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**EFFECT OF CHEMICALS AND BINDERS ON THE DURABILITY
OF FLAME RETARDANT TREATED COTTON NONWOVENS**

A Thesis Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Hatice Mercimek

May 2010

DEDICATION

This thesis is dedicated to:

My family Muharrem Mercimek, Nedim Mercimek,
My Mother Ikbal Kinis, My Father Dursun Kinis,
My sister Gulseren Sezgin, My brothers Vefa Kinis, and Taner Kinis,
My supportive friends, and teachers,
for always believing in me, inspiring me, and encouraging
me to reach higher in order to achieve my goals.

ACKNOWLEDGEMENTS

I would like to thank my advisor Dr. Gajanan S. Bhat who gave me an opportunity to work under his guidance. Without his support and encouragement, this work would not have been possible. Special thanks goes to thank my committee members: Dr. Kevin Kit, and Dr. Roberto Benson for their valuable advices and encouragement.

I would also like to thank to; Prabhakar Gulgunje, Dr. M. G. Kamath, Dr. Raghavendra Hegde, and Dr. Rohit Uppal for assistance during my study and my research. I would also like to thank MSE and UTNRL staff members, especially Chris Eash. Special thanks to Cotton Incorporated and Center of Materials Processing for financial support.

I would also thank to my family especially my husband for his understanding, patience and encouragement during my life and education. I would also thank to my mom who came from overseas to make my life easier during my study. Thanks to all my family members and friends for their support.

ABSTRACT

Cotton based highloft nonwovens have been used in consumer goods such as pillows, upholstered furniture and mattresses for years. Cotton provides comfort, soft hand and cost effectiveness to these products. In contrast to its desirable properties, cotton products have a higher proneness to burning and are characterized as highly flammable materials. During the last decade, the fire safety has been an important issue, and there has been increasing focus on approaches to reduce hazardous fire risks and effects.

Incorporating flame resistant (FR) chemicals and fibers is one of the most effective methods to improve thermal resistance of cotton to ignition, and provide high degree of flame retardancy performance in the final product. The major aim of using flame retardants is to provide more time for people to escape from fire and reduce death and injuries. Most of the approaches to produce FR cotton based nonwovens are for applications where durability is not important. For some of the applications wash durability is desired and needed.

The focus of this research was to develop semi-durable and durable FR treatments for cotton rich nonwovens in an economical way using a binder fiber, going through-air bonding process and treating them with commercially available FR chemicals in the presence of a chemical binder. These FR treated webs have been evaluated for their FR performance before and after washing. Selected FR chemicals and binder types have effect on the wash durability of the produced webs.

Selection of appropriate chemicals and binders in the right combination is important so that desired degree of flame resistancy can be achieved. A neural network model was used to understand these effects, so it can help in selecting the best combination for optimum FR performance and reveal the unknown behavior of FR characteristics. Also, importance of FR chemical type, chemical binder type, chemical add on level and binder percentage based on flammability results was revealed through a statistical analysis.

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1.0 INTRODUCTION AND GENERAL INFORMATION

Cotton is a comfortable material, a natural product, a renewable resource and an environmentally friendly material. It can provide comfortable textile products due to fiber's good moisture adsorption and wicking properties. Cotton is considered as the king of fibers since it is commonly used for most of the clothing, children's sleep wear, home furnishings and mattresses. Cotton based nonwovens have been used in consumer goods such as pillows, upholstered furniture and mattresses for years. In the old days, mattresses have been filled with different kinds of materials such as straw and feathers. Today, mattresses are built with innerspring latex, foams, natural and synthetic fibers, and nonwovens [1, 2].

Like all textile fibers, cotton has a higher proneness to burning [3]. In case of fire, flammable home furnishings and textile materials can ignite easily and contribute to the development of fire. These materials are considered as the main fire risks and called as the first ignited materials [4]. In the US, every year over 3 million fires are reported and these have resulted in 29000 injuries, 4500 deaths and US\$8 billion property losses [5]. Mattress fires are responsible for 440 deaths 2230 injuries and \$274 million in property loss from 1995 through 1999 [4]. In today's World, the safety of humans and their possessions has become a very important issue due to increasing potential of flammable textile materials. Government and textile industries have been involved in investigating and developing new methods to prevent fires and reduce fire risks, and their effects [6].

To decrease the flammability of cotton, inherently flame resistant fibers such as aramids, PBI, novolids, Polyamide imides, melamine and PPS can be used in mattresses with cotton. But the drawback of using these fibers is high cost and the imbalance between cost and product properties [7]. To prevent cotton from burning, flame retardant treatment is one of the most effective methods, which improves thermal resistance of cotton to ignition, reduces flame propagation rate, elevates ignition temperature and

prevents continuous burning [8]. The major aim of using flame retardants is to provide more time for people to escape from fire and reduce death and injuries.

Using flame retardants for textiles goes back to 1735, where borax, vitreal and some other substances were used in England for canvas and linen fabric [9]. Later, cotton was treated with boric acid to impart flame resistance. Around 1821, ammonium phosphate was introduced for linen and hemp [10].

Most flame retardant chemical formulations and additives were invented between 1950 and 1980 [11]. Since this time, new systems and many kinds of products were invented and developed for rapidly growing and developing textile industry. Textile flame retardancy is particularly required in work clothes, protective clothing, children's sleep wear, carpets, military garments, furnishings, drapes and beddings [9, 12.] There are different flame retardants for different fabrics depending on many factors including construction of fiber and the blend type of the fabric [3]. Concerns over the toxological and environmental results of using such chemicals on textile materials are a major barrier to the development and application of flame retardant chemistry [11].

Flame retardant chemicals act in one or more components of combustion: heat, fuel and oxygen [7]. Bromine interferes in burning reaction, forms a protective layer and stops propagation of flame, but after burning its combustion products are toxic. Halogenated flame retardants prevent burning process and production of flammable gases. Inorganic compounds such as alumina trihydrate release water or cooling gases which dilutes flammable gases. Phosphorous compounds cause materials to char and inhibit the pyrolysis process and reduce the amount of fuel for fire. These compounds are nontoxic [13, 14].

In most of the nonwoven applications such as bedding and furniture, flame retardants have a significant role as a consequence of upgrading additives and advanced chemicals to produce the most effective fire retardant material possible [15]. Today, one of the major concerns for mattress industry is to meet the current flammability standards which

determine laws for fabric flammability. In the United States, textile flammability regulations are enforced and administered by the U.S. consumer product safety commission (CPSC) [16].

Effective July 2007, there is a new mattress standard that requires that all the mattresses sold in the US meet the flammability standard FR 1633. This standard addressing the fires by an open flame is designed to provide flame resistance that minimizes flash over and give more time for people to escape from fire. Cotton goods and nonwoven manufacturers have been seeking methods to develop FR treatments for their products to meet the open mattress flammability standard [17].

During the last decade, extensive research has been going on to develop new products to enhance FR of cotton and its consumer usefulness. The inherent properties of cotton make FR cotton the most comfortable flame retardant fabric. For some textile applications durability against water is another concern for manufacturers. Large volumes of FR chemicals used in textile industry are nondurable, which wash off completely after washing [18]. If a fabric can survive water soaking to various degrees this is called a semi durable flame retardant treatment. This type of treatment loses its effectiveness with alkaline detergent or hard water [9]. If fabrics can maintain their basic properties after multiple laundering cycles, these are called as durable flame retardant fabrics [9]. An ideal FR fabric for textile applications must be comfortable, eco-friendly, durable and cost effective.

In 1912, Chemist William Henry Perkins developed stannic oxide FR process, and claimed that garments treated with stannic oxide can withstand two years of regular usage. [19]. In 1950s, serious research was done to obtain durable FR cotton at Albright & Wilson (UK), Hooker Chemical Co., The US department of Agriculture Southern Regional Research Center (SRRC, New Orleans) and Ciba in Europe [9]. American Association of Textile Chemists and Colorists (AATCC) developed a standard laundering procedure for assessment of durability of FR products [20].

The task of developing effective durable FR systems for cotton is required but it is more complicated, more expensive and more difficult to apply compared to non-durable treatments. Durable FR treatments must meet many requirements, most of the flame retardant treated materials showed loss of tensile properties and air permeability because of high loading of chemicals [21].

Research conducted at SRRC showed that durable FR (THPC) results in significant loss in fabric strength. The combination of APO (tris (aziridryl phosphine oxide)) and THPC proved to be one of the most effective flame retardants, but APO's cost and toxic property prevent the use of this formulation commercially [19]. Some FR formulations can give high levels of flame retardancy and wash durability. However, major concern of using these formulations is a big increase in stiffness after chemical treatment. In the literature, it is possible to find many FR chemicals, finishes, formulations and techniques to impart durability to cotton fabrics. However there are only a few those can be used in practice because of environmental and toxicological concerns, commercial availability, process control difficulties, and cost of chemicals [12]. Currently the widely used commercially available durable FR chemicals are proban system and Pyrovatex CP New.

An ideal durable FR cotton treatment must impart durability to washing techniques, be easy to apply, have sufficient air permeability, cause no change in mechanical and aesthetic properties and has a quality and cost balance [22]. Today by taking the advantage of nonwoven technologies it is possible to overcome drawbacks of durable FR treatment and impart desired resiliency, strength and softness. Mostly, bedding products use highloft nonwovens made up of cotton and other fiber blends. Intimate blend of fibers can be prepared by using a well known process called as carding. The nonwoven web can be through air bonded thermally and can be used for successful nonwoven applications and FR treatments.

The focus of this research was to develop semi-durable and durable FR treatments for cotton rich nonwovens using a blend of cotton and FR fibers. Cotton based fiber webs

were treated with seven commercially available nondurable, semi-durable and durable FR chemicals in the presence of chemical binders to impart flame retardancy and wash durability. The FR chemical application to the webs was done by the dipping, squeezing and curing technique to the bonded webs.

New formulations with durable and semi-durable chemicals incorporated have a better durability against water soak and laundering. An important point in this research is to produce nonwoven fabrics that are made of mainly cotton fiber and treated with eco-friendly and non-toxic FR chemicals. Moreover, these fabrics are designed to obtain the desired level of flame retardancy with good performance properties.

2.0 LITERATURE REVIEW

2.1 Highloft Nonwovens and Cotton Blend Highlofts

Nonwoven fabrics can be defined as web structures bonded together either mechanically, thermally or chemically. They are made directly from separate fibers rather than yarns [23].

Highloft nonwoven products have been of growing interest with textile manufacturers and customers. Highloft nonwovens are produced from natural and/or synthetic fibers and have a high ratio of thickness to weight per unit area, which is an indication of high void volume. Development of through-air bonding and bi-component fibers with high melting temperature core with low melting sheath gave chance for the production of thermally bonded highloft nonwovens. Cotton highlofts which are through air bonded using a thermoplastic binder fiber can be obtained without chemical binders. This offers safer production process and working environment for employees. The core polymer of binder fiber maintains homogeneity and integrity while sheath fiber function as glue to bond the fibers [24].

Thermally bonded cotton blend highlofts are used widely in mattress and furniture industries and provide comfort, absorbency, soft hand, wash ability, cost and quality balance in the final product [25]. As it is stated before, cotton has a higher proneness to burning and cotton blend highlofts highly flammable. FR treatment may reduce flammability hazards of flammable highloft and reduce the risk of damage by increased protection [24].

2.2 Natural and Synthetic Fibers

Recently, thermally bonded highloft products have attracted interest of consumers increasingly. Thermally bonded highlofts contains no free chemicals and composed of only synthetic and/or natural fibers. Fibers used for textile and nonwoven industry can be divided into two categories natural fibers and man-made (synthetic) fibers [26].

2.2.1 Natural Fibers

These fibers are produced naturally either from plants or on animals. These fibers can be separated into two groups according to their origin cellulosic fiber and protein fiber [26].

2.2.1.1 Cellulosic Fibers

These fibers are extracted from plants, which mainly contain cellulose, and the most common known type is cotton. Cotton allows fabric to breathe because of its absorbance properties. Cellulosic fibers are economical and can be separated easily from plants. Jute, flax, ramie, sisol, kenaf, and hemp are other types of cellulosic fibers.

They can be used for paper and textile industry. Hemp is produced from stems of carrabis sative plant which can be used by designers in clothing. It can withstand water better compared to other textile products. Ramie is a cheap fiber from an East Asian plant and has a resistance to bacteria and molds. Jute is mostly used in sacks, rope, twine and carpets. These fibers are good liquid and gas absorbers and their heat conducting property is good. Flammability characteristics of these fibers are reasonably poor, as they can ignite and burn very easily [26].

2.2.1.2 Protein Fibers

Protein fibers are produced from animals and most known types are wool, silk and fur. These fibers consist of hydrogen, nitrogen, carbon and oxygen and have both acidic and

basic groups. Protein fibers wrinkle tendency is not as good as cellulosic fabrics and they can retain their shape. One of the disadvantages of these fibers is losing strength with moisture. Wool can lose 40% of its original strength and silk can lose 15% of its original strength. These fibers have higher flame resistance compared to cellulosic fibers. They do not ignite easily and can self extinguish once the heat is removed from the fabric [26, 27]

2.2.2 Manufactured Fibers

Since natural fibers have inherent properties the fiber use was limited in certain applications for thousands of years. Cotton wrinkles easily, silk requires delicate handling and wool shrinks. After developing rayon (first man-made fiber) fibers began to be used for a wide range of applications. With today`s technology one can modify and tailor fibers to improve performance characteristics [28].

The first commercial production of man-made fiber was an artificial silk and developed by French chemist Count Hilaire de Char Dornet in 1889. He built the first rayon plant. In 1931, Nylon the “miracle fiber” was developed by an American chemist. Nylon’s invention is very important because unlike rayon and acetate it is completely synthesized from petrochemicals. Later on modacrylic fiber and olefin fiber were developed by different companies [28].

In 1960’s synthetic fiber production increased by further innovation. Those fibers were modified for different purposes, and at that time synthetic fiber industry was supplying over 40% the fiber [28]

In 1970’s a demand for fire protection of fibers increased because of federal flammability standards for children’s sleepwear, carpet, and other products. Continuous innovation in the manufactured fibers industry leads to a production of numerous fibers that cannot be found in nature. Man-made fibers can be used in apparel, carpets, bedding, upholstered furniture, diapers, artificial organs, construction materials, in nonwoven products and

fabrics [28].

Most manufactured fibers produced by extrusion (fiber spinning) process. Today's most commonly used manufactured fibers are acetate, acrylic, lostex, nylon, aramids, lyocell, olefin, polyester, microfiber, and rayon [29].

2.2.3. Inherently Flame Retardant Fibers

The naturally occurring inorganic fiber asbestos cannot be totally damaged by fire. Asbestos is cheap and has reasonable properties but because of the fine structure it can be breathed easily and cause fatal cancer growth. Glass fibers are heat resistant materials, which have higher temperature resistance and insulation properties however they have limited application in protective clothing as a result of skin irritation [6]. The selection of fiber that is suitable for flame protection should be done on the basis of the specific application.

2.2.3.1 Aramids

The flame retardant polyamides are aramids. The commercial examples are Kevlar (Dupont), Nomex (Dupont), and Twaron (DSM). Aramids show resistance to high temperatures. They char with no melting around 400 °C. Nomex generally is used in protective clothing, military usage, accessories and electrical insulation paper. Nomex can be blended with Kevlar. Kevlar is the most fire protective aramid and mostly used in protective military garments and protective fabrics in vehicles [9].

2.2.3.2 Polyamide Fiber

GE introduced ultem fiber which is useful for woven nonwoven and composite applications. Ultem is a low denier flame retardant fiber [9].

2.2.3.3 PBI (Polybenzimidazole) Fiber

Celanese introduced a non flammable organic fiber, PBI. For short time exposures it can withstand 600 °C and for longer time exposures it can withstand up to 300-350 °C. It is similar to asbestos and can be used in fire blocking fabrics, aircraft seats and fire fighters [6].

2.2.3.4 Rayon

Inherently FR viscose rayon is produced by addition of phosphorous in the spinning dope before extrusion. It is commercially developed by Sandoz and Lenzig AG. This can survive alkaline laundering [6, 9].

Sateri fibers in Finland developed an environmental friendly viscose rayon fibers containing cellulose and polysilicic acid under the brand name visil, and hybrid viscose fibers comprising of polysilicic acid and aluminum ions under trade name visil AP [6, 9, 30]. The flame retardancy of hybrid is enhanced by following mechanism:

- A nonflammable char formation on fiber surface.
- The water release temperature from fiber is decreased.
- The inorganic compounds prevent the flame and show a self extinguishing effect.

These fibers can be used in blends, such as blended with modacrylics to enhance overall flame resistance [9].

2.2.3.5 Polyester Fibers

To obtain inherently FR polyester fibers two methods can be suggested:

- FR co-monomers incorporation during copolymerization
- FR additive addition during extrusion

Commercial FR polyesters are Trevira CS and Trevira FR introduced by Hoeschst [6]. Trevira CS is produced by incorporating a co-monomeric phosphinic acid unit into the PET chains [30]. Hoeschst claims that Trevira is produced by a more environmentally

friendly process compared to other artificial and natural fiber fabrics.

2.2.3.6 Melamine Fibers

Basofil is a melamine based fiber and can be used in mattress, aircraft seating , industrial protective clothing, fiction parts, and automotive insulation. It has an ability to form char without shrinkage when exposed to flame. Its denier distribution enhances thermal insulation performance [9].

2.2.3.7 Polyphenylene sulfide fibers

These fibers can be used for protective clothing because it provides flame and chemical resistance, and conserve its physical properties under adverse conditions [6].

2.2.3.8 Modacrylic

These fibers generally contain a halogenated co-monomer and they are modified acrylic fibers [31]. These fibers can be found under brand names velicren FR and SEF and typically as a copolymer of acrylonitrile, vinyl chloride and vinylidene dichloride [6]. These fibers do not melt when exposed to fire and leave a strong charred residue [31].

Similar to synthetic fibers acrylic fibers shrink when exposed to heat, but if ignited, they burn with a black smoke. So to improve its flame resistance a flame retardant compound introduced is the macromolecule [31, 6]. The flame retardant compound can be a halogen based, typically derivatives [6].

2.2.3.9 Chlorofiber

These fibers generated from polyvinyl chloride are used in furnishing fabrics, nightwear and institutional blankets. These fibers prevent oxidation by lowering the energy and combustible gases [31].

2.2.3.10 Novoloid Fibers

Kynol is produced from phenol formaldehyde resin and it is a well-known novoloid fiber.

When kynol is exposed to heat, it is carbonized with little or no smoke. But it has limitations for making apparel because of its poor strength and abrasion resistance. To improve its mechanical properties kynol can be blended with nomex or FR viscose [6].

2.2.4 Binder Fibers

Binder fibers are bi-component fibers which comprise a sheath of one polymer and a core of another polymer. The sheath polymer melts at a lower temperature and the core polymer melts at a higher temperature [32]. Typical sheath-core fiber cross-section is shown in Figure 1. Using binder fibers is an effective way to provide thermal bonding, self bulking, unique cross sections and fine fibers.

During bonding process of nonwoven with a binder fiber the sheath melts but not the core. Sheath polymer solidifies and act as a glue to bring other fibers together upon cooling [32].

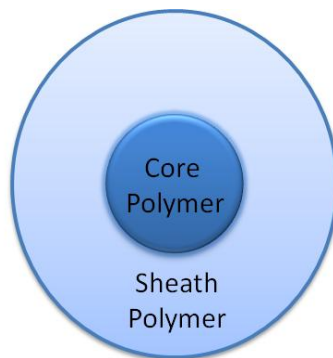


Figure 1 Bi-component binder fiber structure.

2.3. Thermal Bonding of Nonwoven Fabrics

There are three types of bonding processes; chemical bonding, thermal bonding and mechanical bonding. The thermal bonding process started in 1940's, and can meet quality requirements of the market by low energy costs. New raw materials, and improved web formation technologies support using thermal bonding for manufacturing of durable and disposable nonwovens [33].

The advantage of thermal bonding process compared to other bonding processes can be summarized as:

- Quality product
- High amount of energy saving and high economic efficiency
- Low cost machinery
- Uniform and thorough bonding with thicker webs
- No curing process and binder agents are required.
- It is a non-polluting process because of the absence of waste water and exhaust air
- Recyclable products [33].

2.3.1 Binders

Binder fibers, binding powder and binding web can be used as a binder for thermal bonding of nonwovens. Single component and bi-component fibers can be used as binder fibers. The main disadvantage of using single component is narrow temperature range whereas for bi-component a reasonable temperature range for thermal bonding is available. Powdered polymers are used as bonding powders for thermally bonded nonwovens. The most commonly used polymers are PP, PE and PET[33].

2.3.2 Methods of thermal bonding:

- Hot calendering method
- Belt calendering method
- Through air thermal bonding
- Ultrasonic bonding
- Radiant heat bonding [33].

2.3.2.1 Hot Calendering

Calendering is thermal bonding process in which applied heat or pressure applied to a fabric to get a flat surface. Area bonding, point bonding and embossing are three main types of hot calendering [33].

2.3.2.2 Belt Calendering

Belt calendaring is similar to hot calendaring except the time in the nip and degree of pressure applied. Belt calendered products are less dense and papery compared to hot calendared webs. Binders which have sharp melting and flow properties are preferred for belt calendaring [33].

2.3.2.3 Ultrasonic bending:

Rapidly alternating compressive forces are facilitated for ultrasonic bonding. This

bonding is usually used for spot or patterned bonding. If synthetic fibers are used there is no need to use a binder fiber. For natural fibers some synthetic fiber must be blended with natural fiber to bond fibers. Ultrasonic bonding can be used for quilts and outdoor jackets [33].

2.3.2.4 Radiant Heat Bonding

Usage of a radiant energy source in the infrared range is essential for radiant heat bonding. The web temperature is increased by the absorption of energy radiated from the source. Upon the removal of the radiant heat source binder solidifies to bond the webs [33].

2.3.2.5 Through Air Bonding

In through air thermal bonding process nonwoven web exposed to hot air. The hot air flows through openings above the nonwoven. But not pushed through the nonwoven like hot air ovens. Negative pressure pulls the air through the nonwoven, allowing rapid and even transmission of heat. Crystalline binder fibers, bi-component binder fibers and powders can be used in through air thermal bonding. For sheath/core configuration of binder fiber, the sheath is the binder and the core act as the carrier fiber. The main properties of products produced using through air bonding can be listed as: bulky, open, soft, strong, breathable, extensible and absorbent [33].

2.4 Chemical Bonding

In the last century, in order to provide structural integrity all nonwovens required a chemical binder. Much effort has been put into the development and improvement of chemical binders. Binders contribute to improvement in nonwovens performance [34].

In early stages, different types of natural resins and glues are applied to bond nonwovens. Although these give some integrity and strength to webs they had many drawbacks. In 1960s, acrylic based latex binders were introduced to achieve strength as well as stiffness. Despite their price, these binders are still used in nonwovens industry [34].

Synthetic binders have been available with varying binder strength durability and other properties. Cross-linkable and self cross-linking binder introduction are very important for durable nonwovens where durability against wash and dry clean property is desired. Properties desired in a binder can be summarized as:

- Strength
- Flexibility
- Adhesion to fiber
- Resistance to washing and dry cleaning
- Color retention at reasonable cost
- Specific requirements such as chemical and flame resistance [34].

2.4.1 Chemical bonding process

Binder application process include three steps

1-binder application to the nonwoven web

2-curing and removal of moisture or solvent

3-formation of strong bond between the binder and the nonwoven web

The chemical composition of monomer has affect on stiffness/softness properties strength, elasticity, durability and aging. The functional group of binder determines the solvent resistance, adhesive characteristics, and cross-linking nature.

Chemical binders can be applied to webs in differing percentages from about 5% to 60% by weight. The mostly used bonding techniques include saturation, spray, foam, print and powder bonding [34].

2.4.1.1 Saturation Bonding

This bonding may be used together with processes which require rapid binder addition, strength, stiffness and high fiber encapsulation. Fiber is encapsulated by totally immersing the web in a binder solution or by flooding the web near the point of pressure rolls. Excess binder solution is removed by vacuum or roll pressure. Drying can be done with steam heated drying cans or through air ovens. Binder addition can vary between 20% and 60%. This process is simple and strength, softness or amount of binders can be controlled [34].

2.4.1.2 Foam Bonding

In this technique, binder can be applied at low water and high binder solids concentration. It uses air and water as a carrier medium for binder. The foam is produced by passing air into binder solution while agitating the binder solution can include stabilizing agent in order to prevent collapsing during application and curing. This process requires less energy and less binder migration. But it is difficult to control the process and foam levels [34].

2.4.1.3 Spray Bonding

In this technique, binders are sprayed onto moving webs. The binders are atomized by air pressure, hydraulic pressure or centrifugal force, and applied to upper surfaces of the web. After spraying, the web is passed through a hot oven to remove water and achieve curing. This method is preferred for fabric application that requires the high loft maintenance [34].

2.4.1.4 Print Bonding

Print bonding is used for binder application to predetermined areas. It is a preferred application method when it is required that a part of the fabric be binder free. Many light weight nonwovens employ this method. Printing patterns can be changed to enhance the strength, softness and absorbency. Two types of printers can be available: rotary screen and rotogravure printers. Outstanding softness of nonwovens with proper strength can be achieved by using print bonding method [34].

2.5 The Process of Combustion and the Combustion Cycle

One of the most effective methods to provide personal safety, and decrease personal and property losses caused by fires is the use of flame retardant chemicals. To understand FR mechanism better, it is necessary to understand combustion process and combustion cycle.

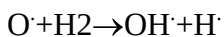
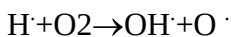
Combustion can be defined as the oxidative reaction of an organic compound which has propagation based on nature of combustible material and thermal energy generated. Combustion consists of generation and emission of heat and light which makes the phenomenon visible. The emitted light color depends on the released amount of energy [31].

The kinetics of a solid material depends on physical factors which makes it complex process. Combustion can improve slowly with smoke emission or quickly with the production of flame. The combustion products depend on the amount of available oxygen and the structure of the flammable material. Flame can be defined as is the visual sign of the light emitted from the combustible material in the gas phase [31].

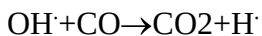
The basic combustion cycle of a solid material, like a textile material, is given in Fig. 2. When a material is exposed to a heat source, the temperature of the material will increase. At a critical ignition temperature and heat transfer rate pyrolytic decomposition of the substrate will occur with release of heat and combustion gases [31, 35]. The gases of this decomposition consist of combustible gases, non combustible gases and carbonaceous char. The decomposition temperature depends on the combustion atmosphere and the nature of the solid material [36].

The combustible gases mix with ambient air and react with its oxygen to produce highly reactive $H\cdot$ and $OH\cdot$ radicals. These radicals play important role in the chain reactions that

lead to decomposition and sustain the burning process. The pyrolysis reaction in combustion cycle can be simply shown below: [35].



The exothermic reaction that produces the thermal energy in a flame is:



The H radicals produced in the reactions turn back into reaction so, the fire becomes a self supporting process which continues as long as enough oxygen is available in the environment. Combustion propagates until the supply of combustible gases becomes insufficient to support burning process [31, 35]. If the solid material does not decompose into flammable gases, it will smolder slowly with smoke emission and self extinguish. If the material becomes a char and form a barrier it will stop penetration of flame to the underlying material [13].

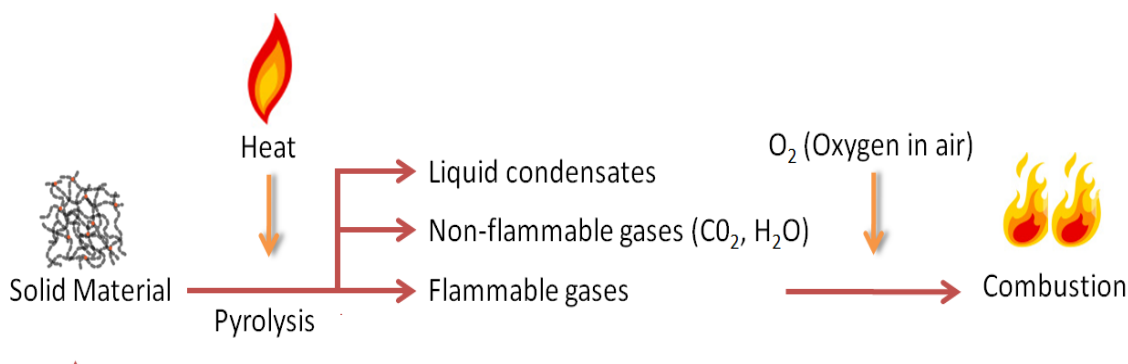


Figure 2 Combustion of a solid material.

2.6 Mechanism of Flame Retardancy

Throughout the history, fire has been a major reason for death and property losses. Modern technology improved flame retardant chemicals to reduce the possibility of burning of wide range of textiles, plastics, and electronics used in commerce and in

homes. it is estimated that hundred million dollars worth of property has been saved by using flame retardant chemicals [37].

The earliest FR formulation was the usage of alum to reduce the flammability of wood around 450 BC. By around 200 BC, to improve fire retardancy in wooden buildings ancient Romans used vinegar with alum. In the mid 1600s, mixture of clay and gypsum was used to reduce flammability of theater curtains. In the early 1870's alum, ferrous sulphate and borax were used for wood and textiles. Ammonium phosphate was introduced for linen and hemp around 1821 [10]. Since then, science and technology of flame retardant has resulted in the use of more than 175 different flame retardant chemicals to fulfill a variety of flammability requirements for different applications [37].

The objective of flame retardants is to prevent the ignition of materials and reduce the flame propagation. The flame retarded materials minimize fire risk but not completely became non-flammable. They function at different stages of the burning process, and allow people more time to escape (Figure 3). Flame retardants decrease ignition time, development of smoke flame propagation, toxic gases release and heat release rate [38]. The flame retardants prevent a small fire from becoming a huge hazard. If a fire is fully developed the flame retardant material will decompose and it cannot become effective in the burning process.

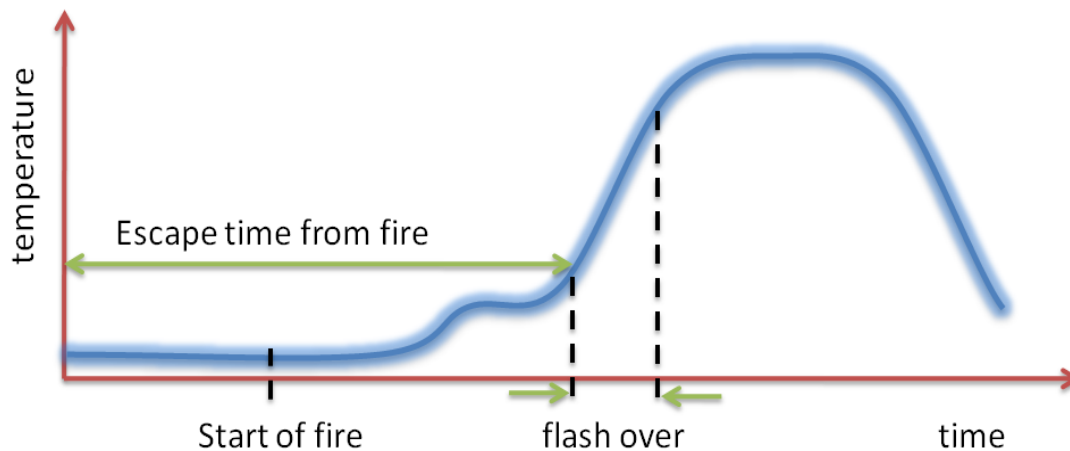


Figure 3 Phases in a fire.

2.6.1 Mode of Action

First patent of flame retardant was obtained by Obdiah Wilde for canvas that used in theaters and public building in 1735. In 1970s usage of flammable materials increased which led to wider usage of flame retardants to break combustion cycle by affecting chemical or physical process occurring in one or both, the gas and condensed phases [10].

Flame retardants function by chemical and/or physical ways in the solid, liquid or gas phase during the particular stages of burning [36, 39]. Flame retardants prevent combustion during particular stages of the fire process e.g. heating, decomposition, ignition, or flame propagation [39]. The physical action of the flame retardants consists of:

- Formation of a protective layer: The chemicals can prevent heat transfer from the heat source and prevent oxygen flow to the flammable material. Also they prevent the supply of pyrolysis gases to the material surface. This mechanism can be observed in phosphorus compounds, silicon compounds, basic base additives and inorganic borates [36, 39].
- Cooling effect: The chemical can trigger the endothermic process which cools down the substrate to a temperature so that ignition temperature is not reached. ATH acts are in this way [36, 39].
- Dilution effect: The additives evolve non-flammable decomposition gases and dilute the fuel in gas and solid phases, so that the flammable gases concentration falls under the ignition limit and it cannot ignite [36, 39].

The most important chemical reactions that flame retardant act in combustion process take place in the solid and gas phase [36].

2.6.1.1 Reaction in the Solid Phase

Two mechanisms can take place in solid phase. One reaction is the accelerated breakdown of polymers by the flame retardant. Second reaction, where FR additive by dehydrating action can cause an insulating layer of carbon (char) formed on the polymer surface [36, 39].

Most phosphorous compounds are effective flame retardants by formation of char. The flame retardant action of phosphorous compounds in cellulose is to propagate by initial phosphorylation of cellulose. The phosphorylated cellulose breaks down to water phosphoric acid and unsaturated cellulose and finally becomes char. Some nitrogen compounds synergize the flame retardant action of phosphorous on cellulose [10].

2.6.1.2 Reaction in the Gas Phase

Flame retardant can terminate the free radical mechanism of the combustion process which takes place in the gas phase. This cools down the substrate and reduces combustible gas supply [36, 39].

2.6.2 Types of Flame Retardants

2.6.2.1 Reactive and Additive Flame Retardants

Flame retardants can be incorporated in the polymer matrix, or as in textile can be positioned on the material. Flame retardants that can be added by reaction are called reactive flame retardants, and these that can be mixed with polymer are called additive flame retardants [14]. Reactive FR additives form chemical bond and cannot migrate from the polymer matrix. Those additives are more expensive than additive FRs. Their application is particularly in duroplastics such as polyester resin, polyurethane. Additive flame retardants can be introduced during polymer production or thereafter. Since these are not chemically bond to polymer, they can be released easily from the polymer matrix. These additives are mainly used in thermoplastics [14].

2.6.2.2 Important Flame Retardant Groups

2.6.2.2.1 Inorganic FR

ATH: It is one of the inorganic compounds that can be used as a FR. This FR additive starts to decompose at 200°C to aluminum oxide and water. The water becomes a barrier for flame and prevents flame from reaching the material surface. It slows the burning by absorbing heat [13].

Antimony trioxide: This compound is not used as a FR on its own, but it can be used in combination with other flame retardants such as halogenated FRs. The addition of antimony compounds enhances the decomposition of halogenated FR to active

molecules. It functions as a catalyst for the FRs. They can also release volatile compounds, which increase the efficiency of the halogenated FR in the burning process [13].

Magnesium hydroxide: This compound can be used for higher processing temperatures as a result of its decomposition temperature around 300°C. Its function in flame retardants has the same mechanism as ATH [13].

2.6.2.2.2 Halogenated flame retardants

Halogenated FRs are generally divided into two groups, chlorinated and brominated FRs. These compounds are active in the gas phase; they remove the hydrogen and hydroxyl radical in the vapour phase. These radicals interfere with the burning process in the production of flammable gases. They can reduce the concentration of fire and terminate fire. At high temperatures these compounds release Br or Cl which react with combustible gases to give HBr or HCl. Then HBr or HCl remove hydrogen and hydroxyl by reacting with these radicals to produce water [13]. Brominated FRs is usually 50%, to 85% of bromine with different properties and act in vapour phase (flame retardant coatings). They can be in liquid powder and pellet form. Disadvantages of those halogen compounds are that they produce corrosive gases (HBr, HCl) and high levels of fume [13]. Even though they are effective and less expensive, they are considered as environmentally hazardous chemicals.

Today non-halogen systems are favored by the FR chemical researchers. The most used halogenated FRs are HET acid, chlorinated paraffins, polybrominated diphenylethers (PBDEs) hexabromacy decadecone (HBCO), tetra bromobisphenol(TBBPA), and brominated polystyrene [14, 40].

2.6.2.2.3 Phosphorous compounds

These compounds act primarily in the solid phase and during heating. They produce phosphoric acid [14, 38], which in turn reacts with the substrate to become a char,

forming a carbon layer. These flame retardants include both inorganic and organic compounds. By forming a carbon layer these compounds prevent further supply of oxygen and flammable gases which makes progression of flames difficult [38]. Phosphorous as a halogen –free alternatives have with great market acceptance, and development for these compounds are very promising [41]. Most important phosphorous compounds are:

- Phosphate esters, they are commonly used in engineering plastics [40].
- Phosphanates and phosphinates: they are used in flexible PU foams for automotive and building application [40].
- Red phosphorous: they are mainly preferred in PA6 and PA66 applications.
- Ammonium polyphosphate is one of the most commonly used FR. in textiles

2.6.2.2.4 Nitrogen based Flame retardant

Nitrogen based FRs have several affect on flame. In the condensed phase they form a cross-linked structure by transformation of melamine which inhibits combustible gases formation. In the gas phase, they release nitrogen or ammonia gas, which dilute flammable gases and reduce flame. Nitrogen based compounds act in synergy with phosphorous based FRs and most of them are based on melamine compounds [38].

2.6.3 Intumescent Coatings

Intumescent coatings were first reviewed in 1970s and primarily applied to paint [39]. Intumescent materials provide a thick fire protection layer by a decomposition process at high temperature, which cause the material to swell into a thermally stable char layer [35]. Intumescent coatings have appearance similar to paint and consist of combination of different products such as [13].

- An inorganic acid source which release an organic acid when heated
- A binder which leaves a thick liquid

- A blowing agent (spumific) compound which releases nonflammable gases [13].

These compounds must undergo a series of decomposition mechanism and physical processes. The flame retardancy of intumescent coatings occur as

- The inorganic acid releases between 150 and 219 °C based on an acid source.
- Esterification of carbon rich compounds at higher temperature (temperature above acid released temperature).
- Melting of the materials during esterification
- Carbonizing the material into foam because of released gases of reactions.
- The foam strengthens and solidification occurs through gelation [39].

The majority of intumescent coatings used zinc borate, ammonium phosphate, melamine phosphate and organic esters as the acid source. Blowing agents are generally nitrogen compounds such as urea, melamine, guanidine etc.

Intumescent coating systems are mostly based on ammonium polyphosphate (acid source) melamine and its derivatives (as blowing agent) and pentaerythritol derivatives as char forming agents [6].

A good intumescent system can expand 50 to 200 times the original thickness [35]. Intumescent coatings are effective in reducing flame propagation and heat release rate and preventing combustion. As an insulator, the foam layer prevents the heat transfer to the polymer and mass transfer from the polymer to the flame [39].

The disadvantages of intumescent systems can be summarized as; poor bonding with substrate, poor durability and aesthetic features, rapid aging and low resistance to wear and erosion [35].

2.6.4 Performance Criteria and Choice of the Flame Retardants

The selection of suitable flame retardants for textile applications depends on different factors which can be listed as:

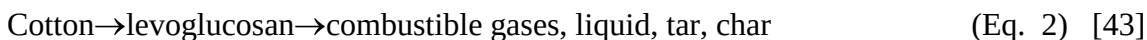
- Flame retardant chemical's potential risk on human and environmental health
- Flammability characteristics of the textile
- The test method that is used to evaluate flame retardancy. Some tests need low level of flame retardants while some need high deposition of effective flame retardants to pass the test.
- Application process of the flame retardant material
- Chemical properties of flame retardant (resistance to water, solvents, acids, bases, oils etc).
- Durability of the flame retardant (resistance to cleaning with water or other cleaning techniques)
- Cost and performance relationship
- Minimal alteration to the physical properties of the fabric (texture, smell, strength) [10].

2.7 Cellulose Burning and FR Mechanism in Cellulose

Burning of cellulose is an oxidation of the material when exposed to heat source which consumes combustible gases, liquids, and solid residues generated during the pyrolysis of materials [42]. The pyrolysis of cellulose is a very complicated chemical process and is supposed to involve two different pathways and takes place above 300 °C. The first mechanism involves dewatering and charring of cellulose, omitting water, carbon dioxide and solids (Eq. 1) [42].



According to second mechanism the cellulose produces non-volatile liquid levoglucosan and cleavage of levoglucosan generates more combustible low molecular weight products, liquids and char [42, 43]. These combustible gases sustain burning and propagation of combustion. This process can continue until char is left. The carbon content of the decomposed products increases and char formation occurs (Eq. 2) [43].



The combustion of char occurs at 600 °C in two steps. First step is the conversion of carbon into carbon monoxide via surface reaction, and the second step is the conversion of carbon monoxide into carbon dioxide (Eq.3, Eq.4) [42].



Since one of the effective ways to make cellulosic fiber more resistant is to use a flame retardant. The pyrolysis of flame retardant cellulose fiber the similar pathways, but exhibits lower decomposition temperatures and reduced formation of combustible gas products (aldehydes, ketones, furans, furfural and nucleoglucosan) due to gas scavenging effect. But flame retardant treatment lead to higher char yield compared to untreated cotton. The amount of water and carbon dioxide released were increased for flame retardant treated cellulose. [42]. Phosphorous based FR imparts flame retardancy to cellulose fiber by this mechanism [44]. Phosphorous compounds decompose to phosphoric acid, which catalyzes the cellulose dehydration reaction, and prevents flame spread. Phosphate derivatives can inhibit afterglow reaction by suppressing levoglucosan formation [42].

2.8 Char formation and Char Forming FRs for Cellulosic

When a polymer burns, it can produce volatile fragments which can ignite when exposed to oxygen or it can form an inert insulating char. This char can be a barrier to inner component from further heating and it can prevent combustion. The aim of flame resistant materials is to promote char formation. In general, char can be defined as a highly cross-linked porous solid and its production consists multiple processes [45]. The most effective flame retardants are those which can transform a combustible polymer to a char structure. This type of FRs do not burn in air and provide a continuous barrier to flame. Char promoting FRs has important place in fire protection [30].

Most phosphorous and nitrogen based flame retardants decrease flammable volatile production and accelerate char formation in cellulose. These compounds can prevent formation of levoglucosan which acts as a precursor for flammable volatile formation. The actual mechanism of char formation of cellulose is little understood. Char yield increases with increase in non-crystalline content, and it is related to cross-linking reactions where cellulose dehydrates to form ether links [30].

The char formation is increased by phosphorous and nitrogen synergism. Flame retardants such as phosphorous salt condensates, Proban CC, Pyrovatex CP and ammonium polyphosphate, produce greatest char in the 300-500 °C range. These retardants generate high levels of aromatic volatiles such as benzene, toluene and phenol after pyrolytic decomposition [30].

2.9 FR Treatments of Cellulosic Fibers

2.9.1 Non-durable FR treatments of Cellulosic Fibers

Non-durable FR treatments involve water soluble chemicals that can be wash off with plain water. These treatments can withstand non-aqueous laundering with dry cleaning solvents. These chemicals can be applied by padding or spraying of aqueous solution. These can be used on products that will not be laundered such as disposable medical gowns, party costumes and wall coverings [9]. Most commonly used non-durable FRs are borax, boric acid, di-ammonium phosphate monoguanidine dihydrogen phosphate, and diguanidine hydrogen phosphate. Also same cheaper water soluble organophosphorous compounds can be used for non-durable or semi-durable FR chemical treatments [9].

2.9.2 Semi-durable FR treatments of Cellulosic Fibers

These treatments can resist water soaking to changing degrees but cannot survive multiple launderings. According to BS 5852 standard, a semi-durable FR fabric can survive soaking in water at 40 °C for 30 minutes [9]. Semi-durable treatment can be used for tents, carpets and curtains [36]. Another definition is that these treatments can be bound to the cellulosic fabric, but lose its effectiveness with alkaline detergent and/or hard water. As a result of breakdown of the phosphate to cellulosic bond, alkaline detergent destroys the flame retardancy of the fabric. Semi-durable treatment cannot resist alkaline laundering. Also in hard water Ca, and Mg cations can be captured by phosphate groups and reduce flame retardancy [9].

One method to obtain semi-durable FR cotton is boric acid and urea treatment as shown by Ciba researchers. Recently, Pyrovatim PBS introduced by Ciba, now marketed by Hunstman, is a popular semi-durable FR. This is a phosphorous based product which can be used for non-durable and soak durable applications. Pyrovatim PBS contains salts of polyethylene with aminoalkylphosphonic acids. The treated fabric should be cured at 160 °C for 160s or 170 °C for 90s to obtain a soak durable FR treatment. Pyrovatim PBS can be applied to interliners, upholstery, curtains, and protective garments [9].

Back coating is another method of semi-durable FR treatment which is commonly used in carpets. Horrocks showed that ammonium polyphosphate in combination with char formers such as pentaerythritol are effective in back coatings on cotton fabric. If greater wash durability is desired, coated ammonium polyphosphates (Clariant's Exolit AP-462 and Budenheim's FRCROS 487) developed and marketed as eco-friendly replacements for the decabromide back coatings are available. Phosphorous containing coatings perform as intumescent which form a foamy char when expose to heat source. Backcoatings with a volatile phosphorous containing flame retardant such as Antiblaze CU, Fyrol 5I or tributyl phosphate provide effective semi-durable treatments. Ammonium polyphosphate, pentaerythritol and melamine combination under the trade name Akro fireguard can be used in carpet back coatings [9].

2.9.3 Durable FR Treatments of Cellulosic Fibers

In the published literature, it is possible to find a lot of different methods for imparting durable FR treatments to cellulose. But few of them are commercially available, and more mostly based on phosphorous compounds. Mostly used and available durable FR systems for cotton are THPX finishes and reactive phosphorous based FR (Pyrovatex CP New) [12].

2.9.3.1 THPX finishes for cellulosic fibers

The most popular durable commercial product in use about for 50 years, is that based on tetrakis (hydroxymethyl) phosphonium salts (THPX), originally developed by Albright & Wilson in the UK. The basic research was carried out by the US department of agriculture southern regional research laboratory in New Orleans [9]. The reaction between formaldehyde and phosphanite in the presence of acid, generally hydrochloric or sulfuric is the basis of the THPX chemistry. The reaction is shown below (Figure 4) [9].

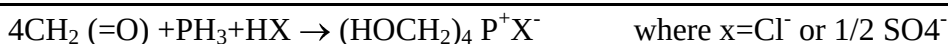


Figure 4 THPX formula.

The concern of the chloride is that small amount of free formaldehyde in the product could form volatile carcinogenic bis(chloromethyl) in the work area [9].

A rich literature is available on the ways to treat phosphonium salts with many kinds of ureas, melamines etc. with cellulose. Proban process is the most popular successful way of using THPX chemistry. In this process THPX is reacted with urea before being applied to cotton in the solution PH adjusted to 5-8. Then cotton fibers are dried and cured with gaseous ammonia in a special ammoniation chamber. After curing, the finish is treated with aqueous hydrogen peroxide to form the end product with a network of $\text{NCH}_2\text{-P(=O)-}$ linkages. This end product has no hydrolyzable links and it is very stable phosphine oxide structure. As a result, this finish can withstand 100 launderings with alkaline detergents [9].

Proban treatment can be used for military applications, hotels and nursing institutions. This process produces fabrics with a fairly soft hand and maintains good tear strength. Treated fabric does not melt or cause flame propagation, but it chars when exposed to flame. A drawback of this process is the requirement for a special ammoniation chamber which cannot be found easily. Since ammoniation chamber is not available in most textile finishes new applications have been tried on THPX process not using gaseous ammonia. American Cyramid has patented a method that uses aqueous ammonia [9].

2.9.3.2 Pyrovatex CP

Pyrovatex CP which is often called N-methylol dimethyl phosphonopropionamide and has a chemical formulation shown in Figure 5 [9].

It is a water soluble product with less bound formaldehyde. Prof. Horrocks and Roberts performed studies to reduce formaldehyde release of Pyrovatex CP New. Prof Horrocks's Laboratory and Ciba developed low formaldehyde grade Pyrovatex CP. Pyrovatex CP

and low formaldehyde grade Pyrovatex CP can pass European Oeko-Tex environmental standard [9].

Under acid –catalyzed environment, Pyrovatex CP New can react with cellulose to form aminol linked structures, mostly on the 6-hydroxyl groups of the cellulose. A nitrogen resin can enhance the phosphorous fixation with Pyrovatex CP. The nitrogen resin can also increase flame retardancy and laundering durability of cotton. A Pyrovatex CP treated cotton textile can withstand 50 or more launderings. But, it is more affected by hypochloride bleach treatment and not as durable as proban treatment [9]. To increase bonding of pyrovatex to cellulose, it can be applied with a methylated melamine resin [12].

The advantage of Pyrovatex CP New is that it does not require any special equipment [6, 12]. Newer versions of Pyrovatex CP New have much improved strength retention [9]. In addition to phosphorous loss alkali metal cations built up from detergent and hard water cations is another problem of Pyrovatex CP New during launderings. This problem can be eliminated with soft water usage [9].

2.9.3.3 Other Durable Finishes for Cotton

A UK company Firestop introduced “noflan, a phosphorous-chlorine based product (mixture of ammonium salt of methyl phosponoamide acid and ammonium chloride) shown in Figure 6. This product is water soluble but when it is cured with melamine formaldehyde resin and urea it can withstand multiple launderings. This product is advised for use in plain cotton or polyester-cotton blends [9].

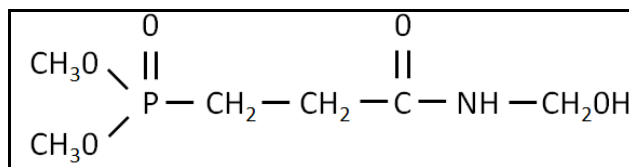


Figure 5 Pyrovatex CP formula [46].

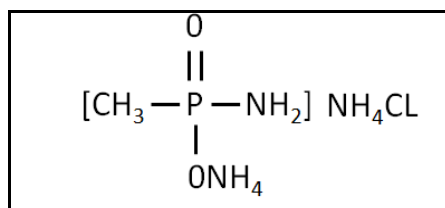


Figure 6 Noflan formula [9].

Amgard LR1 and Amgard LR2 for application to cellulosic or cellulosic rich blends are new systems that provide good soaking durability. These chemicals are ammonium polyphosphate based solutions [6]. Ammonium sulphamate with urea or urea based cross-linking agent can be applied to cotton fabrics by a pad-dry-cure method. Treated cotton fabrics can pass vertical strip test after 50 hard water alkaline launderings [6].

2.9.4 Thermosol Flame Retardant Treatment of Polyester Fabric

Early version of thermosol involved the use of tris (dibromoprophyl) phosphate but after 1970s because of its carcinogenic nature this compound was removed from market. Today, Rhodia's Antiblaze 19 or Amgard CU can be used as a major product in thermosol treatment [9].

The process involves applying the phosphate by aqueous padding and then drying the fabric at 190-210 °C for about 30-40s. The fibers swell, and the phosphanate migrates into the fibers. The flame retardant is held tightly upon cooling [9]. Thermosol treatment of Chemtura's CD 75 M uses hexabromocyclododecane applied as an aqueous solution and dried at 180-205 °C, which allows passing NFPA-701 flammability test after multiple launderings [9].

2.9.5 Coating with Bromine-containing Emulsion Polymers

The emulsion contains 35-45% bromine, poly (pentabromobenzyl acrylate) which is available as 40% solid aqueous emulsion (Textron from ICL). This method is mainly suitable for 100% polyester and for cotton polyester blends. It can provide a flame retardants finish which can withstand to AATCC standard home launderings. This emulsion can be applied to apparels bedding, awning liner and work wear [9].

Water-borne dispersions are available with copolymers of pentabromo benzyl acrylate. These dispersions can be resistant flame retardant finishes or back coatings. These polymeric finishes have environmental and toxicological advantage over non-polymeric bromine flame retardants because polymeric additives are retained by the substrate [9].

2.9.6 Recent Techniques to Obtain Durable FR

One of the major concerns for flame retardants is environmental hazards of the chemical. An important approach in flame retardant textile is to develop eco-friendly flame retardant fabrics. Chitosan is an aminopolysaccharide obtained by alkaline deacetylation of chitin which is a natural material. Chitosan addition during the phosphorylation of the cotton fabric is claimed to give an eco-friendly textile with a reasonable price. In this process, Chitosan was dissolved in a citric acid solution and added to phosphorylation bath containing diammonium phosphate butanetetracarboxylic acid and sodium hypophosphate. Chitosan functions as a nitrogen source and has synergistic effect with

the phosphorous compound. The treated fabric is found to have good wash durability [43].

One method to obtain durable FR is application of encapsulated FR and thermo bonded to the fabric. Boric acid encapsulated in a polymeric blend, which preserves the softness and drape of the fabric. This application survives multiple washings in an economical way. [47].

The researches to obtain cellulose with durable FR quality with cost effective eco-friendly formulations seems to be very promising for today and future textile application

2.10 FR Tests and Regulations:

2.10.1 FR Tests

FR tests are designed to determine the fire risk of materials and products for the application which they are required. Most tests measure the ignition temperature, ignition time, flame time, char length, char area, mass loss, and flame propagation rate. It is more important to select a proper flammability test procedure to get accurate results. The test selection must be based on the type of the fabric to be tested, type of the flame, and flame exposure time. The product must satisfy fire safety requirements defined in the tests ASTM and BSI test methods. [26]. The most popular test for textile materials are limiting oxygen index (LOI), vertical flammability test, horizontal test, 45° angle test and small open flame test (TB604 or 16CFR part 1634).

2.10.1.1 Limiting Oxygen Index (LOI)

Oxygen index method describes the tendency of a material to sustain a flame and widely used to evaluate flammability of polymeric materials. LOI is the minimum oxygen concentration that is sufficient to sustain the flame in a controlled atmosphere of oxygen

and nitrogen [48]. It is a convenient reproducible and inexpensive way of determining numerical measure of flammability [49].

LOI testing can be done according to ASTM 2863. ASTM 2863 is a method to determine the minimum oxygen concentration in an oxygen/nitrogen mixture that will support flaming burn in a specimen. According to ASTM test sample size should be 50mm width and 150mm length. The test sample positioned vertical by placing in a transparent test column and mixture of oxygen and nitrogen is passed in upward direction through column. The sample is ignited at the top by using a flame. The oxygen concentration is adjusted until the sample support sustained burning. A schematic of LOI test setup is shown in Figure 7.

The volume fraction in the O_2 and N_2 gas mixture is defined as the LOI. LOI is commonly reported as a percentage rather than fraction [48]. The effectiveness of fire retardants is determined by the change of critical oxygen concentration they can induce as a function of concentration [49].

It is useful to assign materials into experimentally meaningful groupings based on their LOI. Since air comprises about 20.95% oxygen, if a material's LOI is less than this, it will burn easily in air. So 20.95% can be considered as a threshold value while grouping of materials. According to the most researchers a classification of the materials based on LOI can be done as shown in Table 1 [49].

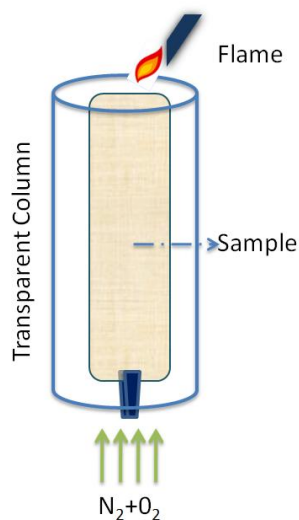


Figure 7 Schematic of LOI test setup.

Table 1 Classification based on LOI values

LOI < 20.95	Flammable
LOI = 20.95	Marginally stable
21 < LOI < 28	Slow burning
28 < LOI < 100	Self extinguishing
100 < LOI	Intrinsically non-flammable

It is good to remind that this classification is specific to limiting oxygen index test, for another test the result can be different and it is not necessary to agree with other test results. In limiting oxygen index test the high LOI value means the safer material [49].

2.10.1.2 Vertical flammability test

This test is designed to determine the flame resistance property of fire retardant fabrics. According to federal test method standard 191A method 5903, the sample is held vertically while 35mm flame is positioned to ignite the fabric at the bottom edge. The

flame is removed after 12sn. The char length and afterglow is measured after the flame extinguished this test means fabric will sustain combustion if it passes the test. Vertical flammability test makes it possible to measure various parameters simultaneously. It is good to remind that as hot air rises, the vertical position of sample allow the flame to propagate faster [26].

2.10.1.3 45° Angle Test

The 45° angle test is similar to vertical test but the fabric sample is mounted in a frame and held at an angle of 45°. The flame is applied to the bottom of fabric for a certain amount of time. The flame propagates up to the length of the fabric. The time required for flame to propagate through the length of the fabric, and ease of ignition are measured and recorded. Most textile materials can be evaluated using 45° angle test except children's sleep wear, protective clothes, footwear, hat and gloves [50].

2.10.1.4 Small open flame test (TB604 or 16CFR part 1634)

In January 2005, consumer product safety commission published an open flame standard for top of the bed items such as pillows, comforters and mattress pads etc. [9]. TB604 is a laboratory scale test for open flame standard. In this test the fabric specimen is held wrinkle free in a horizontal position and ignited with a small open flame (flame length 40mm) at the center of the fabric. The flame is removed after 20s and the fabric allow burning for over 6 minutes until combustion ceases. The specimen passes the test if the weight loss does not exceed 25% of the initial weight. For a mattress pad the specimen passes the TB604 test, if the flame does not create a void more than 50mm in diameter [51].

2.10.2 FR Regulations

In 1953 the flammable fabrics act was passed to regulate the production of high flammable clothing. In 1967 it was amended to permit regulation of a wide of range clothing and interior furnishings. In 1972 the consumer product safety act was passed

which created Consumer Products Safety Commission (CPSC). After that time, responsibilities under FFA transferred to CPSC [52]. Presently, in the U.S. federal textile flammability laws, standards and regulations are administered and enforced by CPSC. CPSC issues much educational news, warnings, and recalls unsafe products [16].

The state of California has developed mandatory and voluntary standards for upholstered furniture and other products. Also they developed independent standard organizations such as ASTM, NFPA, and ISO [12]. Statistics show that UK and California flammability regulations have been very effective in saving lives and property [9].

There are many flammability regulations around the world which varying from country to country. In U.S., regulations for upholstered furniture and other furnishings can vary from state to state, even from city to city. The flammability of materials is determined by LOI tests, open flame tests, cigarette and pill ignition tests, etc. The results of these tests determine if the fabric or fiber is acceptable for a specific use. For textile manufacturers it is important to follow the flammability regulations and standards [12].

2.11 Advantages and Disadvantages of Durable Flame Retardant Treatment for Cotton Based Nonwovens

The advantages of durable FR treatment can be summarized as;

- Durability to water washing or other washing techniques which is an important performance criterion for some application
- Durable flame resistance to range of fabric and fiber constructions; in other words protective properties of the product will be retained after regular use.
- Char formation with phosphorous based FR products

Flame retardants and durable flame retardants can have some adverse effects on fabric. These effects can be listed as [21].

- Change in mechanical properties such as lowered tensile, burst and tear strength, and loss in abrasion resistance
- Lowered air permeability due to deposition of FR chemical to impart FR properties
- For some treatments, increase brittleness
- Color change of the fabric due to high curing temperature
- A harsh handle
- Some applications such as proban treatments need special requirement which increase the total cost of the application process.
- Change in outward appearance and aesthetics of the fabric

Cotton based nonwoven webs may exhibit structural changes. But nonwoven techniques are available to offer suitable solutions and optimizations to overcome these drawbacks of FR treatment. An effective durable flame retardant treatment is still a challenge. So, cotton based nonwovens can be obtained with desirable mechanical structural and physical properties to supply the durable FR systems for cotton.

2.12 Overview of Research

This research is set to produce semi durable or durable FR treatments for cotton based nonwoven webs that are imparting flame resistance with some wash resistance. The nonwoven webs are produced by through air bonding of cotton fiber, FR fibers and binder fiber and treating them with commercially available FR chemicals and binders. An important aspect of this research is to treat fabrics with eco-friendly and nontoxic chemicals in an economical way. These treated webs are evaluated for their FR characteristics before and after washing. Also, wash durability performance and mechanical properties of webs are characterized with appropriate methods.

One of the other objectives of this project is to optimize chemical and binder combinations to get some degree of flame retardancy. Statistical analysis methods are

used to select best combinations for optimum FR performance and to reveal the importance degree of parameters on flammability function.

3.0 EXPERIMENTAL DETAILS

In this research cotton and commercial grade FR fibers, binder fiber, FR chemicals, chemical binders and dispersing agent obtained from different industries and organizations were used. Experiments were carried out to produce semi-durable and durable FR for cotton based nonwoven webs, and to evaluate their structure and properties

3.1. Fibers Used in Construction of Nonwoven Webs

Cotton, bi-component binder fiber, visil (cellulosic FR), and basofil (synthetic FR) fiber were mixed in the desired proportion in order to produce blend of nonwoven webs for further FR treatment. For this research mechanically cleaned, unbleached gray cotton was used which was obtained from SRRC USDA, New Orleans LA. Cotton is the major component of the fiber blend. Visil FR used was obtained from Jones Fiber Products (supplied from Sateri International). It is a brand name of inherently FR rayon which

contains cellulose and polysilicic acid. Basofil fiber was obtained from Basofil Fibers LLC.

A commercial grade bi-component fiber with low melting polyester sheath (80 °C) and regular polyester core (melting 250°C) binder fiber is used for this research. This fiber was obtained from Jones Fiber Products (supplied from Leigh Fibers).

3.2 Nonwoven Web Formation, Carding and Through Air Bonding Process

Cotton fiber, FR fibers and binder fibers were mixed in the desired percentages. Table 2 shows the combination of the fibers used to produce the nonwoven webs. SDS Atlas carding machine was used to prepare uniform blends of fibers and the web. The photograph of the laboratory carding machine is shown in Figure 8.

Table 2 Combination of fiber blend

	Combination
% Cotton	50
% Binder fiber	15
%Visil (Cellulosic FR)	20
% Basofil (Synthetic FR)	15



Figure 8 Atlas carding machine.

Carding is the most commonly known process used to produce nonwoven webs from staple fibers.

After the carding process, the web was bonded by through air bonding in an oven. In previous Cotton FR research the process conditions of through air bonding to impart good strength, loftiness and appearance were optimized. It was found that the optimum bonding conditions for cotton based nonwovens were 175 °C for 3 minutes [53]. As a result of this, the nonwoven webs were kept at 175 °C for 3 minutes in order to obtain good bonding of the fibers. The nonwoven webs produced were having a basis weight of 300g/m² and a thickness of 15mm.

3.3. FR Treatment

3.3.1 Flame Retardant Chemicals Used in FR Treatment

The prepared nonwoven webs were used for the FR treatment applications. Flame retardant chemicals such as Pyrovatex CP New, Pyrovatim PBS, FR CROS 486, Noflan, Eccoshield FR 101 (with Eccoshield UA), Safron 9025 and Diammonium phosphate (DAP) were applied to nonwoven webs from a solution using the Mathis Laboratory equipment by a pad-up cure technique (Figure 9).



Figure 9 Mathis pad dry and cure equipment.

Seven commercially available non-durable, semi-durable and durable FRs were used in this research (Table 3)

Pyrovatex CP New is a phosphorous based durable FR obtained from Huntsman International LLC. Detailed information about Pyrovatex CP New is given in Chapter 2 of this thesis. Huntsman's TDS claimed that, this product includes methanol (3%) and

formaldehyde (1%) in its composition. This product is miscible with water and it has a slight formaldehyde odor.

Pyrovatim PBS is a phosphorous based semi-durable FR obtained from Huntsman International LLC. It is an aqueous solution containing phosphate of organic bases and nitrogen-containing compounds. This product is miscible with water.

FR CROS 486 is a phase II ammonium polyphosphate halogen-free compound, which is obtained from Budenheim. Its main chemical formula is $(\text{PO}_3\text{NH}_4)_n$ and $n > 100$ and supplied in fine white powder form. FR CROS 486 is a silane coated APP grade which provides significant improvements in terms of processability, thermal stability, compatibility, and water durability.

Eccoshield FR 101 (with Eccoshield UA) is a phosphorous based durable FR which is recommended to apply with Eccoshield UA. Eccoshield FR 101 and Eccoshield UA are supplied from Eastern Color Company in liquid and white bead form respectively. It is claimed, Eccoshield FR 101 is composed of mainly urea tetrakisphosphonium sulphate and water. Its formaldehyde content is less than $<0.75\%$.

Safron 9025 is a brominated flame retardant obtained from ICL industrial products. This compound is claimed to be a durable FR for cellulose and synthetic fiber blends. Safron 9025 provides solutions for flame and smoldering suppression when wash durable formulations are required.

Noflan is an organaphosphorous flame retardant based on complex alkylphosphanates supplied from Firestop chemicals. It is supplied as a white powder and designed to provide FR property to fabrics including cellulose and cellulose rich blends. Noflan is soluble in water and can be applied by dipping, padding, and coating techniques.

Diammonium Phosphate (DAP) is a water-soluble ammonium phosphate salt which can be produced when ammonia reacts with phosphoric acid. It contains nitrogen and phosphorous and it leaves char when it is exposed to heat. It is a non durable FR chemical and in this research used as a control.

Table 3 List of FR chemicals

FR Chemical	Supplier	Composition/ Durability
Pyrovatex CP New	Huntsman International LLC.	Phosphorous based/durable
Pyrovatim PBS	Huntsman International LLC.	Phosphorous based/semi durable
FR CROS 486	Budenheim	Phosphorous based/semi or non durable
Noflan	Firestop Chemicals	Phosphorous based/durable
Diammonium Phosphate	Innophos Inc.	Phosphorous based/nondurable
Eccoshield FR 101	Eastern & Color	Phosphorous based/durable
Eccoshield UA	Eastern & Color	Nitrogen based/nondurable
Safron 9025	ICL Industrial Products	Brominated/durable

3.3.2 Chemical Binders Used in FR treatment

FR solution was prepared with FR chemical, distilled water, dispersant and chemical binder. Dispersion agent, triton X-100 was added to ensure sufficient wetting of highloft nonwovens. Chemical binder was mixed in the solution just before FR application to prevent agglomeration. In this research, Rhoplex TR 520, Airflex 4500 and Permafresh CSI-2 were used as chemical binders (Table 4). High wash durability is closely related to binder type and binder amount. As a result of this, binder selection has to be done carefully to achieve the wash durability requirement of the treatment.

Rhoplex TR 520 is an aqueous acrylic type binder supplied from Rohm & Haas Company. The company claimed that this additive provide adequate strength and wash durability for cotton and cotton based nonwoven based blends.

Airflex 4500 is an ethylene-vinyl chloride emulsion which is designed for nonwoven bonding, coating adhesive and saturant applications. This additive was supplied from Air products Company. Airflex 4500 is a mechanically and chemically stable emulsion to improve end-use properties. It imparts fire retardancy, good strength, and water/solvent resistance to nonwoven or textile materials [60].

Permafresh CSI-2 is a modified imidazolidinone chemical binder which is supplied from Omnova solutions Inc. It provides cotton fabrics durability to many home and commercial launderings.

Table 4 List of Chemical Binders

Chemical Binder	Supplier
Rhoplex TR 520	Rohm & Haas
Airflex 4500	Air Products
Permafresh CSI-2	Omnova Solutions Inc.

3.3.3 FR Solution Application and Curing Process

FR solutions was prepared with desired proportions of chemicals and water and incorporated into nonwoven web by dip pad and cure method using a Mathis laboratory equipment. FR Solution was placed in trough of the Mathis equipment for FR treatment. After dipping the web into the solution for approximately 2 minutes, the fabric was passed through the rolls at 0.5 bar pressure. This dip-nip was repeated for three times to get desired chemical add on level [53]. After completing the dip-nip part of the FR treatment, webs were weighed and the weight was recorded as the wet weight of the sample after application in order to use in wet add on calculations. Then the webs were dried and cured at 150 °C for 10-15 minutes. After drying the webs in the oven, the nonwoven webs were reweighed to get dry weight of the web. This weight was recorded as the dry weight of the sample after FR treatment. Since the moisture regain of the fibers affects dry add on calculations and the accuracy of weight loss calculations, it is important to get a fully dried sample after FR treatment.

Before FR treatment the nonwoven web was weighed. This weight was the conditioned weight of the sample but the actual dry weight of the sample was needed for dry add on calculation. The moisture regain of the fiber blend which was used for nonwoven construction was important in this research. The moisture regain of fiber blend (cotton, visil, basofil and binder fiber) was calculated as 5.5 % of the web weight. Then dry weight of the sample was calculated through subtracting this moisture amount from conditioned weight of untreated web sample. Dry add percentage of the webs was calculated using the following formula;

$$\text{Dry add on \%} = \frac{\text{Dry weight of web after FR treatment} - \text{Dry weight of web before FR treatment}}{\text{Dry weight of web before FR treatment}} \times 100 \quad (\text{Eq. 5})$$

3.4 Characterization Methods

Untreated sample and FR treated cotton based nonwoven web samples were tested for flammability, wash durability and physical properties before and after washing. All the samples were conditioned in the laboratory as per the ASTM standard.

3.4.1 Bending Length

Bending length measurement of samples before and after wash was done by using a cantilever bending tester (Figure 10). According to ASTM D1388-08, web samples were cut into rectangular pieces of 8x1 inches size and bending length of samples was recorded in cm.

3.4.2 Tensile Properties

Tensile tests of samples were conducted according to the ASTM D5035-95 using one station United tensile tester (Figure 11). The samples were cut into rectangular pieces of 1x3 inches size and 100 lbs load cell was used for this test. Tensile strength and elongation % measurements were made for washed and unwashed samples. Gauge length was 7.5 cm and the cross head speed was 1 cm/min



Figure 10 FRL Cantilever bending tester.

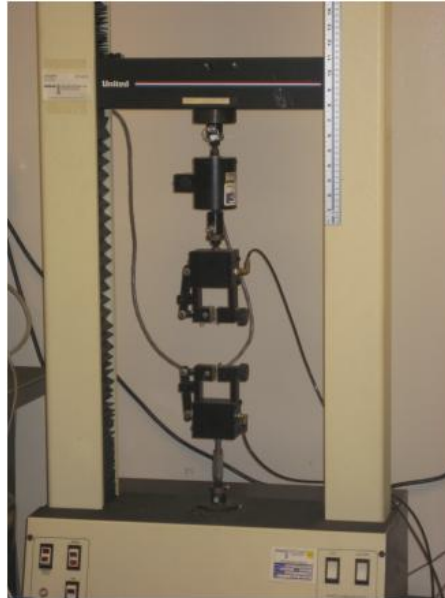


Figure 11 United tensile tester.

3.5 Flammability Tests

The samples produced in the experiments were subjected to flammability test after conditioning the samples for at least 24 hours under standard laboratory conditions (21 ± 1 C° and $65\% \pm 10$ relative humidity).

3.5.1 Limiting oxygen Index (LOI) test

Samples were tested for LOI before and after washing. LOI testing was done by using the General Electric flammability tester (Figure 12) according to ASTM D2863 test method (Figure 12).

According to test method, the specimens were cut into 50mm wide and 150mm long rectangular pieces and positioned vertically in a transparent column. Nitrogen and oxygen cylinders, and propane flame sources were connected to the flammability tester. As mentioned in the literature part, LOI is the minimum concentration of oxygen that supports combustion in a nitrogen and oxygen mixture environment. During LOI testing nitrogen flow is kept constant and oxygen flow varied until the flow rate that supports the flame is reached. The flame height was 35mm and specimen is ignited at the top. The oxygen concentration that supports combustion is recorded and the reported concentration is volume percent.



Figure 12 General Electric flammability tester.

3.5.2 Small Open Flame Test (TB604)

This is a laboratory scale test for items such as bed clothing, mattress pads, comforters and pillows. For this test washed samples were cut into 12x12 inch pieces and placed between two bottoms and two tops of 50% cotton and 50%polyester fabric. Then the sample, together with cotton fabrics are placed on an insulation board horizontally. The insulation board is placed on a scale to record the weight of the sample continuously. According to the test procedure, the center of the specimen was subjected to 30° oriented 35mm height flame for 20 seconds. Then the burner was removed from the surface of the material. After ignition the flame start to propagate over the sample and allowed to burn for 6 minutes until the flame extinguishes (Figure 13).



Figure 13 TB604 Test Setup.

While conducting the TB604 test, the video records weight of the pad and temperature of the sample center. To measure the temperature of the sample center a sensor was located under the web sample. The sample passes the test if weight loss does not exceed 25% and there is no flash over. A mattress pad passes the test if the flame does not create a void more than 50mm in diameter.

3.6 Washing procedure

3.6.1 Water Soak Test

For the first part of this research, washing of samples were done by using water soak tests. To do water soak tests, FR treated cotton based web samples were cut into 6x6 inch size. Before washing these prepared samples were pre-dried in the oven at 120 °C for 20-30 minutes in order to remove the moisture in the sample and start with an actual dry sample. After drying, the samples were weighed, and the dry weight of the samples before water soak tests were recorded. Also, pre-drying will eliminate the error for weight loss calculations of the web samples. Then the samples were soaked in hand soap containing 1 Lt plain water at 40 °C for 30 minutes. Water soak test was applied to FR treated webs twice as described. After second water soaking, samples were re-dried in the oven at 120 °C for 20-30 minutes. The dry weight of sample was recorded after two water soak tests. During water soaking tests, the uniformity of water temperature was maintained by using magnetic stirrer and temperature variances were minimized by agitation of water.

3.6.2 Hand Laundering

In the second part of the study washing of samples were done by using hand laundering. Hand laundering of samples was done according to ASTM D2724. According to hand laundering procedure 20g of laundry detergent was dissolved in 7.6 Lt of water at 41 ± 3 °C in a 9.5 Lt pail. Then two specimens were added to water and washed by lifting each specimen out of the bath followed by reimmersion at least ten times. Before the last reimmersion, the center of each specimen was rubbed by hand and rinsed by water at 41 ± 3 C°. The specimen did not get twisted or wringed during washing and drying. After washing, specimens were dried by hanging two corners in air at room temperature.

4. 0 RESULTS AND DISCUSSIONS

4.1. Wash Durability and Weight loss results

Chemical binder is an important additive that imparts strength and wash resistance to nonwoven webs. Chemical binder is also effective on adherence of FR chemicals to the fabric. With the aim of determining semi-durable and durable flame retardant systems for cotton based nonwovens, it is important to investigate binder influence on wash durability of nonwoven webs.

In order to determine the effect of binder level on wash durability of cotton based webs, flame retardant treatments were applied with flame retardant solutions that include FR chemicals with varying percentage of chemical binders (no binder (0%), 1% binder, 5% binder and 10% binder based on FR solution).

Rhoplex TR 520 was found to be a successful chemical binder in previous FR cotton nonwoven mattress pad research [53]. Since we had three types of chemical binders, we decided to study Rhoplex TR 520 effect on wash durability. As mentioned in the experimental section, seven commercially available semi durable and durable FR chemicals were used in this research (Pyrovatex CP New, Pyrovatim PBS, FR CROS

486, Noflan, Eccoshield FR 101 (together with Eccoshield UA), Safron 9025 and Diammonium phosphate). As a starting point, Pyrovatex CP New, Pyrovatim PBS, FR CROS 486 and DAP with various levels of Rhoplex TR 520, dispersing agent and desired amount of distilled water were mixed to prepare different FR solution combinations. So, one set of FR treatment on cotton nonwoven webs was finished with different FR chemicals at different levels of Rhoplex TR 520.

After flame retardant chemical treatment to cotton webs, water soaking was applied to the samples twice, as described in experimental section. Weight loss of samples was calculated based on dry weight of samples after wash by using Eq. 6.

$$\text{Weightloss\%} = \frac{\text{Dry weight of sample after wash} - \text{Dry weight of sample before wash}}{\text{Dry weight of sample before wash}} \times 100 \quad (\text{Eq. 6})$$

For all the FR chemicals observed weight loss decreased with increasing binder level. The weight loss results are presented in Table B1. The bar chart of weight loss (%) of FR vs. Rhoplex TR 520 binder percentage (%) is represented in Figure 14.

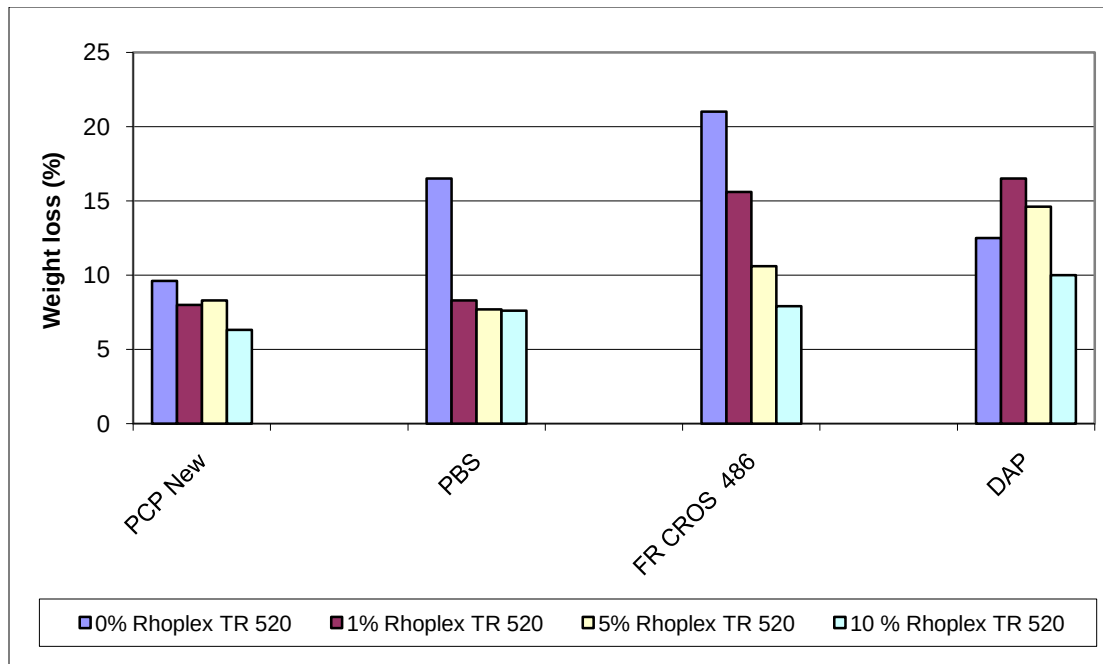


Figure 14 Weight loss (%) of FR vs. Rhoplex TR 520 binder (%).

Since FR treated webs have different chemical dry add on levels (chemical percentage deposited on the web calculated based on the dry web weight after FR treatment) using the weight loss results (calculated by Eq. 6) to evaluate and compare wash durability of different flame retardant chemical may be misleading. A different calculation based on total chemical weight on sample before wash and total weight loss after wash was used to determine weight loss % and wash durability of FR treated samples; wherein

$$\text{Weightloss\%} = \frac{\text{Total weightloss of sample due to washing(gr)}}{\text{Total chemical weight on sample before wash(gr)}} \times 100 \quad (\text{Eq. 7})$$

After evaluation weight loss results of first FR treatment sample set (Rhoplex TR 520 treated samples) it is observed that 10% Rhoplex TR 520 containing FR treated samples had lower weight loss % compared to 0%, 1% and 5% chemical binder treated samples (Figure 14). As a result of this, we decided that most FR treatments with the other binders (Airflex 4500 and Permafresh CSI-2) can be done with 10% binder. Weight loss results calculated by equation 7 related to the durability performance of each FR chemical when applied with different binders and binder levels. Weight loss results are presented in Tables B2, B3 and 5.

Weight loss (%) of FR vs. Rhoplex TR 520 percentage (%) for all FRs is represented in Figure 15. Also, weight loss (%) of FR vs. chemical binder type for all FRs is represented in Figure 16. Weight loss results are presented in Tables B2, B3 and 5.

Table 5 Weight loss percentage of FR after two water soak tests (Permafresh CSI-2 as binder)

Flame Retardant Chemicals	Weight loss (%) (10% binder)

Pyrovatex CP New	50
Pyrovatim PBS	69
Noflan	66
Safron 9025	42

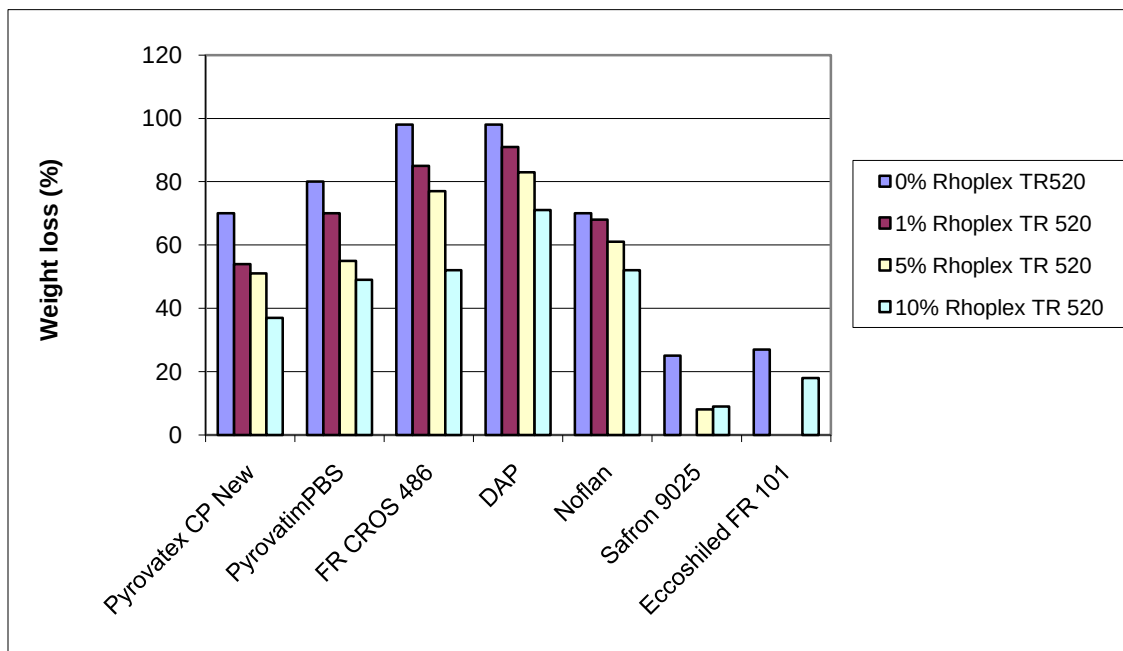


Figure 15 Weight loss (%) of FR vs. Rhoplex TR 520 binder (%) for all FR chemicals.

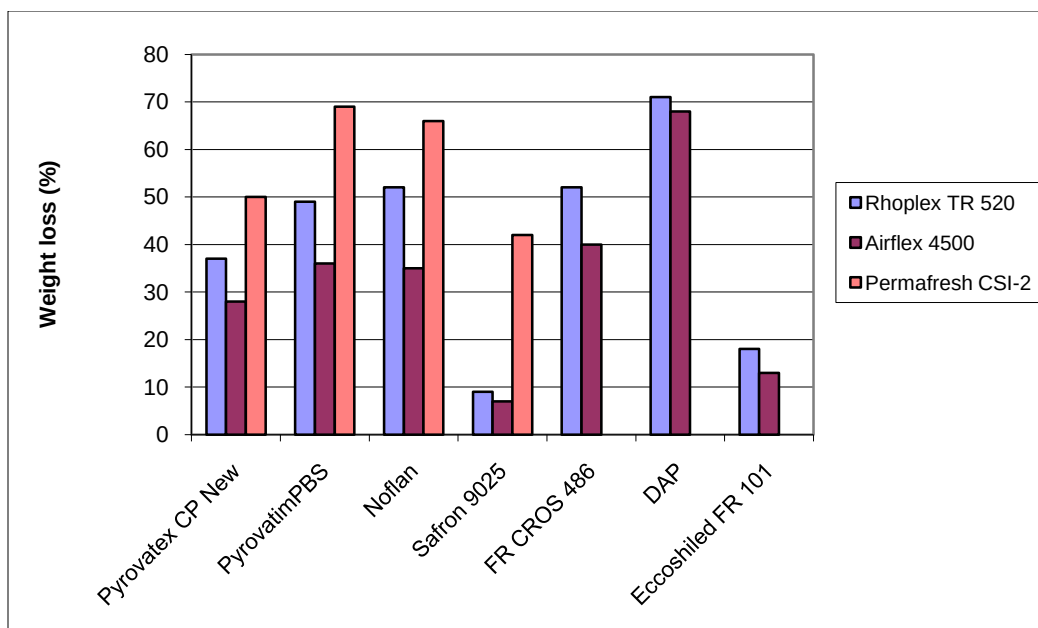


Figure 16 Weight loss (%) of FR vs. chemical binder type for all FRs.

As the binder level increased in the flame retardant solution formulation, weight loss of treated samples due to washing decreased with varying percentages for all types of FR chemicals. While weight loss difference between 1% and 5% binder treated samples was small, there was significant weight loss difference between 1% and 10 % binder treated samples. It is observed that for all FR chemicals studied in this research FR solution, formulation with 10% binder level gave the best wash durability after water soak tests.

From Figure 15, it can be seen that, Safron 9025 and Eccoshield FR 101 (with Eccoshield UA) treated samples with all type of binders had the highest wash durability (lowest weight loss) compared to other FR chemical treated samples. Also, Pyrovatex CP New treated samples showed a higher level of wash durability performance among the FR chemicals studied. DAP treated samples had the lowest wash durability. Since DAP is a nondurable FR this result was as expected.

Also, weight loss results showed that except for Safron 9025 and Eccoshield FR 101 treated samples, most of the flame retardant chemical applied to nonwoven webs were removed after two water soak cycles when no binder was used (Table B2 and Figure 15).

After washing, almost all chemical applied to webs was removed for FR CROS 486 and DAP treated samples (Table B2). This result indicates that, to provide wash durability to cotton based nonwoven webs usage of chemical binder is a must for the flame retardants investigated in this research. A binder can react with cellulose and form a network which should improve resistance to hydrolysis.

As it can be seen from Figure 16, weight loss result comparison of FR chemicals with different kinds of chemical binders showed that when binder level was kept constant (10%), highest wash durability (lowest weight loss) was obtained with Airflex 4500 treated samples, whereas lowest wash durability (highest weight loss) was obtained with Permafresh CSI-2 treated nonwoven samples.

4.2. Flammability Test Results

Flame resistance is a crucial property for textile products in terms of fire safety. In this research, we tested the effect of washing on flame retardancy performance of commercially available semi durable and durable FR chemicals which are applicable to cotton based fabrics. LOI of samples were tested before and after wash. Since chemical loss of samples treated with 10% binder was found to be low, LOI tests were done for samples that had 10 % binder in the FR formulation.

After two water soak cycles, LOI tests were done to samples and amount of chemical remained on samples after wash were calculated with the formula below;

$$\frac{\text{Total weight of chemical remained on sample after wash (gr)}}{\text{Weight of cotton web sample before FR treatment (original sample weight) (gr)}} \times 100 \quad (\text{Eq. 8})$$

LOI result of samples before and after wash and amount of chemical wt (%) remained on sample after two water soak tests are presented in Tables B4, B5 and B6.

LOI results of samples before and after wash with all types of FR chemicals and different types of chemical binders are represented in Figures 17, 18 and 19.

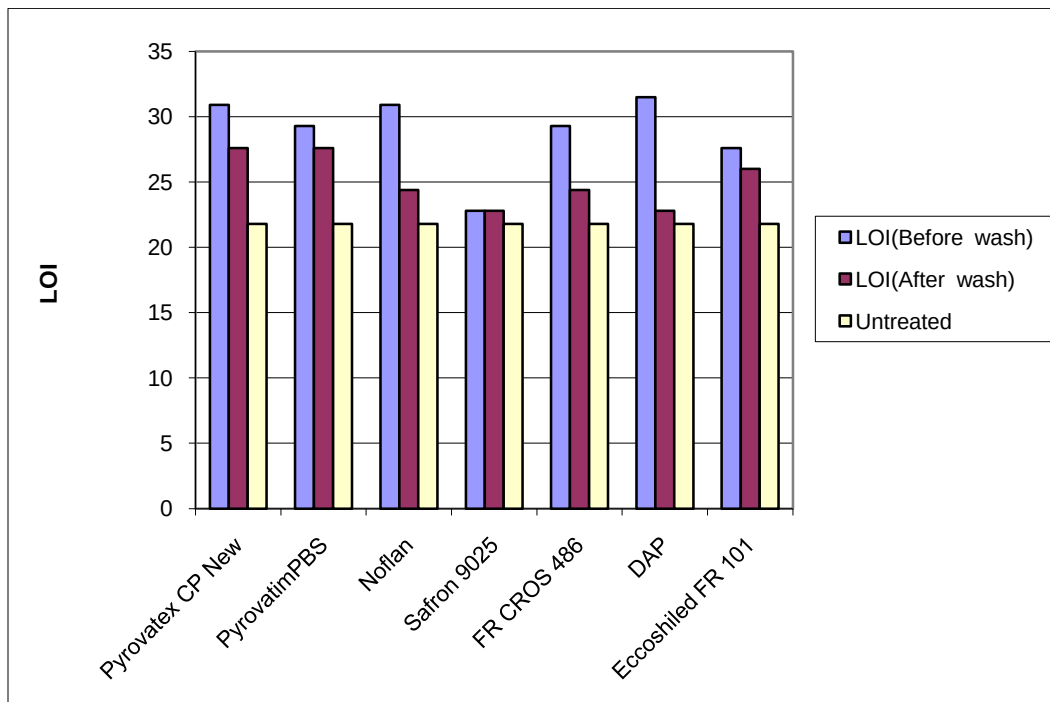


Figure 17 LOI results of FR treated samples before and after wash for all FR chemicals when 10% Rhoplex TR 520 used as binder

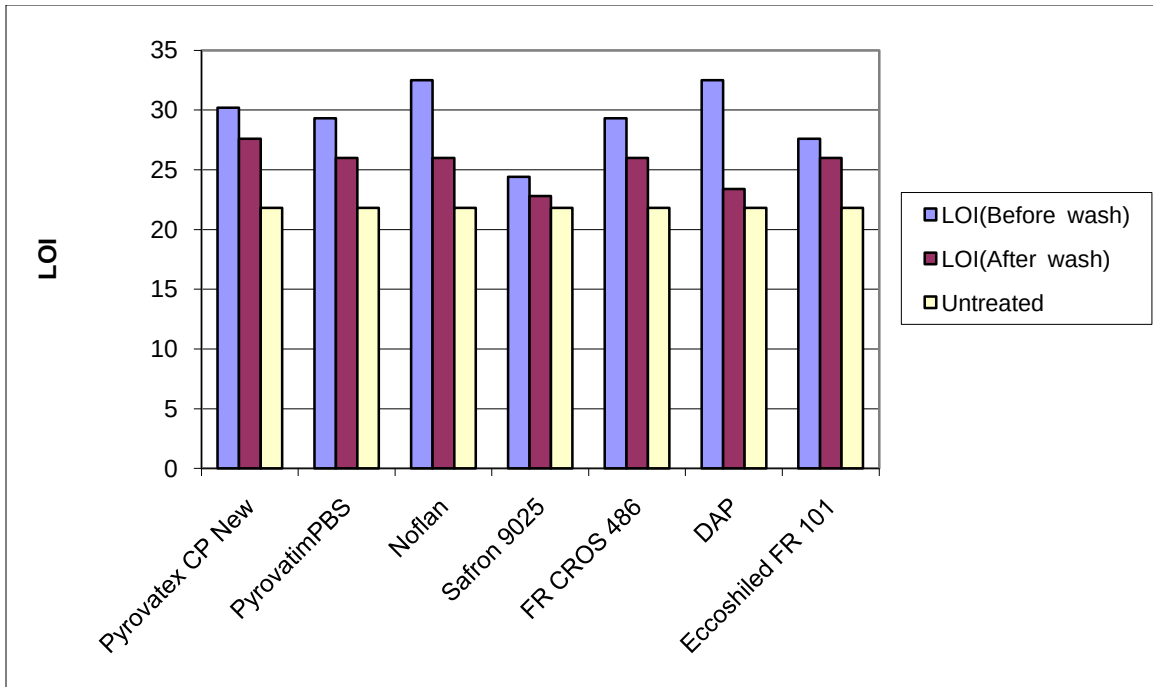


Figure 18 LOI results of FR treated samples before and after wash for all FR chemicals when 10% Airflex 4500 used as binder.

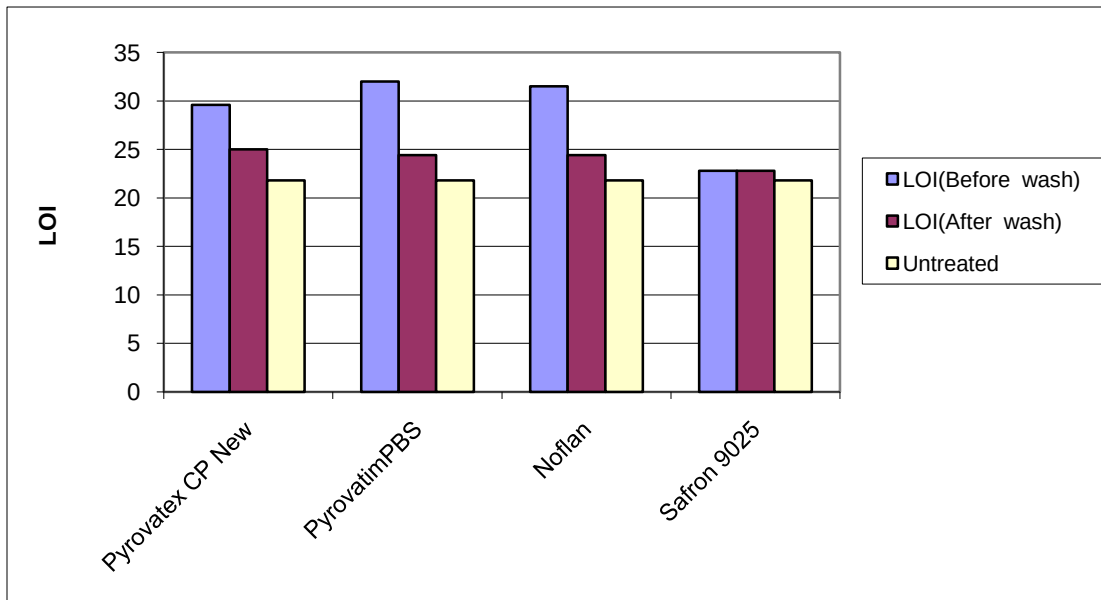


Figure 19 LOI results of FR treated samples before and after wash for all FR chemicals when 10% Permafresh CSI-2 used as binder.

LOI result for untreated cotton based nonwoven web was found to be 21.8. As it can be seen from Figures 17, 18 and 19, with all types of chemical binders flame retardancy of nonwoven samples showed a significant improvement after FR chemical treatment (see before wash LOI results). Most of the FR chemicals studied in this research exhibited an LOI value higher than 29% before washing.

It is given in the literature, phosphorous flame retardants phosphorylate cellulose under initial thermal degradation and this stage inhibits the production of levoglucosan and accelerates char formation. These compounds provide flame resistance by lowering decomposition temperature through dehydration reaction [62]. Our LOI data showed that phosphorous based FRs inhibit the combustion of cotton drastically which supports the fact that protective layer formation on the substrate functions as a fire barrier as given in the literature. Before wash LOI results clearly demonstrate that semi durable and durable FR solutions studied in this research can be potential effective FR systems for cotton rich nonwovens to reduce flammability. Only, Safron 9025 treated samples had LOI value close to untreated sample with all types of chemical binders and failed the LOI test (Figures 17, 18 and 19).

With all types of binders studied, FR chemical treated webs showed higher LOI compared to that of untreated webs. LOI results revealed that after washing, Pyrovatex CP New with Rhoplex TR 520, Pyrovatim PBS with Airflex 4500 and Rhoplex TR 520 treated samples had higher LOI values compared to other samples. These samples can be classified as slow burning materials according to classification based on LOI (Table 1). These chemicals have good durable flame retardancy performance for cotton rich nonwovens. Also, Eccoshield FR 101 (with Eccoshield UA) treated samples had good LOI level compared to other samples studied (Figures 17 and 18).

The durable FR performances depend on the type of compound and its chemical composition. The higher FR performance of some samples after wash may be explained either by FR reaction with cellulose, or network film formation on the substrate, which is resistant to hydrolysis. The durable FR property of Pyrovatex CP New is due to its bonding with cellulose repeat unit by N-Methylol group. This linking to cotton cannot be removed during washing conditions and, leads to durability to washing. The possible reaction between Pyrovatex CP New and cotton are shown in Figure 20 [46]. There may be some other reactions taking place between Pyrovatex CP New, cellulose and chemical binder. Spectroscopic techniques can be used to reveal possible reactions of chemicals and fibers which provide wash resistance property.

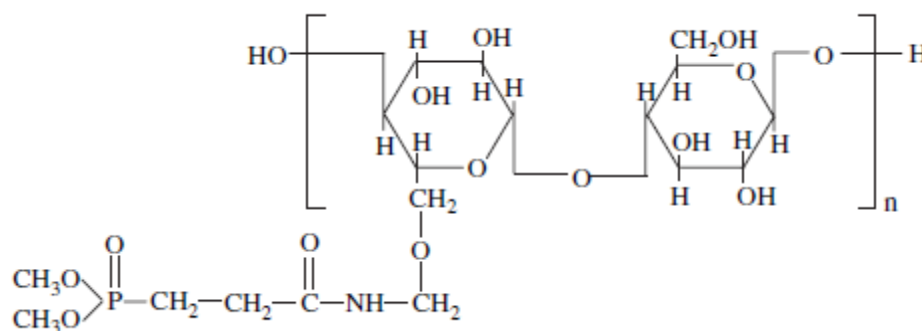


Figure 20 Pyrovatex CP New bonding to cotton [46].

Similar to Pyrovatex CP New, reacting onto cellulosic fabric provide wash resistance to Pyrovatim PBS [9]. Our LOI results showed that linkage of these FR chemicals with cotton gave high durability and reasonable LOI values after water soak tests. Also, the presence of chemical binder enhanced the durable FR performance of these chemicals. Our findings are consistent with literature studies.

It can be seen from LOI results, with all types of binders, Safron 9025 and DAP treated samples had the lowest LOI values after washing. In addition to this, Safron 9025 treated samples had same LOI values before and after wash. This result means that Safron 9025 has a low FR performance but it is resistant to washing.

As it can be seen from Figure 19, LOI results of Pyrovatex CP New, Pyrovatim PBS and Noflan with Permafresh CSI-2 treated samples had same LOI values after washing.

4.3. Mechanical Test Results

Bending length (BL) and tensile properties of samples were tested using the Cantilever bending tester and tensile tester, respectively. The modulus of samples before and after wash was calculated by using the slope of stress-strain curve in elastic deformation region created during tensile test. Mechanical test results of untreated web are presented in Table 6. The bending length for untreated nonwoven web was measured as 7.3 cm (Table 6). The bending length increase % for FR treated samples was calculated with the formula below;

$$\text{Bending length increase \%} = \frac{\text{Bending length of FR treated} - \text{Bending length of untreated web}}{\text{Bending length of untreated web}} \times 100$$

(Eq. 9)

The Bending length results of FR chemical treated webs are presented in Figures 21, 24 and 27 (data in Tables B7, B8 and B9).

Mechanical test results of FR treated samples before and after wash for all FR chemicals with different binders (Rhoplex TR 520, Airflex 4500 and Permafresh CSI-2) are represented in Figures 22, 23, 25, 26, 28-31, with data values listed in Tables B7-B20 in Appendix B.

Table 6 Mechanical test results of untreated nonwoven web.

	Bending Length (cm)	Tensile Force (N)	Elongation (%)	Modulus (N)
Untreated sample	7.3	0.8	40	0.9

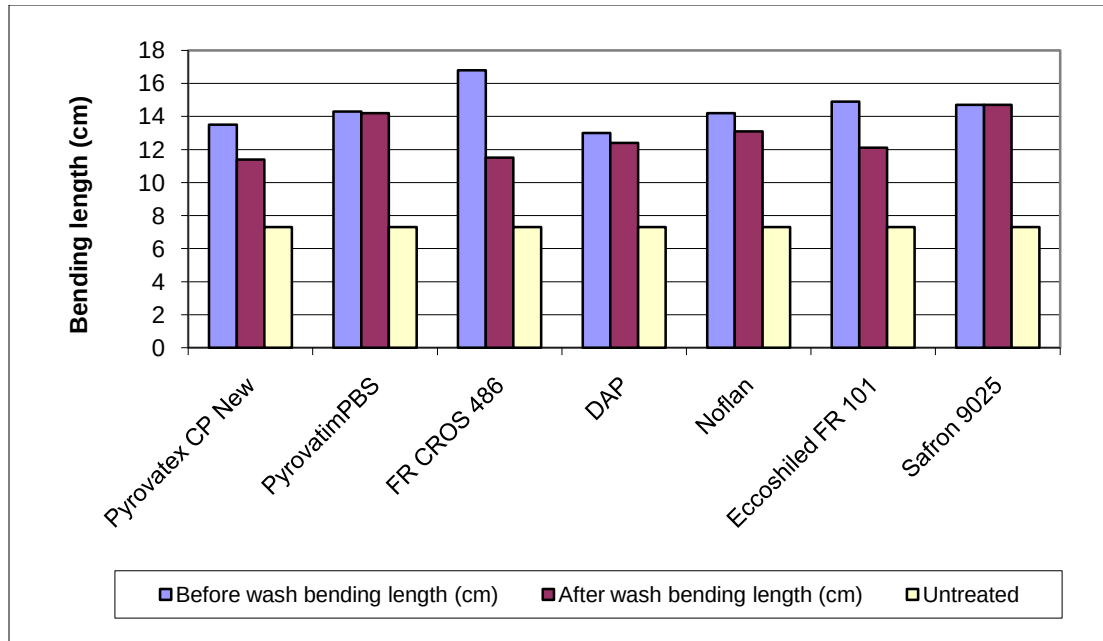


Figure 21 Bending length results of samples before wash and after wash when 10 % Rhoplex TR 520 used as binder.

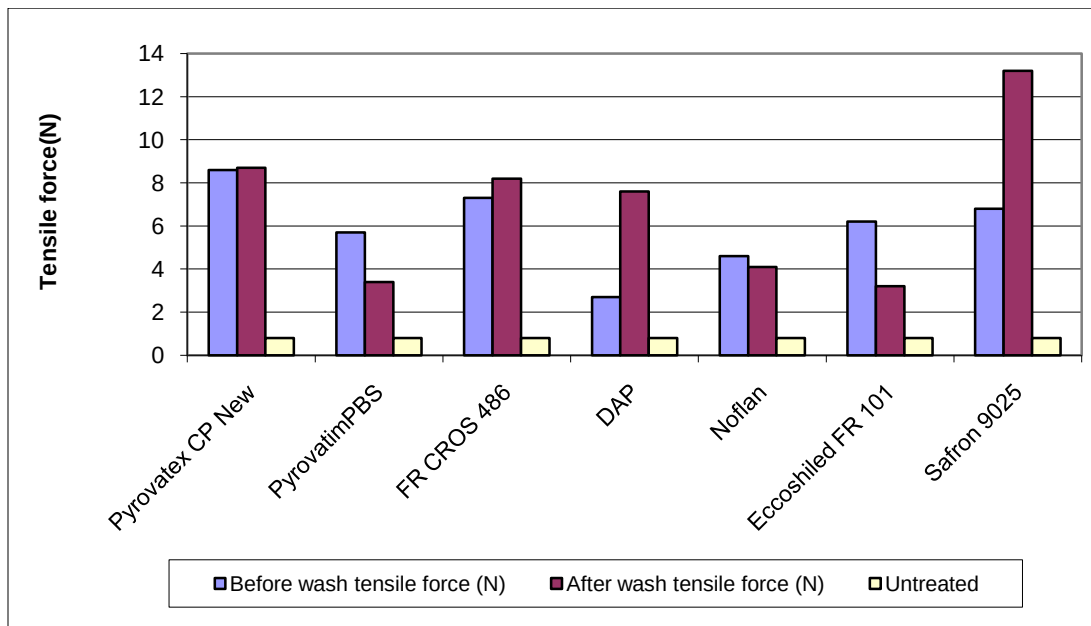


Figure 22 Tensile force results of samples before wash and after wash when 10 % Rhoplex TR 520 used as binder.

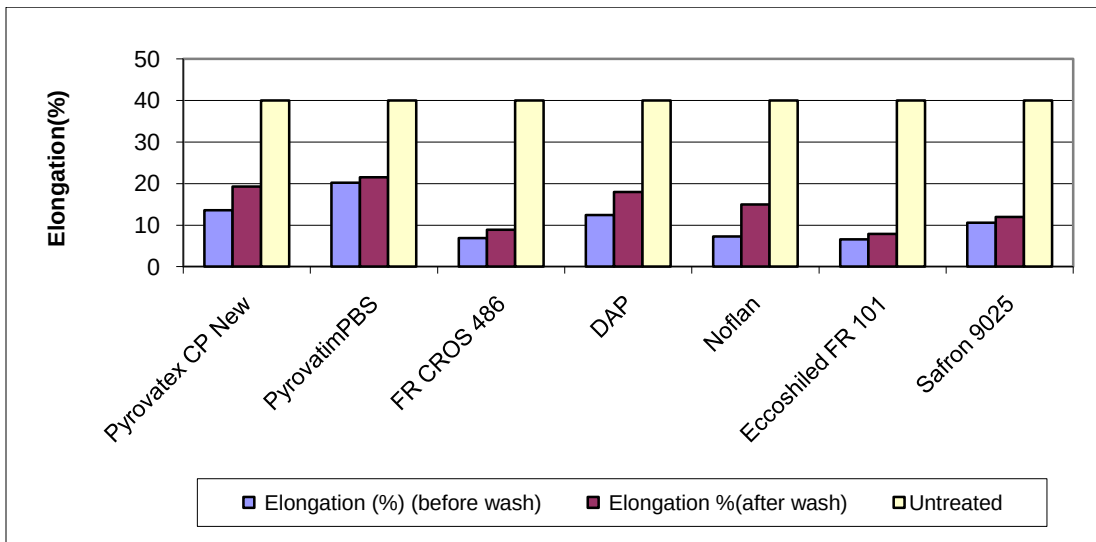


Figure 23 Elongation results of samples before wash and after wash when 10 % Rhoplex TR 520 used as binder.

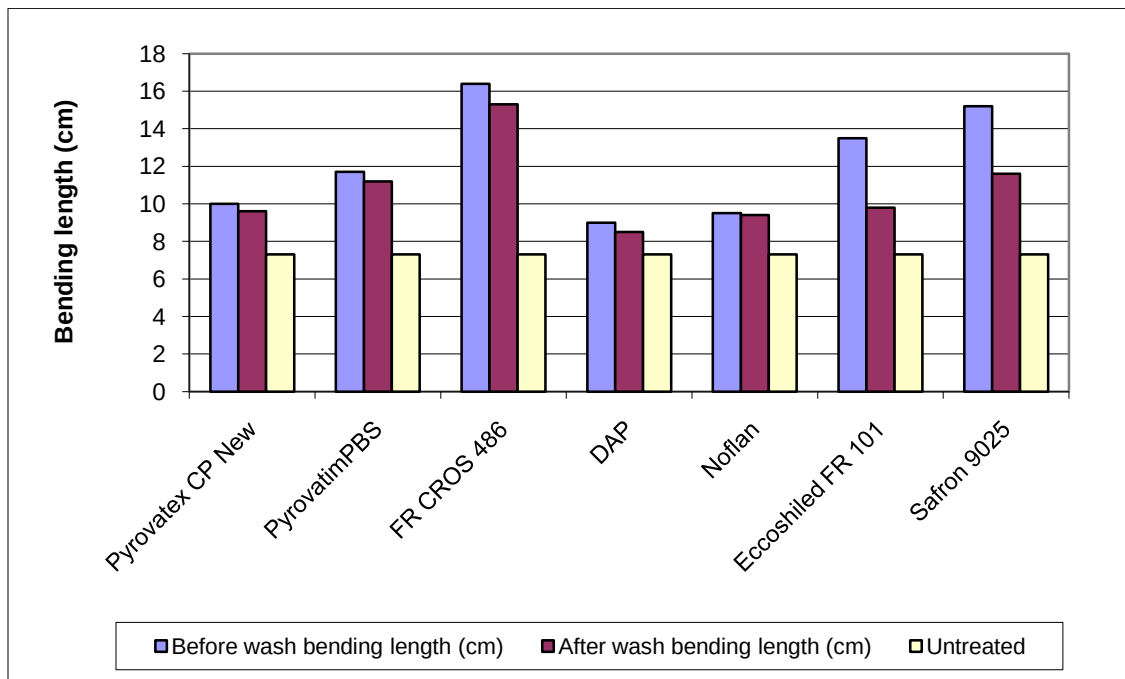


Figure 24 Bending length results of samples before wash and after wash when 10 % Airflex 4500 used as binder.

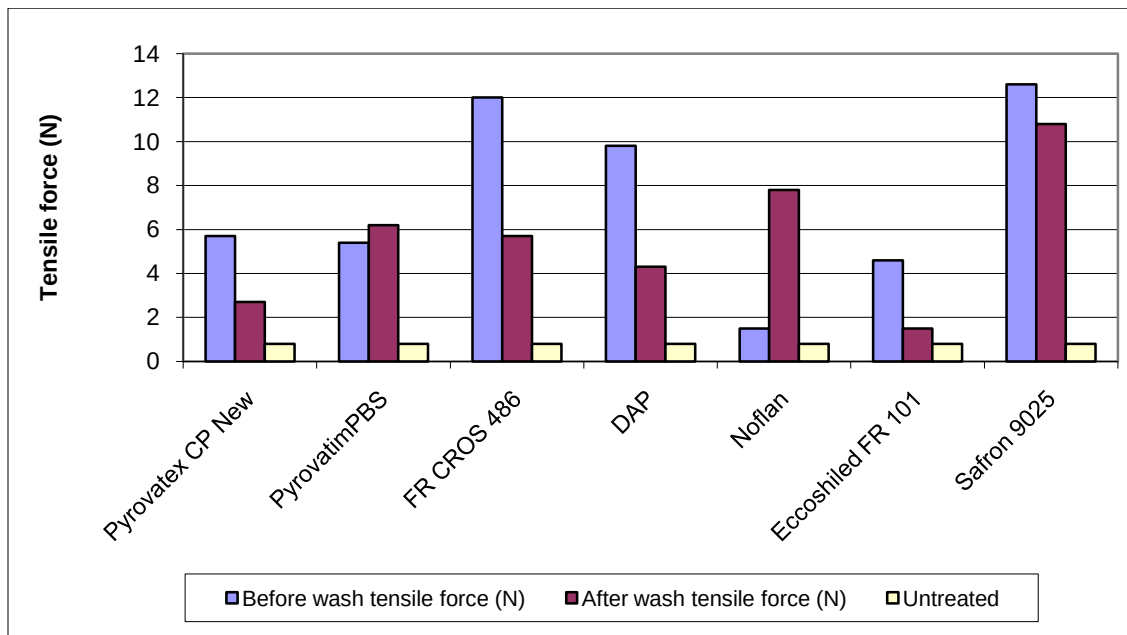


Figure 25 Tensile force results of samples before wash and after wash when 10 % Airflex 4500 used as binder.

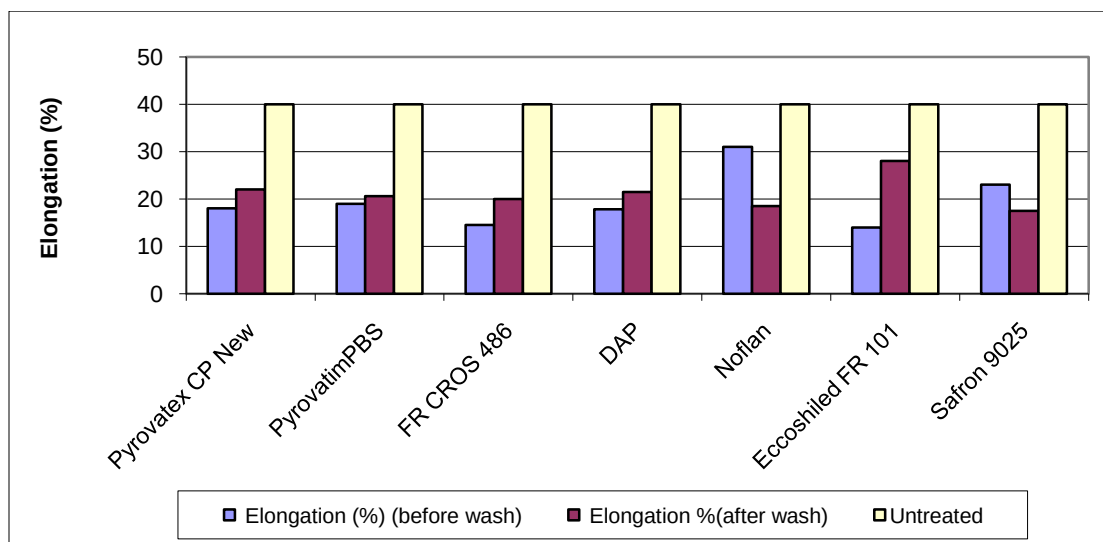


Figure 26 Elongation results of samples before wash and after wash when 10 % Airflex 4500 used as binder.

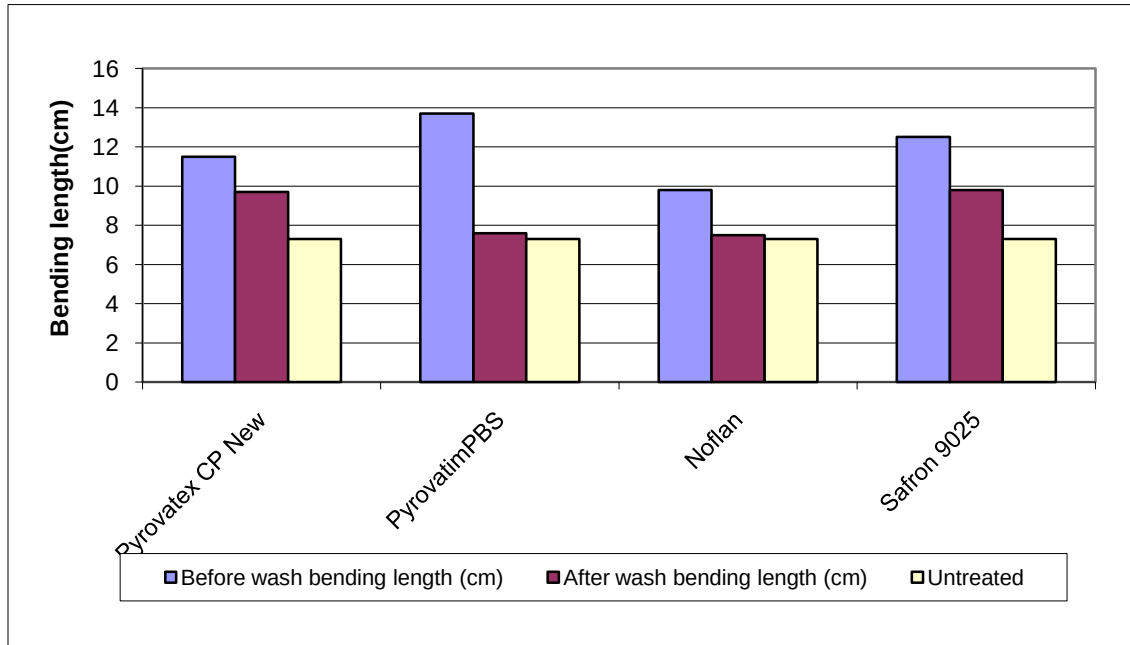


Figure 27 Bending length results of samples before wash and after wash when 10 % Permafresh CSI-2 used as binder.

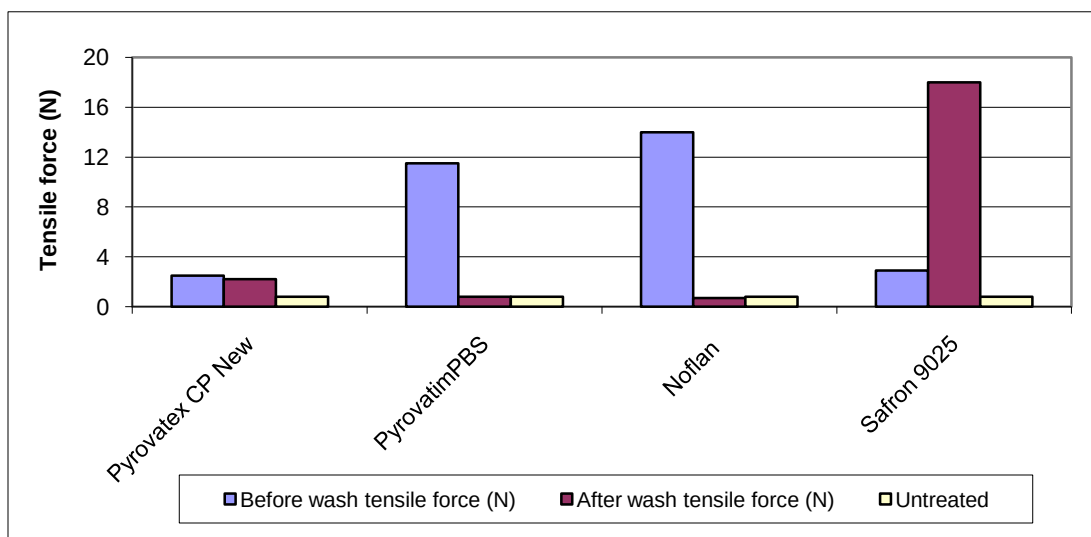


Figure 28 Tensile force results of samples before wash and after wash when 10 % Permafresh CSI-2 used as binder.

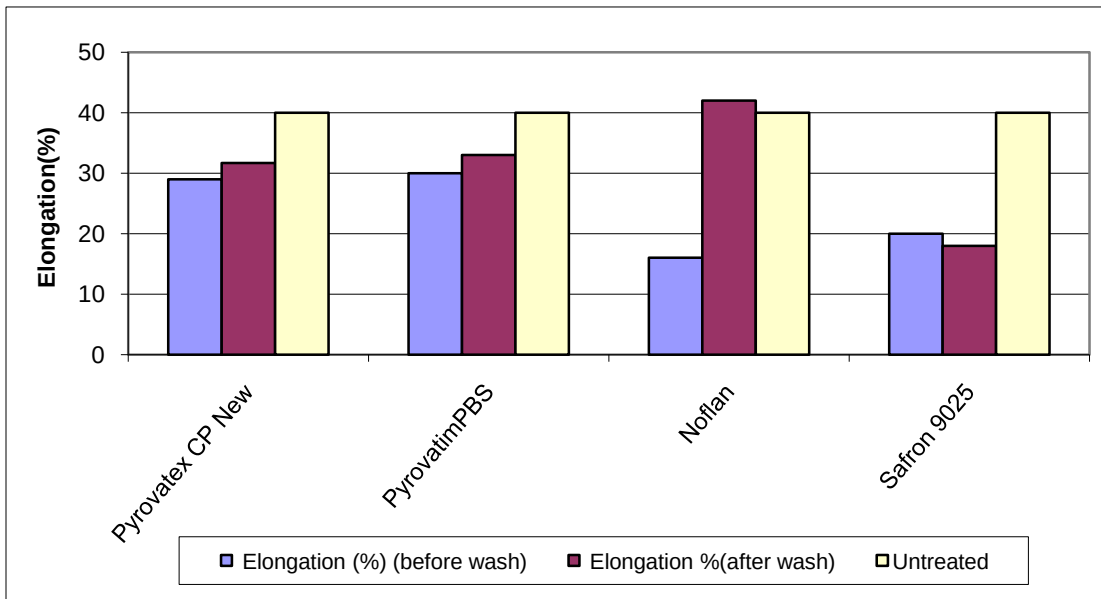


Figure 29 Elongation results of samples before wash and after wash when 10 % Permafresh CSI-2 used as binder.

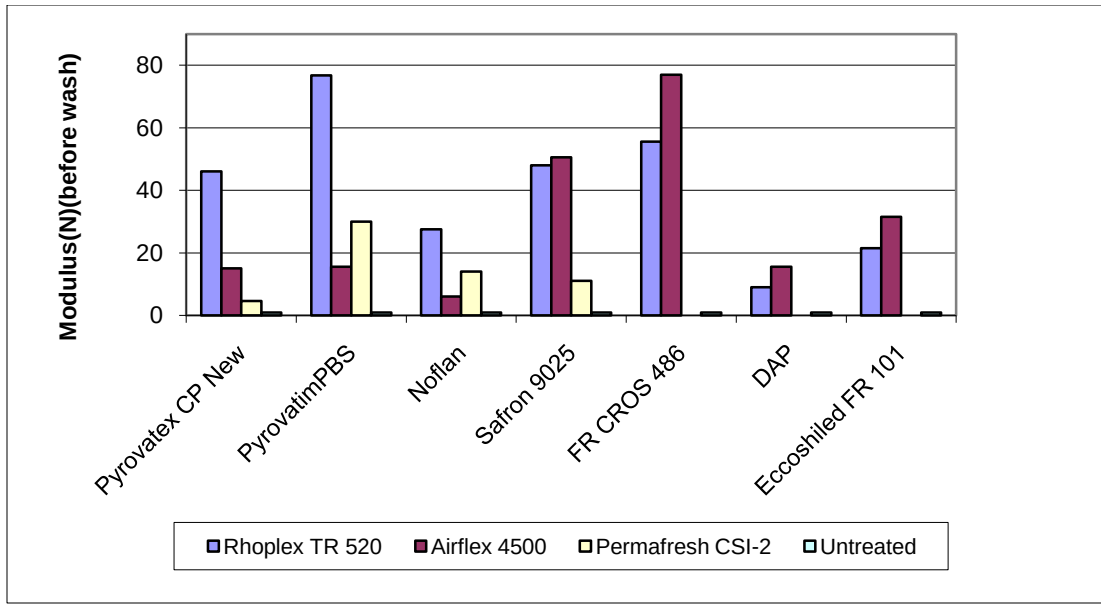


Figure 30 Modulus results of FR treated samples before wash for different binders.

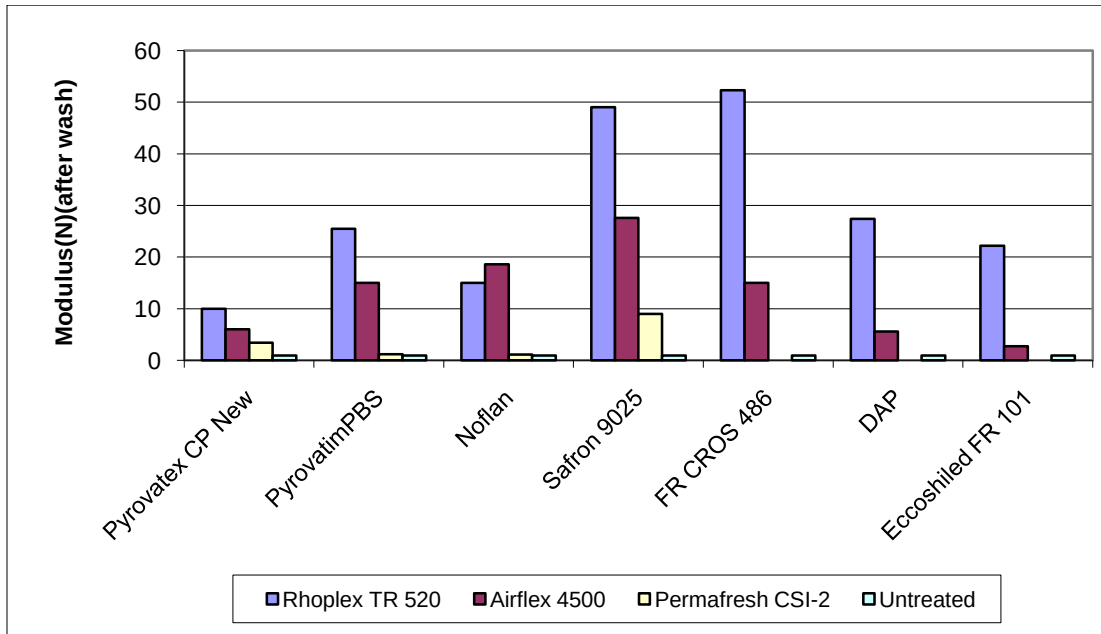


Figure 31 results of FR treated samples after wash for different binders.

Stiffness of FR treated samples significantly increased compared to untreated nonwoven web stiffness. These results revealed that the mechanical properties change as a result of flame retardant treatment. Compared to other chemical binder treated samples, Rhoplex TR 520 treated samples had higher stiffness increase effect on cotton rich nonwoven webs (Figures 21, 24 and 27). Also, results from tables in Appendix B revealed that the stiffness of samples increases as the binder percentage increases according to Rhoplex TR 520 stiffness results (Appendix B13-B18). SEM study of FR treated webs revealed that chemical binder tends to form film like layer on the fabrics [53]. This formation of bridging fibers and reduces the flexibility for movement. SEM pictures are shown in Flame Retardant Mattress Pads research of our group [53].

Mechanical tests clearly showed that binder type and binder level have critical affect on stiffness increase of FR treated samples. From mechanical results it can be seen that, when binder type and binder level was kept constant, Safron 9025 and FR CROS 486 treated samples had higher stiffness increase compared to other FR chemicals (Tables B7, B8 and B9). Even after washing, FR treated webs had higher bending length compared to untreated sample (Figures 21, 24 and 27). These results are further verification of chemical retention, and wash durability property of studied FR chemicals.

Before washing, FR chemical treated webs exhibit higher tensile peak force and lower elongation compared to untreated webs. This result indicated that FR chemical increases the strength of the cotton based nonwoven fabric.

Elongation of FR treated and washed samples were lower than that of untreated samples which show chemical retention on fabric after washing. Elongation of FR treated and washed samples were higher than the elongation of FR treated and unwashed samples which indicates some chemical loss during washing for each sample (Figures 23, 26 and 29).

As it can be seen from Figures 30 and 31, before and after wash modulus of FR treated samples were found to be higher than untreated nonwoven web sample. Similar to stiffness results modulus of samples increased as the binder percentage increased before and after washing (Appendix B13-B18). All these results clearly indicate that the chemical treatment acts as adding chemical binder on the web.

4.4 Statistical Data Analysis Results

Statistics, a mathematical science, enables analysis, interpretation and presentation of the data. When there is a diversity of possibilities and uncertainties, statistical models help explain the data and solve the problems. In short, statistical models are useful to make decision based on numerical values [63, 64]. In past years, statistical models used mostly linear models but today nonlinear models such as neural networks and new models are widely used for data analysis. A number of commercial statistical computer packages such as SAS are now available.

In this research, JMP 7 statistical software and neural networks (NN) were applied to our experimental data for statistical analysis. Having chemical binder type, chemical binder percentage, chemical add on percentage, and FR chemical type as the LOI function parameters, the effectiveness of each parameter on the function was ranked. Also, the effectiveness of these parameters on the modulus result of samples was ranked using JMP 7.

In addition to JMP 7, NN were used to find a nonlinear function approximation with the help of obtained input-output vector pairs. Since the LOI has too many values for each experimental set up, NN was used to ease the burden of working for hours on different LOI parameter combinations. Known LOI function parameters and corresponding outputs are introduced to NN during the training stage. For the testing stage, the NN was asked to

produce LOI outputs for randomly created new input sets to find out the parameter combinations which can pass the LOI test.

4.4.1 JMP 7 Software Analysis Results

JMP is a statistical software package which provides improved explanation of data [65]. By using JMP it is aimed to reveal the importance of the degree of the flame retardant chemical type, chemical binder type, chemical add on percentage and chemical binder percentage on LOI and stiffness results. All LOI results were used as the basis of JMP 7 analysis. JMP plot of residuals based on LOI data of treated and unwashed samples are presented in Figures 32 to 35. JMP plot of residuals based on LOI data of treated samples after wash are presented in Figures 36 to 39.

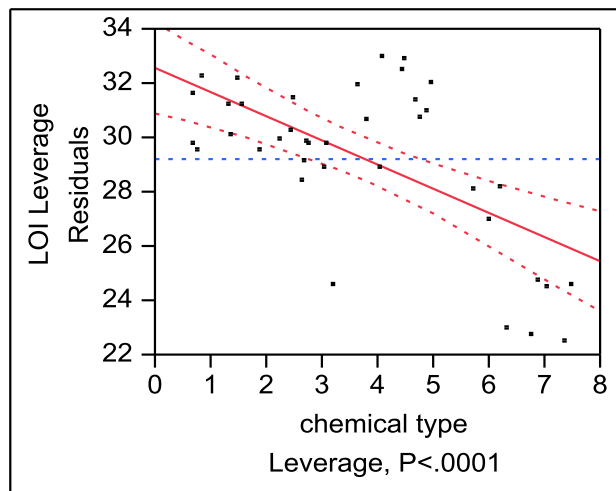


Figure 32 LOI residuals vs. FR chemical type (before wash).

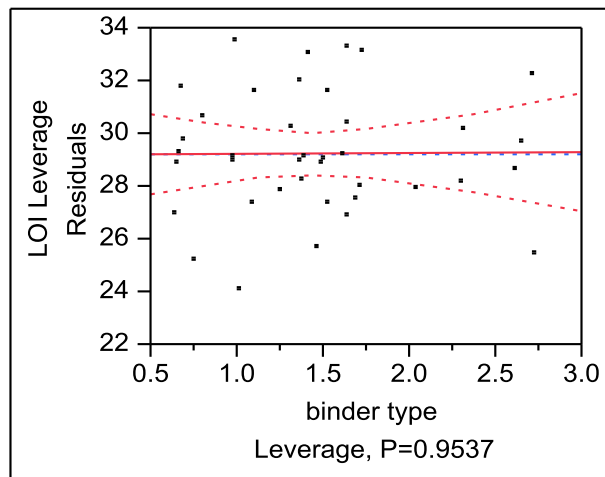


Figure 33 LOI residuals vs. chemical binder type (before wash).

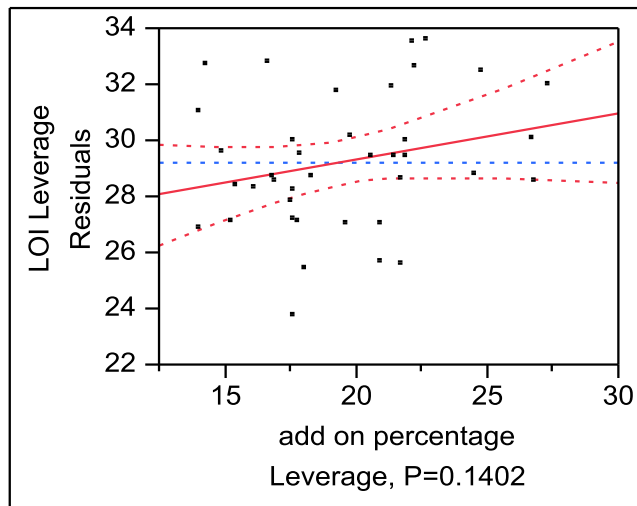


Figure 34 LOI residuals vs. chemical add on percentage (before wash).

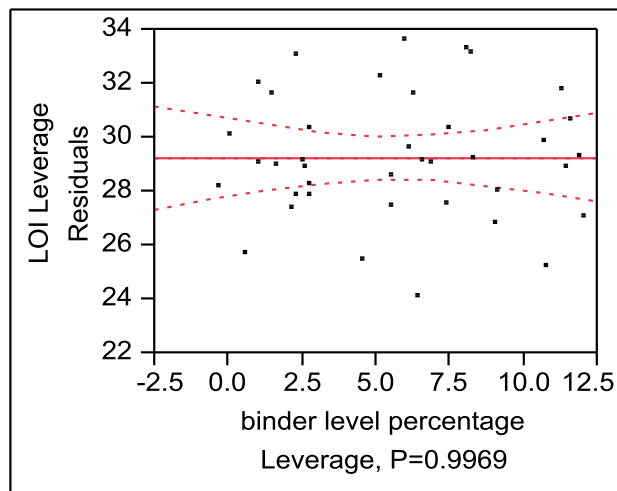


Figure 35 LOI residuals vs. chemical binder percentage (before wash).

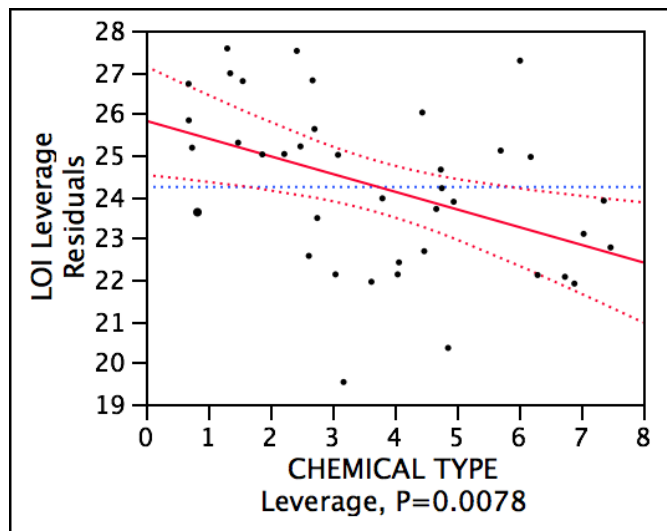


Figure 36 LOI residuals vs. FR chemical type (after wash).

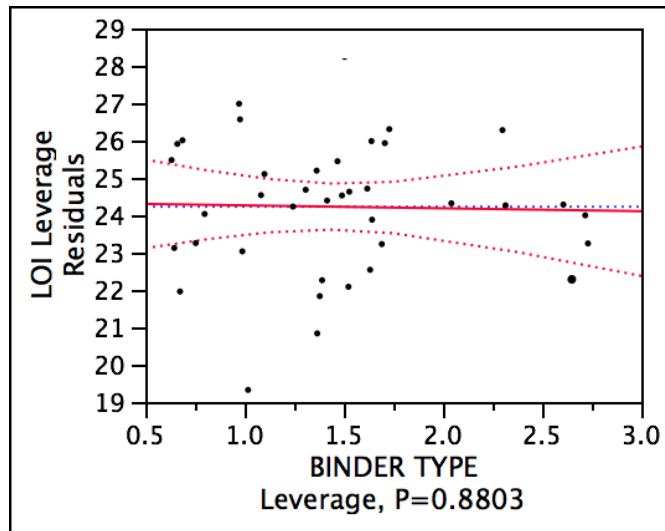


Figure 37 LOI residuals vs. chemical binder type (after wash).

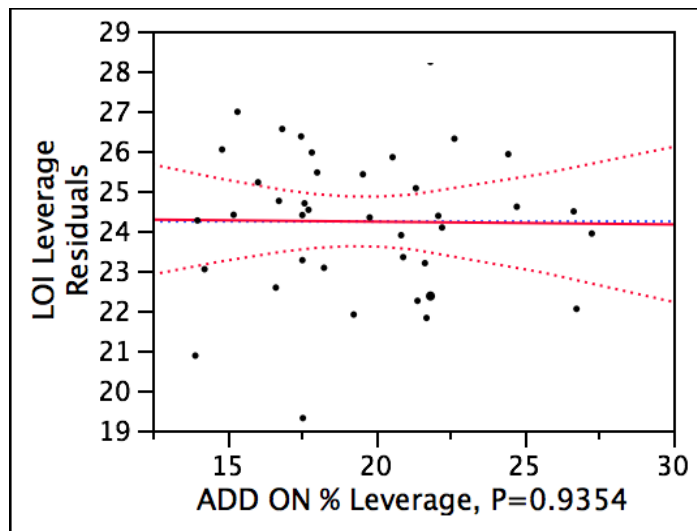


Figure 38 LOI residuals vs. chemical add on percentage (after wash).

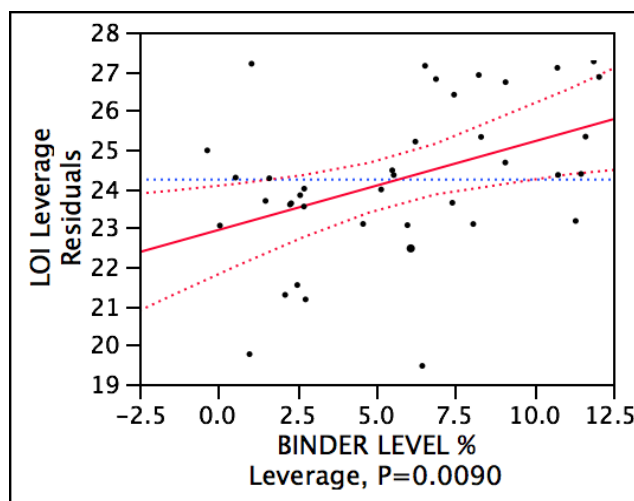


Figure 39 LOI residuals vs. chemical binder percentage (after wash).

JMP analysis results revealed that chemical type has the biggest effect on LOI values before and after washing. Also, statistical analysis showed that after washing, binder percentage had an important effect on LOI result of treated samples, whereas before washing, chemical add on percentage has a significant effect on LOI result. In other words, before washing, chemical type and chemical add on percentage are two effective factors determining the flammability of FR treated samples. But after washing, instead the chemical add on percentage, binder percentage becomes an important factor that determines LOI of FR treated cotton rich nonwoven samples. Therefore, for samples needing wash durability, binder level has to be appropriately selected.

JMP plot of residuals based on modulus data of treated samples before wash are presented in Figures 40 to 43 and modulus of treated samples after wash in Figures 44 to 47.

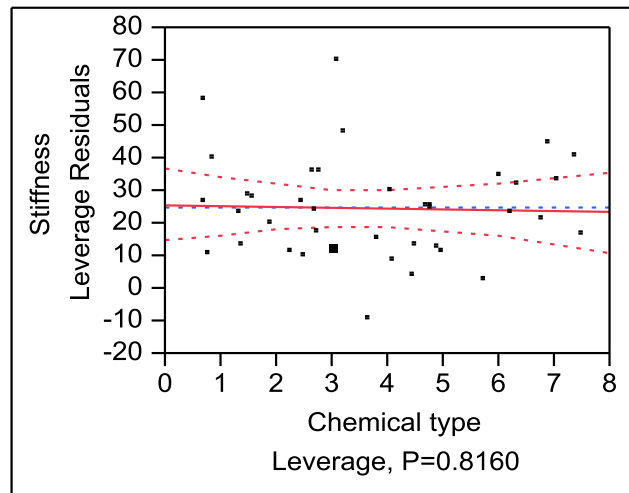


Figure 40 Modulus residuals vs. FR chemical type (before wash).

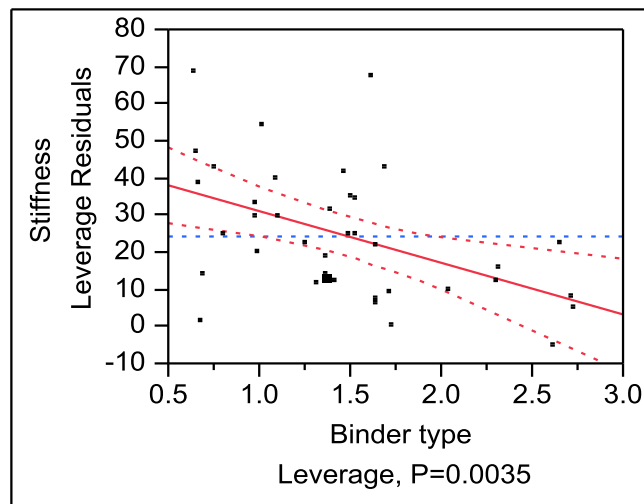


Figure 41 Modulus residuals vs. chemical binder type (before wash).

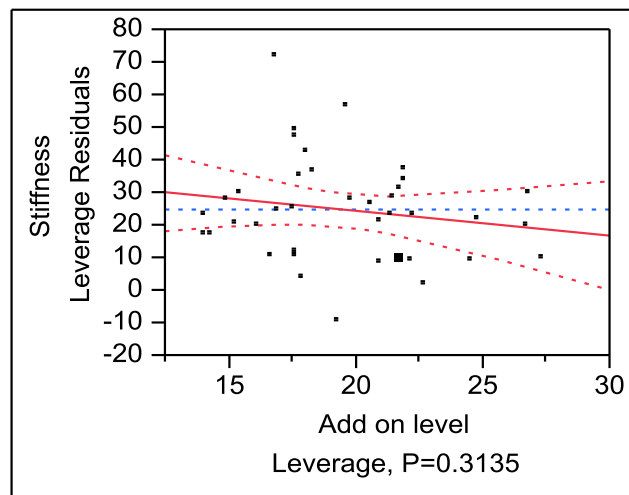


Figure 42 Modulus residuals vs. chemical add on percentage (before wash).

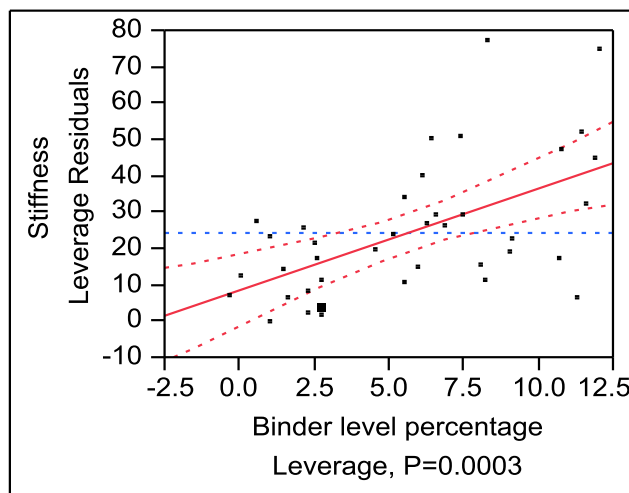


Figure 43 Modulus residuals vs. chemical binder percentage (before wash).

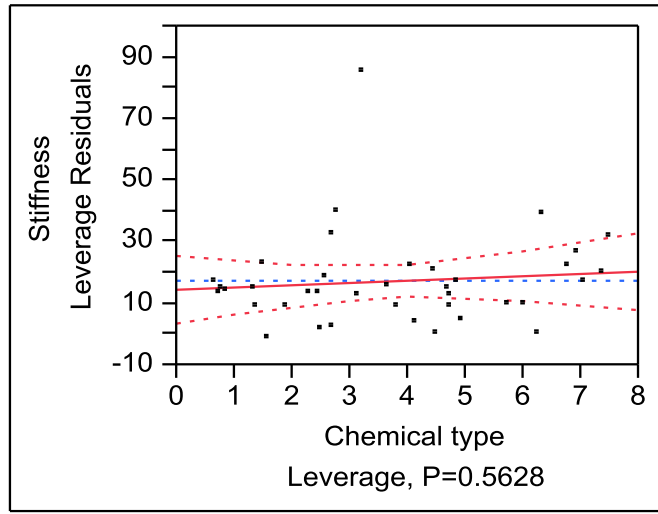


Figure 44 Modulus residuals vs. FR chemical type (after wash).

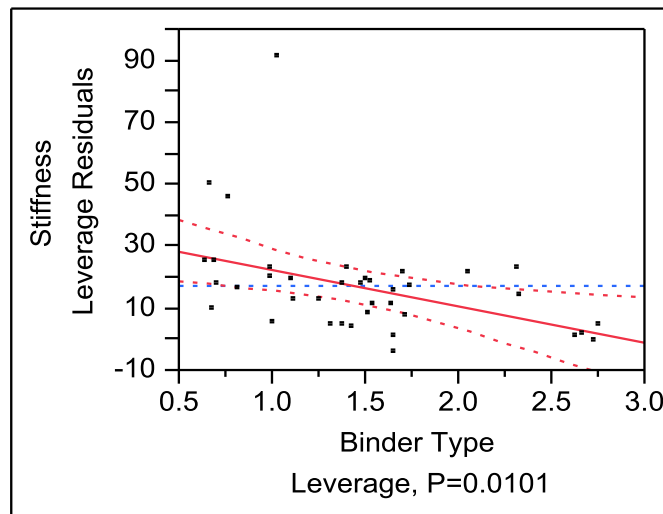


Figure 45 Modulus residuals vs. chemical binder type (after wash).

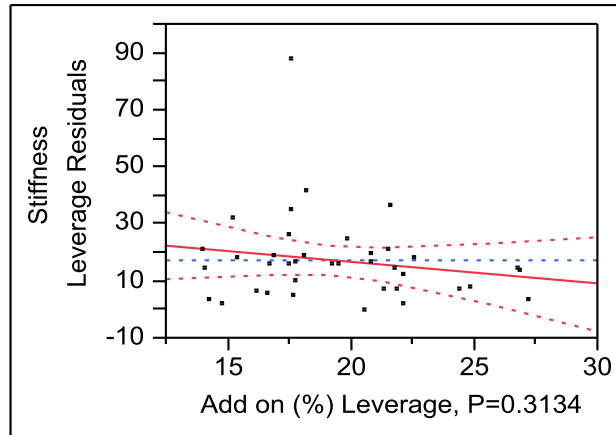


Figure 46 Modulus residuals vs. chemical add on percentage (after wash).

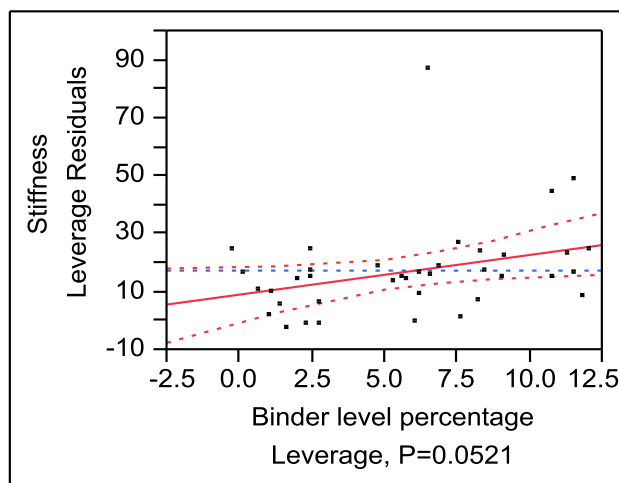


Figure 47 Modulus residuals vs. chemical binder percentage (after wash).

The Modulus data analysis showed that before and after washing, chemical binder type and chemical binder percentage are the most significant parameters on the modulus of the FR treated webs. It is obvious that if the modulus of the cotton webs is considered, significance of chemical binder type and binder percentage must be kept in mind. The flame retarding performance must be balanced with fabric stiffness when choosing a proper FR formulation for cotton based nonwovens.

4.4.2 Neural Network Analysis Results

Neural networks have been called as universal approximators, and provide solution to an arbitrarily function fitting problem. Neural networks are good at recognizing patterns where inputs have been mapped nonlinearly. Such networks use nonlinear models of simple algorithms where the form of nonlinearity can be obtained from the training data [66].

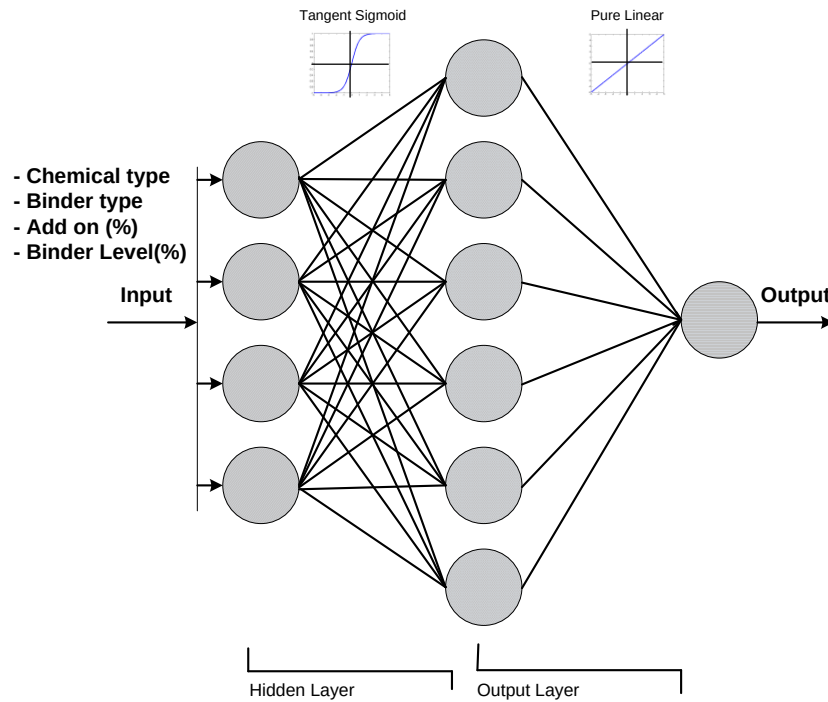


Figure 48 Schematic Neural Network (NN) presentation.

In this research 4×6×1 neural network was used. Neural networks are used for function fitting when inputs and corresponding outputs are known by user. The general accepted methodology consists of three parts:

1. Dividing the already obtained data after experimental study into two groups, training and test data
2. Training the net with the first group, testing the net with the test data that is unknown by the net but known by the user. Therefore the success of net can be evaluated by using the test data outputs as the ground truth.
3. Introducing the net possible randomly selected inputs and having the outputs. The success in the first and second stages affects the third stage.

For the training stage of data, known parameters and values of flame retardant chemical type, chemical binder type, chemical add on percentage, and binder level were introduced to NN as the inputs and corresponding LOI values as the outputs (Figure 49 and 50). 39 experimentally obtained data were divided into two groups. 30 of data were used for training and 9 of it as the testing data. To the net, 30 experimental data are introduced and outputs are tried to reach as the goal of net training. Testing data results by using 9 experimental data are presented in Figure 47. Output of the net was compared with corresponding experimentally observed LOI results (Figure 51).

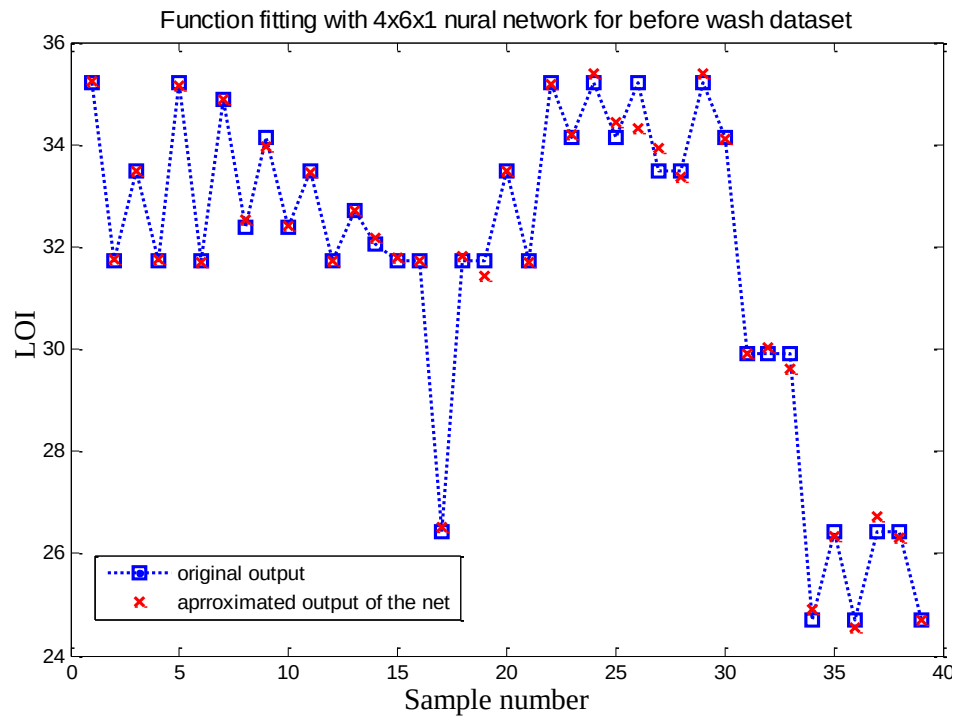


Figure 49 Function fitting (training) before wash LOI data set.

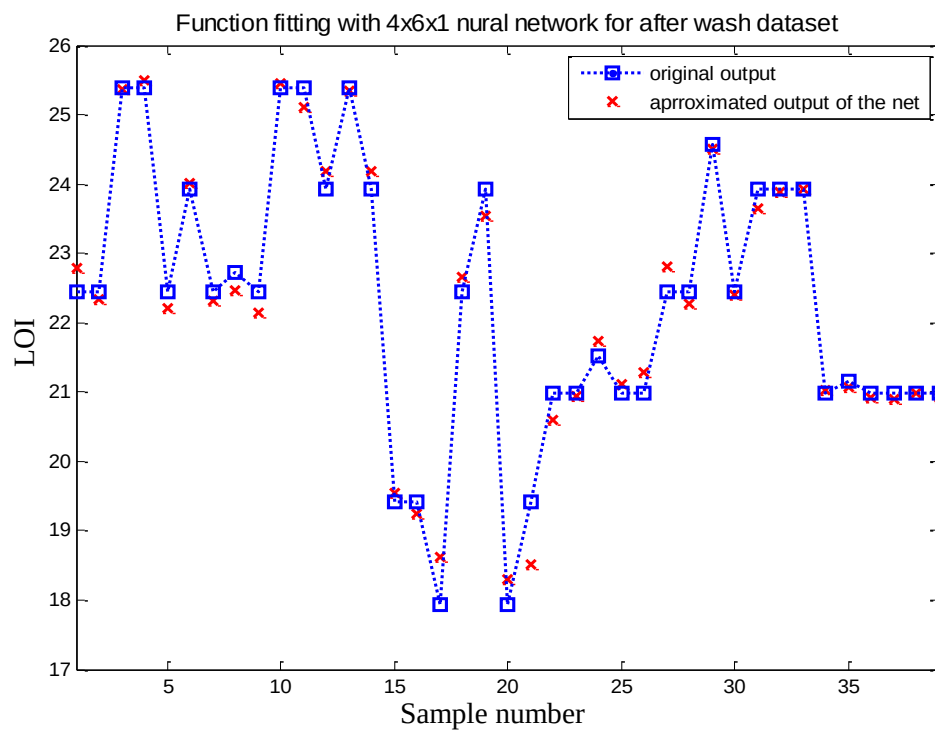


Figure 50 Function fitting (training) after wash LOI data set.

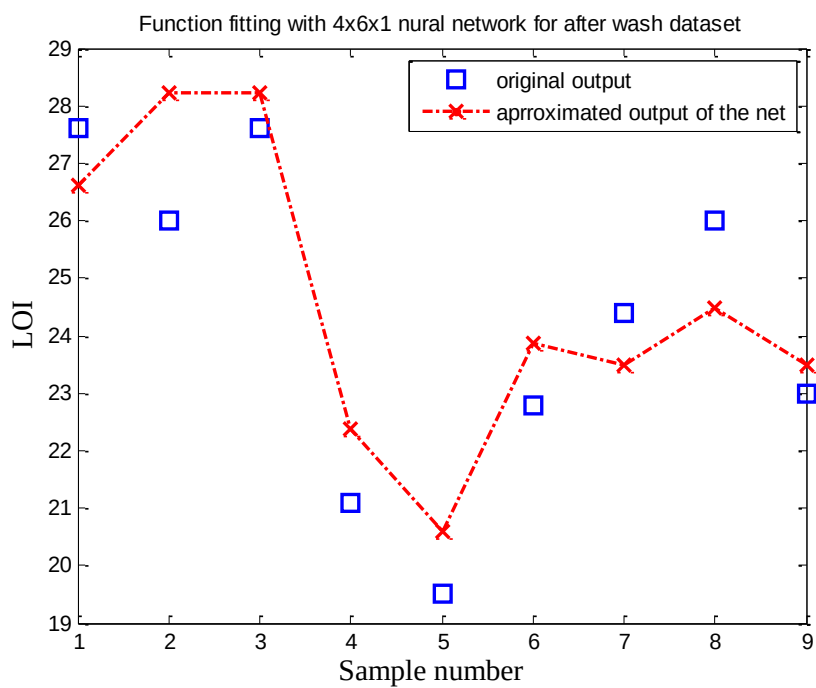


Figure 51 Testing the data stage and experimental LOI results.

As the third stage of NN data analysis, randomly selected 252 new input data combinations were created and NN was asked to produce approximated LOI values for the new data set. Approximated LOI results obtained by NN are presented in Figures 52 and 53.

In Figure 52, approximated LOI results produced by NN are grouped based on FR chemical type, which can be listed as;

0-36: LOI results of Pyrovatim PBS combinations, **37-72:** LOI results of Pyrovatex CP New combinations, **73-108:** LOI results of FR CROS 486 combinations, **109-144:** LOI results of DAP combinations, **145-180:** LOI results of Noflan combinations, **181-216:** LOI results of Eccoshield FR 101 with Eccoshield UA combinations, **217-252:** LOI results of Safron combinations.

In Figure 53, approximated LOI results produced by NN are grouped based on chemical binder percentage which can be listed as;

0-63: LOI results of all FR chemicals with 10% of Rhoplex TR 520, 10% Airflex 4500 and 10% Permafresh CSI-2, **64-126:** LOI results of all FR chemicals with 5% of Rhoplex TR 520, 5% Airflex 4500 and 5% Permafresh CSI-2, **127-189:** LOI results of all FR chemicals with 1% of Rhoplex TR 520, 1% Airflex 4500 and 1% Permafresh CSI-2, **190-252:** LOI results of all FR chemicals with 0% of Rhoplex TR 520, 0% Airflex 4500 and 0% Permafresh CSI-2.

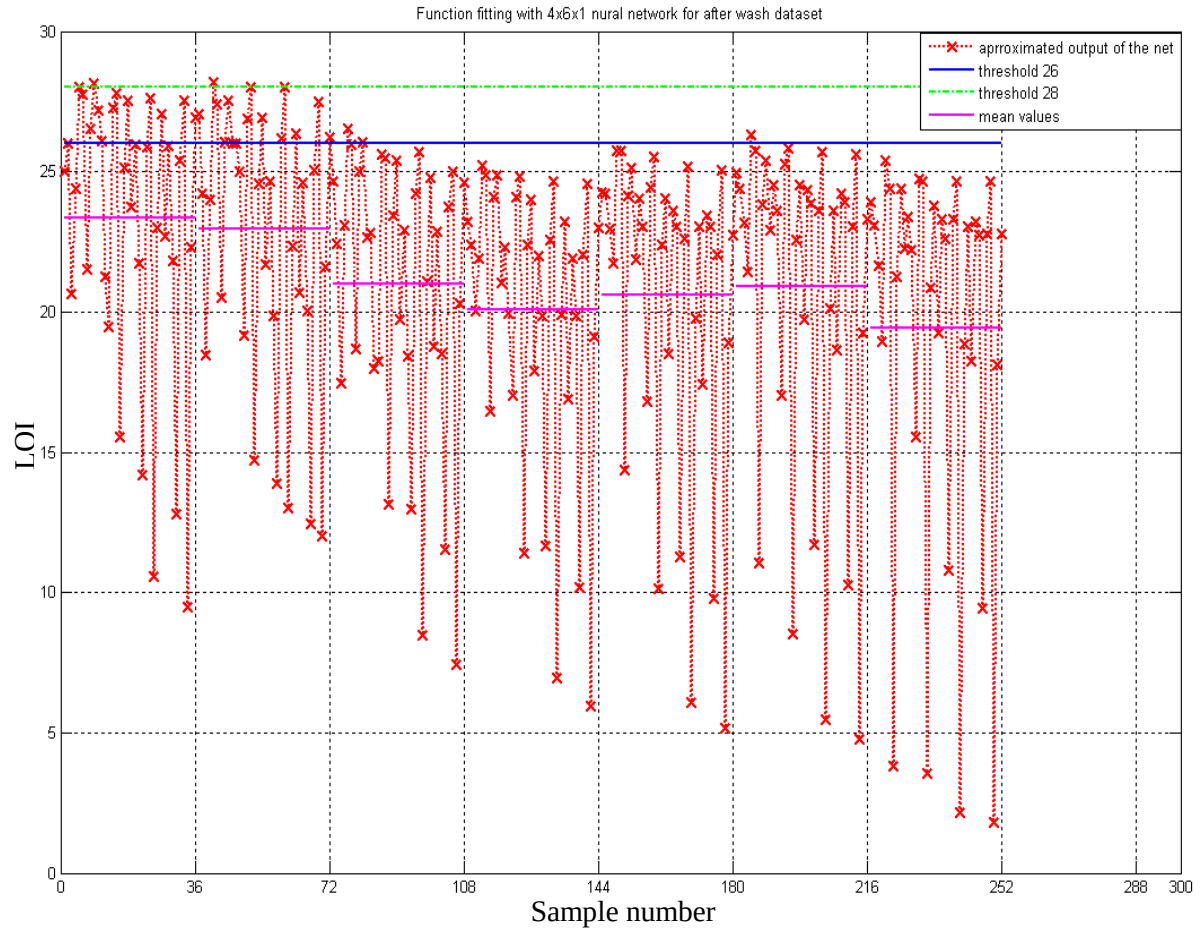


Figure 52 Approximated LOI results after wash which are produced by NN for 252 different FR formulations (lines indicate mean values of approximated LOI data).

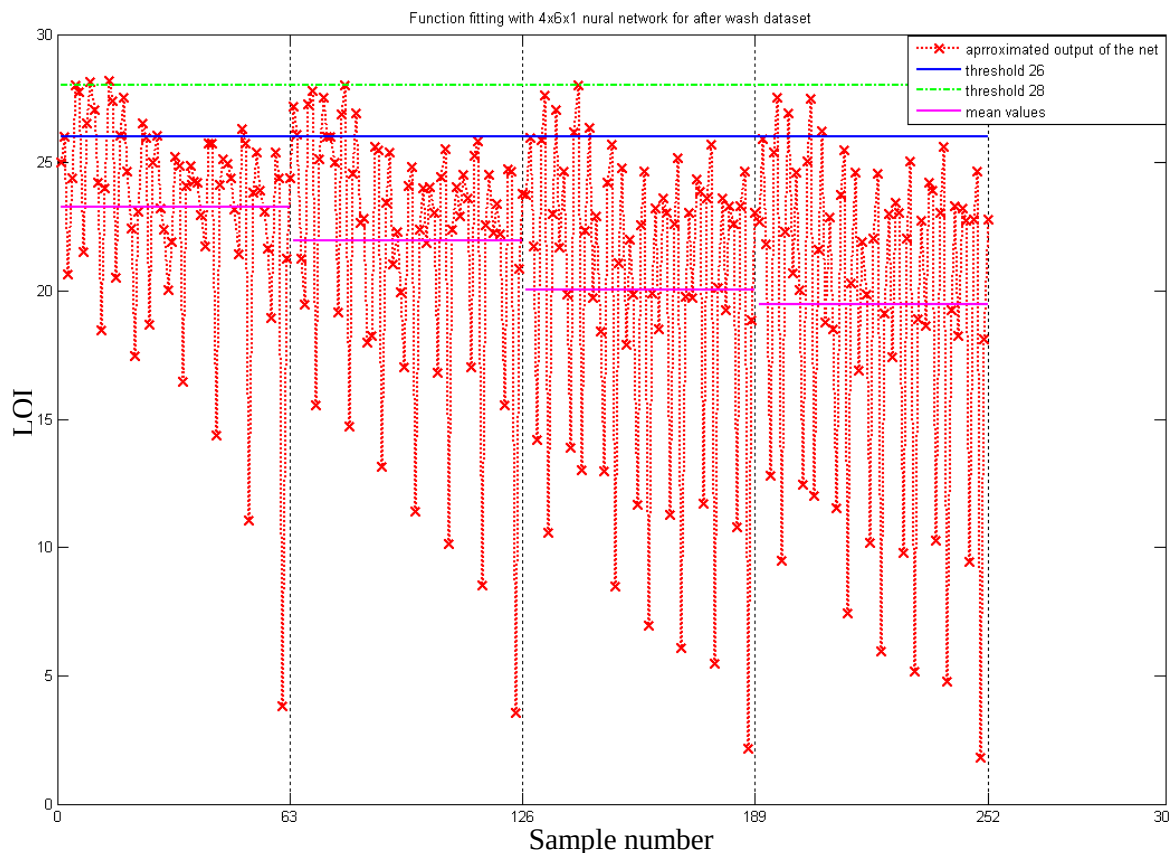


Figure 53 Approximated LOI results after wash which are produced by NN for 252 different FR formulations (lines indicate mean values of approximated LOI data).

Data analysis with NN revealed that Pyrovatim PBS and Pyrovatex CP New combinations produced higher LOI results after washing compared to other flame retardant chemicals studied in this research (Fig. 52 mean values). NN analysis showed that Safron 9025 and DAP combinations produce the lowest LOI results after wash tests (Fig. 52 mean values). Also, our statistical data analysis supported our previous experimental results.

Testing data with NN showed that 10% binder percentage combinations produce higher LOI results compared to 5%, 1% and 0% binder combinations (Fig. 53 mean values).

After wash LOI results decreased as the binder level percentage of the sample decreased (Fig. 53 mean values). The statistical data analysis supports the experimental results. NN data analysis was used for selection of best chemical and binder combination for having an optimum FR performance. Based on NN results, we decided to use the combinations which contain Pyrovatex CP New and Pyrovatim PBS in the presence of 10% Rhoplex TR 520 and Airflex 4500 for our further tests as the next step of the study.

4.5. Hand Laundering and Flammability Test Results

For the first part of study FR treated samples were tested for LOI to determine flammability characteristics of each sample after soak tests. Also statistical analysis based on experimental LOI data was done to reveal the appropriate chemical and binder combination to obtain reasonable FR performance.

Based on statistical analysis, it is obvious that with FR formulations containing Pyrovatex CP New and Pyrovatim PBS chemicals in the presence of 10 % chemical binder desired degree of flame retardancy and wash durability will be achieved.

Based on NN results, we decided to use the combinations with Pyrovatex CP New and Pyrovatim PBS in the presence of 10% Rhoplex TR 520 and Airflex 4500 for our further hand laundering test.

For hand laundering, FR solutions were prepared with desired proportion of Pyrovatex CP New or Pyrovatim PBS and chemical binder as described (part 3.3.4). Each of these FR solutions was applied to three nonwoven webs. One of these treated webs was used as control (no washing), the second treated sample was subjected to one hand laundering cycle, and the third treated sample subjected to two hand laundering cycles. After one and two hand laundering cycles, samples were tested for LOI to determine the effect of laundering on flammability characteristics.

The LOI test results of samples are presented in Tables 7, 8 and 9. LOI results of FR treated samples before and after hand laundering are represented in Figure 54. Also, LOI decrease (%) of FR treated samples after one and two hand laundering compared to unwashed sample is represented in Figure 55.

Table 7 LOI results of FR treated samples before hand laundering

FR Chemical Type	Chemical Binder type	Dry Add-on%	LOI
Pyrovatex CP New	Rhoplex TR 520	23	29.3
Pyrovatex CP New	Airflex 4500	27	29.9
Pyrovatim PBS	Rhoplex TR 520	29	30.9
Pyrovatim PBS	Airflex 4500	28.5	30.9

Table 8 LOI results of FR treated samples after one hand laundering cycle

FR Chemical Type	Chemical Binder type	Dry Add-on%	LOI
Pyrovatex CP New	Rhoplex TR 520	29.8	27.6
Pyrovatex CP New	Airflex 4500	28	28.3
Pyrovatim PBS	Rhoplex TR 520	28	26
Pyrovatim PBS	Airflex 4500	28.4	26

Table 9 LOI results of FR treated samples after two hand laundering cycles

FR Chemical Type	Chemical Binder type	Dry Add-on%	LOI
Pyrovatex CP New	Rhoplex TR 520	27	28.3
Pyrovatex CP New	Airflex 4500	27	28.3
Pyrovatim PBS	Rhoplex TR 520	27	26
Pyrovatim PBS	Airflex 4500	31	26

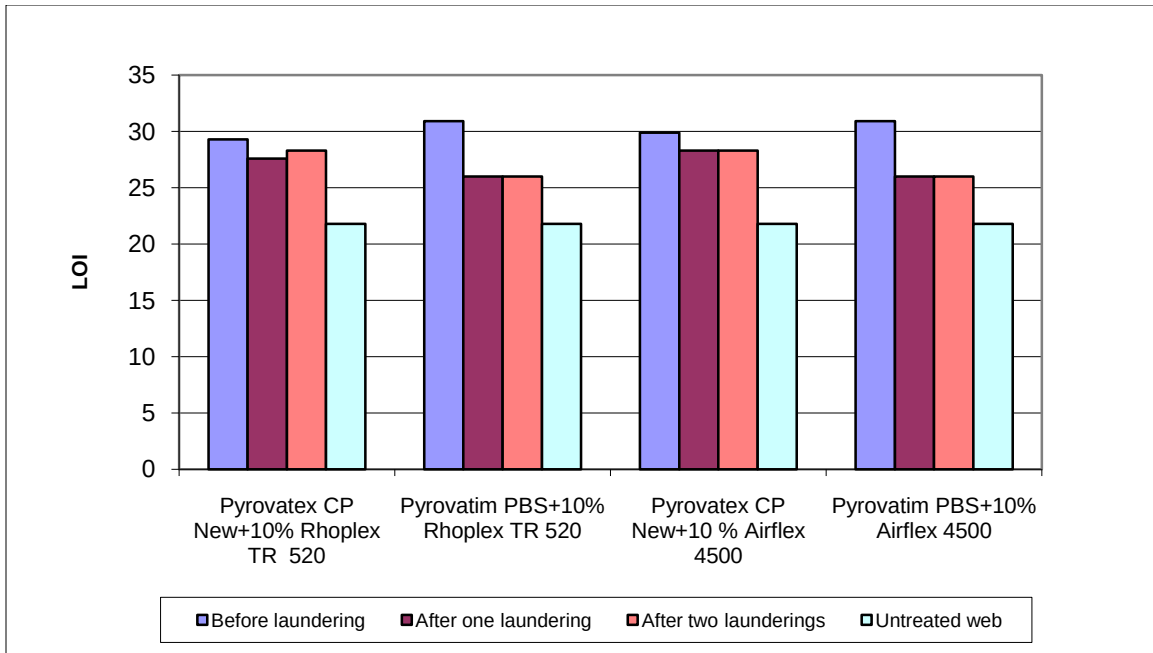


Figure 54 LOI results of FR treated samples before and after hand laundering.

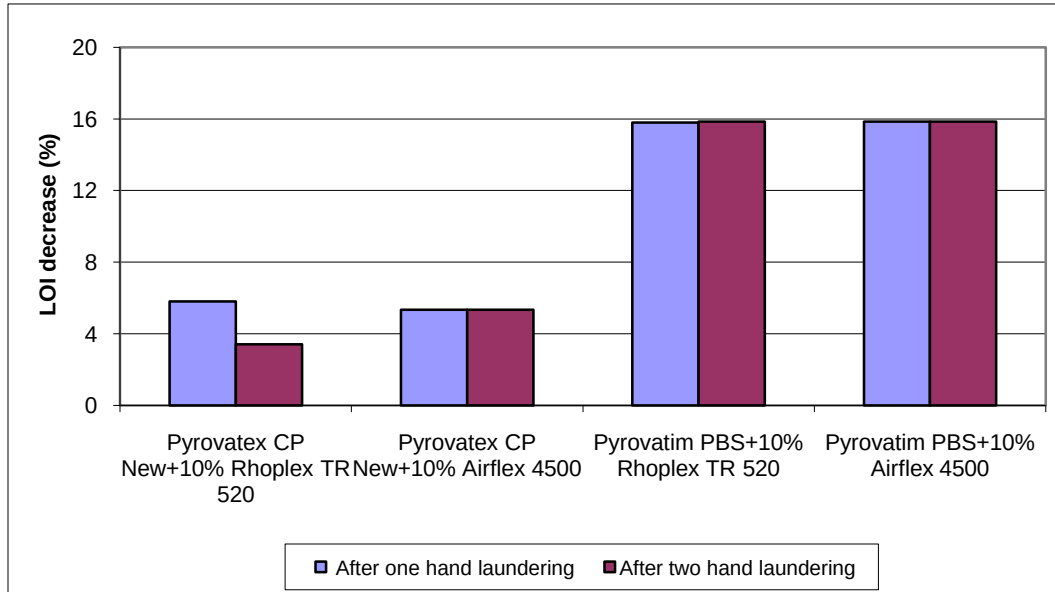


Figure 55 LOI decrease (%) of FR treated samples after one and two hand laundering.

As it can be seen from Figure 54, before and after laundering these samples had higher LOI values compared to untreated web as expected. It is obvious that, Pyrovatex CP New and Pyrovatim PBS treated samples in the presence of binder had a reasonable degree of FR performance after one and two hand laundering cycles.

LOI decrease of Pyrovatex CP New treated samples (Figure 55) is lower than Pyrovatim PBS treated samples. The LOI results of FR treated samples were found to be same after one laundering and two laundering. After washing, Pyrovatim treated samples can be classified as slow burning material and Pyrovatex CP New treated samples can be classified as self extinguishing based on LOI values (based on Table 1).

As it is reported in the literature, Pyrovatex CP New bind to the cellulose repeat unit via its N-Methylol group. This linking cannot be removed during regular washing [46, 67, 68]. Pyrovatim PBS reacts with cellulose and forms phosphate-cellulose bond. LOI results after hand laundering indicated that, Pyrovatex CP New and Pyrovatim PBS provided desired degree of durable flame retardant property and the presence of a binder and the amount of binder increased the amount bonding to cotton. These results can be considered as the confirmation of the previous results. Our results are consistent with observations from other researchers.

Also, to reveal whether these FR formulations can qualify open flame standard, these samples were tested using the test described by California Technical bulletin or, 16CFR part 1634 (TB604 test, described in experimental section). TB604 test results are presented in Tables 10 and 11.

As it can be seen from Tables 10 and 11, FR chemical treated samples passed the TB604 test before laundering and after two hand laundering cycles. The samples pass the test because their weight loss was less than 25% and they did not form any void at the center. Flame spread was very little and slow for both unwashed and washed samples (Figure 56). These results demonstrates that these FR formulations would be suitable candidates to qualify the latest open flame standard.

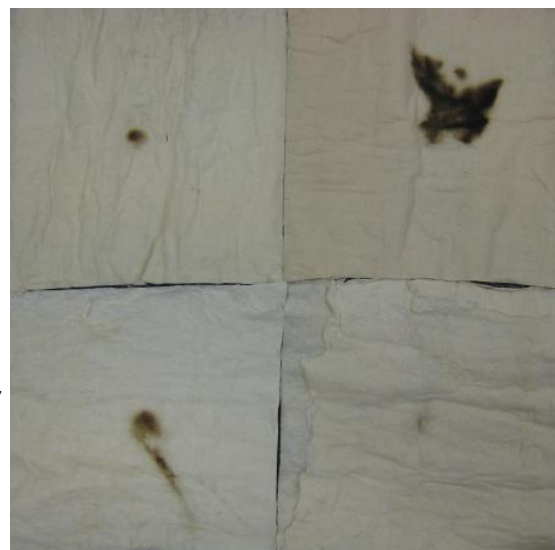
Considering all the results, FR formulations containing Pyrovatex CP New and Pyrovatim PBS chemicals in the presence of 10 % chemical binder are expected to be potential FR systems when wash durability is desired

Table 10 TB604 results of FR treated samples before laundering

FR Chemical Type	Chemical Binder type	Dry Add-on%	Result
Pyrovatex CP New	Airflex 4500	27	pass
Pyrovatim PBS	Airflex 4500	28.5	pass

Table 11 TB604 results of FR treated samples after two hand laundering cycles

FR Chemical Type	Chemical Binder type	Dry Add-on%	Result
Pyrovatex CP New	Airflex 4500	27	Pass
Pyrovatim PBS	Airflex 4500	31	Pass



a

b

Figure 56 Nonwoven web pictures after TB 604 test (a) front side (b) back side.

5.0 CONCLUSIONS AND RECOMMENDATIONS

In this research, effect of different FR chemicals, binders and the level of binders on wash durability, flame retardancy and physical properties of cotton-based nonwovens was investigated.

For FR treated samples, after washing, as the binder level increases in the FR solution formulation, weight loss of treated samples decreased with varying percentages for all types of FR chemicals for all FR chemicals studied. FR solution formulation with 10% binder gave the best wash durability after water soak tests. When 10% binder containing FR applications were considered, highest wash durability was obtained with Airflex 4500 treated samples whereas lowest wash durability was obtained with Permafresh CSI-2 treated nonwoven samples.

Safron 9025 and Eccoshield FR 101 (with Eccoshield UA) treated samples with all type of binders had the highest wash durability. Also, Pyrovatex CP New treated samples had a high level of wash durability performance among the FR chemicals studied. DAP treated samples with all types of binders had the lowest wash durability. The wash durability was dependent on the chemical nature of the FR additive.

Without binder most of the flame retardant chemical applied to nonwoven webs was removed after two water soak cycles. To provide wash durability property, usage of chemical binder is a must for the studied flame retardants.

After FR treatment, flame retardancy performance of unwashed samples showed a significant improvement compared to untreated sample. Selected semi-durable and durable FR chemicals can be used in potential FR systems for cotton rich nonwovens to reduce flammability. Only, Safron 9025 treated samples had LOI value close to untreated sample and exhibited low degree of flame retardancy before washing.

After washing, Pyrovatex CP New with Rhoplex TR 520, Pyrovatim PBS with Airflex 4500 and Rhoplex TR 520 and Eccoshield FR 101 (with Eccoshield UA) treated samples had higher LOI values compared to other produced FR combinations. These samples can be classified as slow burning materials according to classification based on LOI. Pyrovatex CP New, Pyrovatim PBS and Eccoshield FR 101 had reasonable durability performance for cotton rich nonwovens. The additives that had chemical groups that could react with cellulose showed higher durability and LOI performance, as one can expect.

With all types of binders Safron 9025 and DAP treated samples had the lowest LOI values after washing. Pyrovatex CP New, Pyrovatim PBS and Noflan in the presence of Permafresh CSI-2 had same FR performance after washing.

Stiffness of samples significantly increased after FR treatment. Rhoplex TR 520 treated samples had higher stiffness increase effect on cotton rich nonwoven webs. For Rhoplex TR 520 treated samples, % stiffness was higher as the binder percentage in the FR solution increased.

When binder type and binder percentage in the FR combination were kept constant, Safron 9025 and FR CROS 486 treated samples had higher % stiffness increase

compared to other FR chemicals studied. Chemical retention and wash durability property of studied FR chemicals was reflected in mechanical properties of samples after washing as well. Before wash, FR chemical treated samples exhibit higher tensile peak force and lower elongation % compared to untreated web sample. FR chemical strengthened the cotton based nonwoven fabric. Modulus of FR treated samples was higher than untreated nonwoven sample. Before and after washing, modulus of samples was higher as the binder percentage of the FR solution was increased.

To ease the burden of conducting too many experiments statistical tools are effective to reveal information related to experimental data. Also, it will help selection of best chemical and binder combination for having an optimum FR performance. JMP analysis showed that before washing, chemical type and chemical add on percentage are two effective factors determining the flammability of FR treated samples. But after washing, instead of chemical add on percentage, binder percentage becomes an important factor that determines the LOI of FR treated cotton rich nonwoven samples.

Statistical analysis showed that before and after washing, chemical binder type and chemical binder percentage are the most significant parameters on the modulus of the FR treated webs.

Neural Networks analysis revealed that Pyrovatim PBS and Pyrovatex CP New combinations produced the highest LOI results while Safron 9025 and DAP combinations produced the lowest LOI results after washing. Neural Networks analysis also showed that in the presence of 10% binder, samples produce higher LOI results compared to 5%, 1% and 0% binder containing FR combinations. After wash, LOI values decreased as the binder percentage of the FR combination decreased.

After two hand laundering cycles, Pyrovatim PBS treated samples can be classified as slow burning material and Pyrovatex CP New treated samples can be classified as self

extinguishing based on LOI values. These chemicals have the ability to react with cellulose which leads to improved resistance to washing.

Formulations containing Pyrovatex CP New and Pyrovatim PBS with 10% chemical binder passed the TB604 test before laundering and after two hand laundering cycles. Flame spread was very little, and slow for these samples. These FR formulations would be suitable candidates to qualify the latest open flame standard.

Considering all the results, FR formulations containing Pyrovatex CP New and Pyrovatim PBS chemicals in the presence of 10 % chemical binder provided desired degree of durable flame retardant property and the presence of a binder and the amount of binder increased the wash fastness cotton. These formulations are expected to be potential FR systems when wash durability desired.

Things that must be kept in mind while selecting FR chemicals for future applications are; Noflan Treated samples turn to brown (almost a color of burned web) very easily during drying process in Mathis equipment and in the oven. Eccoshield FR 101 had high wash durability and flammability performance but, the supplier company recommended applying Eccoshield FR 101 together with Eccoshield UA. Combination of these chemicals gives very bad smell during FR application and curing process. This bad odor of the chemical is not appropriate for nonwoven processing and applications.

Recommendations for Future work

Understanding the chemical retention before and after treatment is important. FTIR and other spectroscopic techniques can help. Also, SEM analysis of the treated webs will help understand where and how the chemicals are deposited.

Surface morphology of char of fiber can give useful information about FR efficiency of especially phosphorous based FRs. SEM analysis of the charred samples can help in understanding the char characteristics.

Processing conditions and methods can be modified and optimized to obtain higher degree of flame retardancy and wash durability.

Thermal properties of untreated, treated unwashed samples and treated washed samples can be done to see effect of FR treatment and washing on decomposition temperature and char amount.

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APPENDICES

APPENDIX A

Abbreviations

- FR Flame Retardant
- PBI Polybenzimidazole
- ATH Aluminum Trihydrate
- PP Polypropylene

- PU Polyurethane
- PA Polyamide
- DAP Diammonium Phosphate
- APP Ammonium Polyphosphate
- TDS Technical Data Sheet
- MSDS Material Safety Data Sheet
- FFA Federal Fabric Act

APPENDIX B

Table B1 Weight loss results of FR after two water soak tests (10% Rhoplex TR 520 as binder)

	0% Rhoplex TR 520		1% Rhoplex TR 520		5% Rhoplex TR 520		10% Rhoplex TR 520	
	Dry Add on (%)	Weight Loss (%)	Dry Add on (%)	Weight Loss (%)	Dry Add on (%)	Weight Loss (%)	Dry Add on (%)	Weight Loss (%)
PCP New	16	9.6	17.5	8	19.1	8.3	20	6.3

PBS	26.4	16.5	13.7	8.3	16.3	7.7	18.8	7.6
FR CROS 486	27	21	22.5	15.6	17.6	10.6	18	7.9
DAP	14.6	12.5	22	16.5	21.6	14.6	19.5	10

Table B2 Weight loss percentage of FR after two water soak tests (Rhoplex TR 520 as binder)

Flame Retardant Chemicals	Weight loss (%) (0% binder)	Weight loss (%) (1% binder)	Weight loss (%) (5% binder)	Weight loss (%) (10% binder)
Pyrovatex CP New	70	54	51	37
Pyrovatim PBS	80	70	55	49
FR CROS 486	98	85	77	52
DAP	98	91	83	71
Noflan	70	68	61	52
Eccoshield FR 101 +Eccoshield UA	27	-	-	18
Safron 9025	25	-	8	9

Table B3 Weight loss percentage of FR after two water soak tests (Airflex 4500 as binder)

Flame Retardant Chemicals	Weight loss (%) (0% binder)	Weight loss(%) (1% binder)	Weight loss(%) (10% binder)
Pyrovatex CP New	70	50	28
Pyrovatim PBS	80	62	36
FR CROS 486	98	-	40

DAP	98	-	68
Noflan	70	-	35
Eccoshield FR 101 +Eccoshield UA	27	-	13
Safron 9025	25	-	7

Table B4 LOI results of FR treated samples before and wash (10% Rhoplex TR 520 as binder)

Flame Retardant Chemicals	Chemical add-on (%) (Before wash)	LOI (before wash)	LOI (after wash)	Chemical remained on sample (%) (after wash)
Pyrovatex CP New	20	30.9	27.6	12.5
Pyrovatim PBS	18.8	29.3	27.6	9.2
FR CROS 486	18	29.3	24.4	8.8
DAP	19.5	31.5	22.8	7.8
Noflan	27.6	30.9	24.4	13.2
Eccoshield FR 101+ Eccoshield UA	18.5	27.6	26	15
Safron 9025	22.6	22.8	22.8	20

Table B5 LOI results of FR treated samples before wash (10% Airflex 4500 as binder).

Flame Retardant Chemicals	Chemical add-on (%) (Before wash)	LOI (before wash)	LOI (after wash)	Chemical remained on sample (%) (after two water soakings)
Pyrovatex CP New	23.4	30.2	27.6	15.6

Pyrovatim PBS	19.5	29.3	26	12.5
FR CROS 486	18	29.3	26	9.7
DAP	16.2	32.5	23.4	5.2
Noflan	22.5	32.5	26.7	14.9
Eccoshield FR 101+ Eccoshield UA	21.6	27.6	26	18.6
Safron 9025	18	24.4	22.8	17

Table B6 LOI results of FR treated samples before wash (10% Permafresh CSI-2 as binder)

Flame Retardant Chemicals	Chemical add-on (%) (Before wash)	LOI (before wash)	LOI (after wash)	Chemical remained on sample (%) (after two water soakings)
Pyrovatex CP New	20	29.6	25	8.3
Pyrovatim PBS	18.7	32	24.4	6
Noflan	21.6	31.5	24.4	7
Safron 9025	20.9	22.8	22.8	12

Table B7 Mechanical test results of samples before wash (10% Rhoplex TR 520 as binder)

Flame Retardant Chemicals	Bending length (cm)	Tensile Force (N)	Elongation (%)	Modulus (N)	BL Increase (%)

Pyrovatex CP New	13.5	8.6	13.6	46	85
Pyrovatim PBS	14.3	5.7	20.2	76.8	95
FR CROS 486	16.8	7.3	6.9	55.6	130
DAP	13	2.7	12.4	9	78
Noflan	14.2	4.6	7.3	27.5	94
Eccoshield FR 10 +Eccoshield UA	14.9	6.2	6.6	21.5	104
Safron 9025	14.7	6.8	10.6	48	101

Table B8 Mechanical test results of samples before wash (10% Airflex 4500 as binder)

Flame Retardant Chemicals	Bending length (cm)	Tensile Force (N)	Elongation (%)	Modulus (N)	BL Increase (%)
Pyrovatex CP New	10	5.7	18	15	40
Pyrovatim PBS	11.7	5.4	19	15.5	60
FR CROS 486	16.4	12	14.5	77	124
DAP	9	9.8	17.8	15.6	23
Noflan	9.5	1.5	31	6	30
Eccoshield FR 10 +Eccoshield UA	13.5	4.6	14	31.5	84
Safron 9025	15.2	12.6	23	50.6	108

Table B9 Mechanical test results of samples before wash (10% Permafresh CSI-2 as binder)

Flame Retardant Chemicals	Bending length (cm)	Tensile Force (N)	Elongation (%)	Modulus (N)	BL Increase (%)
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Pyrovatex CP New	11.5	2.5	29	4.6	57
Pyrovatim PBS	13.7	11.5	30	30	87
Noflan	9.8	14	16	14	34
Safron 9025	12.5	2.9	20	11	71

Table B10 Mechanical test result of samples after two water soak tests (10% Rhoplex TR 520 as binder)

Flame Retardant Chemicals	Bending length (cm)	Tensile Force (N)	Elongation (%)	Modulus (N)
Pyrovatex CP New	11.4	8.7	19.3	10
Pyrovatim PBS	14.2	3.4	21.5	25.5
FR CROS 486	11.5	8.2	8.9	52.3
DAP	12.4	7.6	18	27.4
Noflan	13.1	4.1	15	15
Eccoshield FR 10 +Eccoshield UA	12.1	3.2	7.9	22.2
Safron 9025	14.7	13.2	12	49

Table B11 Mechanical test result of samples after two water soak tests (10% Airflex 4500 as binder)

Flame Retardant Chemicals	Bending length (cm)	Tensile Force (N)	Elongation (%)	Modulus (N)
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Pyrovatex CP New	9.6	2.7	22	6
Pyrovatim PBS	11.2	6.2	20.6	15
FR CROS 486	15.3	5.7	20	15
DAP	8.5	4.3	21.5	5.6
Noflan	9.4	7.8	18.5	18.6
Eccoshield FR 10 +Eccoshield UA	9.8	1.5	28	2.7
Safron 9025	11.6	10.8	17.5	27.6

Table B12 Mechanical test result of samples after two water soak tests (10% Permafresh CSI-2 as binder)

Flame Retardant Chemicals	Bending length (cm)	Tensile Force (N)	Elongation (%)	Modulus (N)
Pyrovatex CP New	9.7	2.2	31.7	3.4
Pyrovatim PBS	7.6	0.8	33	1.2
Noflan	7.5	0.7	42	1.1
Safron 9025	9.8	2.5	18	9

Table B13 Mechanical properties of FR treated samples without binder before wash

Flame Retardant	Bending	Tensile	Elongation (%)	Modulus (N)
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Chemicals	length (cm)	Force (N)		
Pyrovatex CP New	9.43	2.1	23.6	11
Pyrovatim PBS	8.53	3.3	23	11.6
FR CROS 486	11.2	7.15	19.8	20.5
DAP	9.9	2.86	20	7
Noflan	9.8	4.27	17	11.3
Eccoshield FR 101 +Eccoshield UA	10.9	1.87	7.1	22.8
Safron 9025	11.3	9.8	17.9	31

Table B14 Mechanical properties of FR treated samples without binder after wash

Flame Retardant Chemicals	Bending length (cm)	Tensile Force (N)	Elongation (%)	Modulus (N)
Pyrovatex CP New	7.33	1.16	31	2
Pyrovatim PBS	12.1	4.25	18	10
FR CROS 486	8.6	5.7	20.1	10.4
DAP	9	7	18.3	18
Noflan	7	2.7	19	5.62
Eccoshield FR 101 +Eccoshield UA	10.2	1.25	9	4.9
Safron 9025	10.1	7.1	18.6	17.4

Table B15 Mechanical properties of FR treated samples before wash (1% Rhoplex TR 520 as binder)

Flame Retardant Chemicals	Bending length (cm)	Tensile Force (N)	Elongation (%)	Modulus (N)
Pyrovatex CP New	10.2	1.48	27.4	4.81
Pyrovatim PBS	12.6	7.3	21.6	17.8
FR CROS 486	10.5	2.88	20.46	5.28
DAP	11.9	5.5	19	21.6
Noflan	9.5	1.39	40.5	1.91
Eccoshield FR 101 +Eccoshield UA	13.8	5.61	11.6	53.9

Table B16 Mechanical properties of FR treated samples after two water soak tests (1% Rhoplex TR 520 as binder)

Flame Retardant Chemicals	Bending length (cm)	Tensile Force (N)	Elongation(%)	Modulus (N)
Pyrovatex CP New	8.1	1.26	30	1.96
Pyrovatim PBS	10.4	4.94	20.8	11.3
FR CROS 486	10.2	2.54	25	2.77
DAP	10.5	7.73	25	19.2
Noflan	9.3	1.08	44	0.8
Eccoshield FR 101 +Eccoshield UA	10.5	2.7	15.96	9.36

Table B17 Mechanical properties of FR treated samples before wash (5% Rhoplex TR 52 as binder)

Flame Retardant Chemicals	Bending length (cm)	Tensile Force (N)	Elongation (%)	Modulus (N)
Pyrovatex CP New	11.1	7.9	12.4	20.9
Pyrovatim PBS	13.2	4.73	20.3	21.6
FR CROS 486	15.3	14.5	7.6	91.3
DAP	10	1.84	16.7	7.7
Noflan	10.3	4.3	21	11.9
Safron	16	11.5	21.5	22

Table B18 Mechanical properties of FR treated samples after two water soak tests (5% Rhoplex TR 520 as binder)

Flame Retardant Chemicals	Bending length (cm)	Tensile Force (N)	Elongation (%)	Modulus (N)
Pyrovatex CP New	11.2	8	15.2	34.9
Pyrovatim PBS	12	7.95	14.4	30.6
FR CROS 486	15.5	6.24	5.09	54
DAP	10.6	3.34	13.3	21.7
Noflan	13.6	5.41	14	27
Safron	14	13.2	18.5	38

Table B19 Mechanical properties of FR treated samples before wash (1% Airflex 4500 as binder)

Flame Retardant Chemicals	Bending length (cm)	Tensile Force (N)	Elongation (%)	Modulus (N)
Pyrovatex CP New	10.1	4.89	19.9	5.6
Pyrovatim PBS	8.8	3.05	18	8.6

Table B20 Mechanical properties of FR treated samples after two water soak tests (1% Airflex 4500 as binder)

Flame Retardant Chemicals	Bending length (cm)	Tensile Force (N)	Elongation (%)	Modulus (N)
Pyrovatex CP New	9.6	2	20.6	20.6
Pyrovatim PBS	8.7	3	21.8	9.79

VITA

Hatice Mercimek was born in Turkey. She went to Yildiz Technical University in Istanbul and graduated in 2001 with BS. in Chemical Engineering. Then, she went to Bogazici University in Istanbul and graduated in 2005 with MS. in Chemical Engineering. For two years she worked in a construction chemicals production factory as a research and development laboratory manager in Turkey. She came to USA in 2007 and she currently enrolled in MS program at the University of Tennessee, Knoxville.

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