied to a polyester cotton blend. Both the natural antistatic properties of cotton and the functional sites have potential for minimizing the concentrations of chemicals used. The poly(acrylic acid) would be more effective in covalently bonding to the fabric as cotton has reactive sites available for attachment. Nylon is also a candidate for this treatment because of its poor antistatic properties and available functional sites.

## 6. Recommendations for Future Research

The most important future work to be done is the optimization of the processes and concentrations of chemicals used. One process that was recommended within the research is rinsing the fabric after the sample is treated with sodium hydroxide as sodium hydroxide causes irritation to the skin. The fabric should be tested to determine if the low concentrations of sodium hydroxide warrant this additional process. Further optimization of the amount of sodium hydroxide could warrant the water rinse unnecessary.

A significant amount of antistatic properties were lost after one accelerated laundering equivalent to five home launderings. An accelerated laundering could be completed on a sample excluding the sodium hydroxide to determine if the sodium hydroxide is what was being removed. The finish should also be applied to polyester fabrics that have previously been dyed to determine if the dyeing process has any effects on the antistatic properties and durability of the finish. Other factors to optimize include the temperature and duration of curing. The experiments performed were all performed keeping both temperature and the duration of curing constant. It would be beneficial to determine the impact of these variables.

Some experimental findings were not fully understood. One phenomenon included the improvement of antistatic properties after deionized water rinses at low humidity values. One potential reason was because of moisture hysteresis. To test this theory, samples could be completely dried and tested for surface resistivity throughout the humidity range starting

with the lowest humidity and working up. A comparison could be made with the surface resistivity values obtained with starting at the highest humidity and working down.

Other chemicals should be tested with the use of poly(acrylic acid). The phosphate ester can be experimented with by replacing o-phosphorylethanolamine with a phosphate ester that has a longer chain. This may provide added durability as phosphate esters have increased durability with increasing size. The phosphate ester could also be replaced with a quaternary ammonium compound which has high affinity. Another base such as potassium hydroxide could be used to replace sodium hydroxide and determine if charge carrying of the ions can be improved depending on the base used.

The textile material is suspected to have a big impact on the durability of the finish. The application of this technology should be applied to polyester cotton blends to determine if the functional groups in cotton aid in the attachment of the finish. Nylon would also be a candidate for this finish as reactive sites are available for attachment and the need for antistatic properties is also present. Successful use of this finish on nylon has potential for providing value to the floor covering industry.

## 7. References

- Alder, A., Suter, M., Giger, W., & Fernandez, P. (1996). Determination of the quaternary ammonium surfactant ditallowdimethylammonium in digested sludges and marine sediments by supercritical fluid extraction and liquid chromatography with postcolumn ion-pair formation. *Analytical Chemistry*, 68(5), 921.
- American Association of Textile Chemists and Colorists. (2007). *Technical manual of the american association of textile chemists and colorists*. New York, N.Y.: Published for the Association by Howes Pub. Co.
- Bhattacharya, A., Rawlins, J. W., & Ray, P. (2009). *Polymer grafting and crosslinking*. Hoboken, N.J.: John Wiley.
- Brenntag. Retrieved 3/9, 2010, by phone (919) 596-0681.
- Brown, T., Lemay, H., Bursten, B., & Burdge, J. (2003). In Folchetti N., Draper P. (Eds.), *Chemistry, the central science* (9th ed.). Upper Saddle River, NJ: Pearson Education, Inc.
- Cotton, Inc. Retrieved 01/19, 2010, from <http://www.cottoninc.com>.
- Edelstein, S. M. (1953). From philosopher's toy to industry's headache-the story of static electricity. *Am. Dystuff Rep.*, 42, 70.



Grossman, R. F. (1993). Antistatic agents. *15*(3)

Harper, W. (1951). The volta effect as a cause of static electrification. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, *205*(1080), 83.

Hersh, S. P. (1975). Resistivity and static behavior of textile surfaces. In M. J. Schick (Ed.), *Surface characteristics of fibers and textiles* (pp. 226). NY, NY: Marcel Dekker, Inc.

Horrocks, A. R., Anand, S., & NetLibrary, I. (2000). *Handbook of technical textiles*. Boca Raton Fla.; Cambridge, England: CRC Press; Woodhead Pub. Ltd., in association with The Textile Institute.

Kirk, R. E., Othmer, D. F., Grayson, M., & Eckroth, D. (1978). *Encyclopedia of chemical technology* (3d ed.). New York: Wiley.

Levinson, M. (1999). Rinse-added fabric softener technology at the close of the twentieth century. *Journal of Surfactants and Detergents*, *2*(2), 223.

Liu, Y., Xiong, Y., & Lu, D. (2006). Surface characteristics and antistatic mechanism of plasma-treated acrylic fibers. *Applied Surface Science*, *252*(8), 2960.

Mark, H. F., & Kroschwitz, J. I. (1985). *Encyclopedia of polymer science and engineering* (2nd ed.). New York: Wiley.

Morton, W. E., Hearle, J. W. S., & Textile Institute. (2008). *Physical properties of textile fibres* (4th ed.). Cambridge, England; Boca Raton, FL: Woodhead Publishing in association with the Textile Institute; CRC Press.

Pionteck, J., & Wypych, G. (2007). *Handbook of antistatics*. Toronto: ChemTec Pub.

Ranney, M. W. (1976). *Antistatic compositions for textiles and plastics*. Park Ridge, N.J.: Noyes Data Corp.

Sarma, S. (2009). Ionic-modified antistatic finishes Retrieved from <http://www.lib.ncsu.edu/theses/available/etd-07102009-165459/unrestricted/etd.pdf>.

Schindler, W. D., & Hauser, P. J. (2004). Antistatic finishes. *Chemical finishing of textiles* (pp. 121). Cambridge, England: Woodhead Publishing.

*ScienceLab.com*. Retrieved 2/28, 2010, from <http://www.sciencelab.com>.

Sherrill, J., Michielsen, S., & Stojiljkovic, I. (2003). Grafting of light-activated antimicrobial materials to nylon films. *Journal of Polymer Science. Part A, Polymer Chemistry*, 41(1), 41.

Shishoo, R., & Textile Institute. (2007). *Plasma technologies for textiles*. Cambridge: Woodhead.

*Sigma-aldrich*. Retrieved 11/20, 2009, from [www.sigmaaldrich.com](http://www.sigmaaldrich.com).

- Slade, P. E. (1998). *Handbook of fiber finish technology*. New York: Marcel Dekker.
- Stamm, M. (2008). *Polymer surfaces and interfaces : Characterization, modification and applications* (1st ed.). Berlin ; London: Springer.
- Stock, J., & GmbH, C. (2004). *Surfactants in producing and processing of fibres*. Berlin Germany.
- Test fabrics, inc.* Retrieved 4/05, 2010, from <http://www.testfabrics.com>.
- Tobiesen, F. A., & Michielsen, S. (2002). Method for grafting poly(acrylic acid) onto nylon 6,6 using amine end groups on nylon surface. *Journal of Polymer Science*, 40, 719.
- Tyner, D. (2007). Evaluation of repellent finishes applied by atmospheric plasma. Retrieved from <http://www.lib.ncsu.edu/theses/available/etd-02262007-091239/unrestricted/etd.pdf>.
- Uyama, Y., Kato, K., & Ikada, Y. (1998). Surface modification of polymers by grafting. *Advances in Polymer Science*, 137, 1.
- Warfield, R. W., & Petree, M. C. (1961). Electrical resistivity of polymers. *I*(2), 80.
- Wei, Q., & Textile Institute. (2009). *Surface modification of textiles*. Boca Raton : CRC Press ; Oxford; Cambridge: Woodhead; In association with the Textile Institute.

Wilche, J. C. (1757). *Disputatio physica experimentalis de electricitatibus contrariis.*

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