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Flame Retardant Mattress Pads

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To the Graduate Council:

I am submitting herewith a dissertation written by Manjeshwar Ganeshaq Kamath entitled "Flame Retardant Mattress Pads." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Polymer Engineering.

Gajanan S. Bhat, Major Professor

We have read this dissertation and recommend its acceptance:

Roberto Benson, Kevin Kit, Jimmy Mays

Accepted for the Council:
Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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Flame Retardant Mattress Pads

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Manjeshwar Ganesha Kamath
August 2009

DEDICATION

This thesis is dedicated to:

My family, friends, and teachers

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ABSTRACT

Focus of this research is on developing cotton-based nonwoven mattress pads with flame retardant (FR) properties by blending cotton with other commercially available fibers, binders, and followed by chemical treatments; offering a cost-effective recipe to meet the upcoming flammability standards. Furthermore this research explores the opportunities taking advantage of possible synergistic effects to achieve maximum performance.

Recent changes in the flammability regulations require improvements in the flame resistance of cotton-containing consumer goods such as upholstered furniture, mattresses, and pillows. Cotton, synthetic fibers, fabrics, and foam are the basic constituents of these goods that are often the first to be engulfed by fire. Hence there is a need to impart certain degree of flame resistance based on their end use. In case of real fires, these improvements in flame retardancy would provide more time for people to escape from a fire with fewer injuries, and result in savings of life as well as property.

Cotton being a highly flammable fiber, to achieve higher degree of flame resistance, it is necessary to incorporate additional fibers and chemicals into cotton products. Choice of appropriate materials can help to achieve a synergistic role in the combustion process to slow down burning, reduce flame spread, or even extinguish the fire. Many of these chemicals are expensive and lead to a spike in the product cost. Moreover there are certain FR chemicals that are likely to pose environmental and health hazards. The FR chemicals used in this research are halogen free and have been considered safe. Finally, a cost effective recipe for constructing mattress pads that passes the latest flammability tests was developed. As planned, these nonwoven pads were produced by blending cotton with other commercially available fibers, binders, and followed by chemical treatments that take advantages of various synergistic effects to achieve maximum performance at low cost. The product of this research is a good candidate for mattress pads as well as other products such as upholstered furniture, mattress ticking, and pillows, which are required to comply with the open flame standards.

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1.0 INTRODUCTION AND GENERAL INFORMATION

Currently scientific research on cotton-based consumer goods such as upholstered furniture, mattresses, and pillows is focusing on the flame retardancy regulations enforced by the legislature. Every year about 14000 household fires occur, leading to 330 deaths and $300million in property loss[1]. Moreover open flames and burning cigarettes cause about 80% of these fires. In case of real fires, these improvements in flame retardancy would provide more time for people to escape from a fire with fewer injuries, and result in savings of life as well as property.

In the recent years, several agencies such as the U.S. Consumer Product Safety Commission (CPSC)[1], California Bureau of Home Furnishings[2], and National Fire Protection Agency[3] are continually developing new flammability regulations for upholstered furniture, mattresses, pillows, bedclothes, carpets, work clothes, sleepwear, and personal protection garments etc. As a result, the demand for flame retardant fibers and fabrics is increasing to comply with the time-to-time changes in these regulations. Regulatory details are available in Chapter 16, Code of Federal Regulations (CFR)[4] parts 1602 through 1634.

Depending on the application, the degree of FR treatment varies[5] (Figure 1). Personal protective garments need extremely high degree of FR, whereas toys need FR of lower degree. Sleep products fall in the medium FR category. Currently primary concern of the mattress industry is to pass open flame tests[6] such as CFR Part 1633[4] compliance for mattresses effective since 2007 and soon extending to over the mattress products such as mattress pads, comforters, and pillows as CFR Part 1634[4]. Hence sleep product manufacturers are looking for FR treatment of their products to meet these standards at minimum add-on cost. Chemicals employed in FR treatment must be easily available at an affordable price. This highlights the vast market potential for a techno-economically viable product with a desired degree of flame Retardancy suitable for over the mattress products.

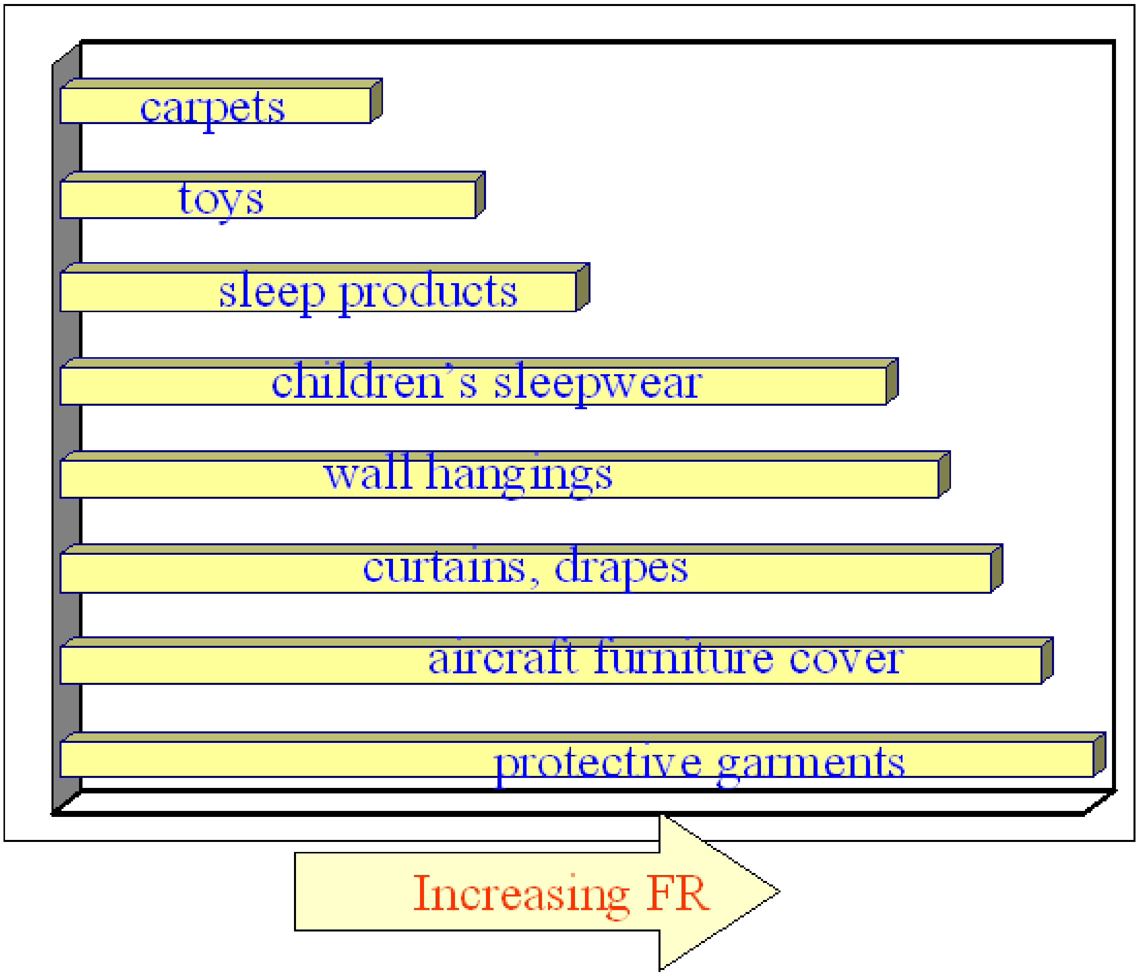


Figure 1 Degree of FR Varies with the Application[5].

Basically cotton is comfortable, a natural product, and is obtained from a renewable resource. Cotton based nonwovens[7] have been used in consumer goods such as comforters, pillows, upholstered furniture, and mattresses for years. A bed is a piece of furniture[8] upon which a person may sleep or recline; in many cultures the bed is considered the most important piece of furniture in the house and a status symbol. Ancient furniture[9] was developed out of the desire for protection, comfort, and sometimes to mark status.

Beds provide support to the whole body, improve the quality of sleep, and for centuries beds were used for sleeping as well as eating, and entertaining socially[8]. Sleeping on the bare ground or even on mats, a practice prevailing since ages is not comfortable, especially in a cold climate or rainy season. Even today the poor, who has no choice, follow this practice. Today, a typical mattress in the United States is constructed of several layers of foams, natural and synthetic fibers, and springs.

Today, a typical mattress in the United States is constructed of several layers of foams, natural and synthetic fibers, and springs. A mattress can be used alone, or on the floor, but is usually placed higher off the ground on a wooden frame with metal springs inside known as foundation. A fabric cover fixed permanently onto the mattress is called ticking. Main purpose[10] of the mattress is to provide adequate comfort. Research[11] indicates that a mattress that conforms better to the shape of the body provides better support and comfort. Also, natural fibers such as cotton and wool have the ability[11] to take perspiration away from the skin and keep one comfortable.

Naturally existing materials such as stone, brick, and manmade products like concrete, and glass are intrinsically flame resistant that simply do not burn. Obadiah Wyld[12] first attempted to introduce FR properties to cotton in early 1730s. Later in 1970s, boric acid[7] treatment of cotton became a popular method to meet standard cigarette ignition resistance that imparts a certain level of flame resistance, but is inadequate to meet present open flame standards. Performance limitations[12] are determined by stability of the chars produced following interaction of the FR chemicals and the fiber when heated. Synthetic fibers such as aramids, novoloids, polyamide imides, carbonized acrylics, and melamines that are self-extinguishing flame resistant[13], but these fibers are very expensive. Moreover, increasing crude oil prices directly impact on all these synthetic fibers unlike cotton, which is less sensitive to changes in the crude oil price.

Flame retardants function by interfering in at least one of the three components of combustion[13]: heat, fuel and oxygen. In the case of melamine fibers, it functions as a heat sink at the early stages, then it degrades to evolve nitrogen that dilutes the vapor and in the later stage the residue acts as a barrier between air and fuel. There are a few chemicals such as bromides, that interfere in the burning reaction and stop the spread of flames, but their combustion products are toxic. Metal hydroxides are safe, since they quench the fire by releasing cooling gases (water vapor), but loading metal hydroxides into the fiber to the desired level (~50%) is not feasible[14]. Phosphorus compounds are good char forming agents to incorporate into a polyester fiber to a desired extent ~10%. Also there are chemicals to provide intumescence effect[15], a foamy barrier that prevents further decomposition of the fuel.

Generally bedding products use high loft nonwovens made up of cotton and other fibers. Pretreated cotton is blended with a tailored mixture of FR fibers. Earlier studies[16] showed that improved flame resistance could be obtained by diammonium phosphate (DAP) treatment, using dimethylol dihydroxyethylene urea (DMDHEU) as a bonding agent. Various FR chemicals[17], FR finishes[18], and microencapsulating[19] techniques are found in commercial applications. Earlier researchers have explained the feedback processes[20] during thermal decomposition of treated cotton, effect of various phosphorus[21] compositions and mechanism[22] involved in FR pads. Enhancement of FR along with antibacterial properties has been tried[23]. Rhoplex[24] is a binder chemical available in the market to adhere FR chemicals onto fibers. Incorporation of FR flexible foam or a Spunfab[25] dry adhesive in a sandwich pattern is another method to impart FR properties.

Mattress pads are generally made of fiber-based nonwovens. Our earlier experience[26] in fiber-based nonwovens proves that an intimate blend is the key to success. Carding is a well-known process for making an intimate blend of fibers. Through-air thermo-bonding method integrates the web as well as cures the adhesive resulting in high-loft nonwovens of desired strength to withstand the stresses exerted on it during downstream processes.

This research is focused on developing FR nonwovens using feedstock consisting of cotton and other FR fibers treated with FR chemicals that are commercially available in sufficient quantities at a reasonably low price. Moreover, the product of this research would be tailored precisely for mattress pads, or barrier pads fitted over the mattress sets such that they meet the upcoming open flammability standards. In addition to evaluating the flammability and physical properties of developed products, the structure of the treated fabrics and the mechanisms involved in achieving flame resistance has been investigated.

2.0 LITERATURE REVIEW

Literature review presented here is based on the technical information extracted from technical papers, trade catalogs, proprietary publications, supplier's web pages, and technical discussions with the scientists and engineers in the field. History and development portion includes the names of the inventors as appeared in earlier publications.

2.1 History and Evolution of Beds

A bed is a piece of furniture upon which a person may sleep or recline; in many cultures the bed is considered the most important piece of furniture in the house and a status symbol. Ancient furniture[9] was developed out of the desire for protection, comfort, and sometimes to mark status. Beds provide support to the whole body, improve the quality of sleep[8], and for centuries beds were used for sleeping as well as eating and entertaining socially. Sleeping on the bare ground or even on mats, a practice prevailing since ages is not comfortable, especially in cold climate or rainy season; moreover it is sometimes dangerous because of crawling insects and snakes found on the ground. Even today the poor, who has no choice, follow this practice.

Prehistoric humans[27] simply huddled in groups for warmth at night and slept on the ground either inside the cave or a hollow tree trunk to escape from wild animals. Most probably, about 10,000 years ago the earliest "mattress" invented was a pile of leaves or straw with animal skins over it[9]. Table 1 provides details on evolution of beds compiled from several published literature. Around 1500BC Persians invented the earliest waterbeds by filling water into the bags made of goatskins. Romans combined bed, couch and sofa into one piece and used it for both sleeping and eating. It had a wooden bedstead or headboard that served as a backrest for reclining. Bed supporting legs had carvings, an inlay and plaiting of gold. Cords stretched across the frame and blankets or cushions were piled on top of them. Interestingly a few were 1 to 1.5meter (3'-5') high that there were also footsteps for ascending and descending the bed.

Table 1 Evolution of Beds: a Timeline

TIME	DETAILS
Early humans	Slept on ground inside caves or inside hollow tree trunks - Nomads
8000 BC	Leaves/straw/feathers stuffed in animal skin - the earliest mattress
3600 BC	The first water-filled beds were goatskins filled with water - Persia
200 BC	Bags of cloth stuffed with hay, wool, or feather - Roman Empire
200 BC	Warm water beds in cradle, sleep until drowsy - Roman Empire
15th Century	Mattress made of straw, feathers, stuffed into bags made of silk/velvet
16th Century	"Sleep soundly" on a wooden frame with ropes across like hammock
18th Century	Mattress stuffed with cotton, wool, or down (feathers)
1850s	Tufted mattress to hold the fillings and cover together.
1865	The first coil spring construction for bedding patented
1871	The first innerspring mattress in Germany - by Heinrich Westphal
1873	Waterbed designed to treat bedsores - by Neil Arnott.
1900	The pocket coil mattress invented - by James Marshall
1906	Sealy Mattress Company formed - bought all patents on mattress
1929	The first mattress with the synthetic material, rubber - Dunlopillow
1940	Futons were introduced to North America.
1950	Foam rubber mattresses and pillows appeared on the market
1953	First Flammable Fabrics Act by the Federal Trade Commission
1960	Synthetic vinyl waterbeds introduced
1980	Inflatable airbeds introduced - made with synthetic vinyl
1990s	Visco-elastic memory foam mattress introduced – Temper Pedic
2000s	Adjustable firmness or comfort sleep numbers appeared
2007	Increased fire/ flammability safety standard introduced
2008	Organic and environmentally friendly contents

Around 16th century, the beds were made of shallow chests in which the bedding was placed[9]. The mattress was a bag filled with straw or wool that was covered in cheap fabric. A typical soft bed in its simplest form consisted of a wooden framework with a rope or leather stretched across like a hammock[27]. In 18th century, the natural fibers such as coconut fiber, cotton, wool and horsehair were used as filling material and the mattresses with tufted or buttoned fillings and edge-stitched cover became popular. In the late 19th century iron and steel replaced the wooden frames. 'Dunlopillow' is the first synthetic material in which latex rubber used in mattress field in 1929. Soon pocket spring mattresses with individual spring sewn into fabric bag were introduced.

Today, a typical mattress[28] (Figure 2) with foundation or box spring in the United States is constructed of several layers of foams, natural and synthetic fibers, and springs. Wooden slats are used in the support structure to reduce noise. Module coil structure provides spring action without swaying away. The fabrics is wrapped all around the box spring have FR properties. Pads inside the mattress insulate the spring and they are made up of cotton that imparts comfort and durability.

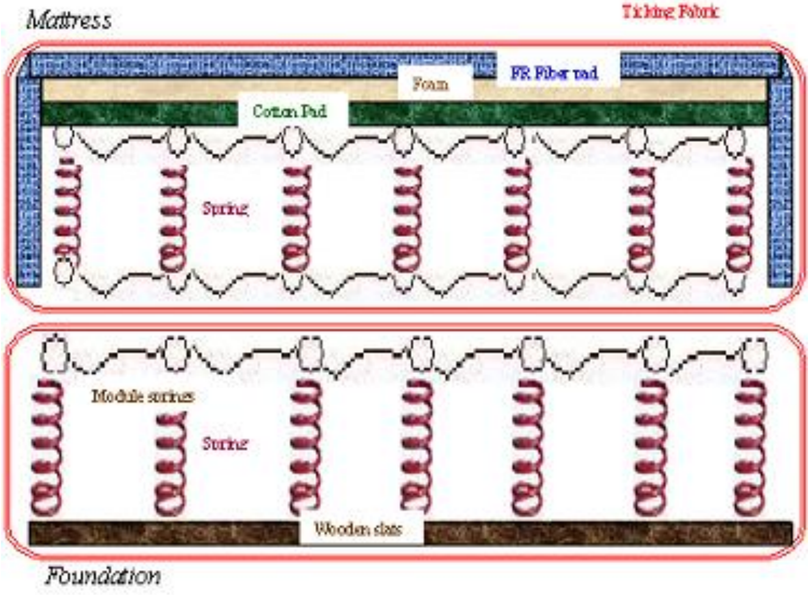


Figure 2 Mattress Construction.

FR properties are imparted while constructing these pads and lower grade cotton is used to keep costs low. Pads are stitched or needled and thermo-bonded to reduce clumping on use. A mattress can be used alone, on the floor, but is usually placed higher off the ground on a wooden frame with metal springs inside known as foundation. There are mattresses with the support systems such as air, water, foam, or springs. A fabric cover fixed permanently onto the mattress is called ticking. The pad beneath the ticking both on top and the sides must withstand the two-burner open flame test**2** TB603. Considering this, a new mattress pad with proprietary FR formulation[29] is available that are snug-fit over an older mattress set and get in compliance with the open flame test.

2.2 Mattress

A mattress is one of the most important pieces of furniture in the house because almost one-third of our life is spent in the bed for relaxing and sleeping. The quality of the sleep determines how effectively one functions during next day. The main purpose of the mattress is to provide adequate sleep comfort[10].

Why do we sleep? Scientists have discussed this question for centuries[30]. In fact sleeping activity recharges and prepares our body system for the next day Sleep is also considered a healing phenomenon that rejuvenates, and reenergizes our body and mind. During sleep, digestion slows down and system goes into an energy saving mode. The brain processes new information gathered, archives memories, and simultaneously looks for answers to the teasing questions.

More activities taking during the sleep are: self-repairing of muscles, tissues, and strengthening the immune system. Good food, exercise, and rest or sleep is necessary for survival of all beings. Lack of sleep affects memory, reduces cognitive skills, causes mood swings, and hallucinations. In an already stressed life, it contributes in alleviating the stress further.

Sleep is of an adaptive in nature[30]. Most of us, who take food in daytime, sleep at night whereas nocturnal creatures sleep during the day. There are three main sleep positions: back, stomach and side. One may change sleeping positions frequently, even 40 times during the sleep. The sleeping position determines which part of the body will interface with the mattress that in turn determines the amount of stress on to the body[10]. A pillow can provide extra support and take pressure off certain parts of the body. For example, when sleeping on the back, placing a pillow under the knees takes stress off the low back. Similarly, when sleeping on the side, placing a pillow between the knees helps to keep the spine in alignment. In simple words the research indicates that a mattress that conforms better to the shape of the body provides better support and thereby better sleep[10].

Mattresses should be designed to distribute pressure evenly across the body that helps circulation, decreases body movement and enhances sleep quality. The doctors recommend a mattress or sleep support system[11] that is adequate to conform to the spine's natural shape and to keep the spine in alignment while sleeping or lying down. Generally orthopedists recommend medium to firm mattresses. This is because if the sleep surface is too hard, it can give rise to uncomfortable pressure on contact points such as shoulder, hip, and knee, which can cause deterioration of the joints over time. There is an easy way to check softness: just by lying on the back on the mattress. If there is no space between the person’s back and the bed, it is too soft. If it takes a lot of effort to roll over, then the bed is too soft. On the other hand mattress is considered too firm/hard if one is able to slide hand in the gap under the small of the back easily, and this makes one to feel uncomfortable at the shoulders, and hips.

Generally doctors recommend a firmer mattress to a back or stomach sleeper, and a softer mattress to a side sleeper to minimize the pressure points, especially if the person has a very curved or rounded body shape. In fact statistics indicate that side sleepers[11] are in majority. Mattress pads play an important role in altering the firmness of existing mattresses[10] if desired so.

Doctors recommend a mattress pad of thickness ranging from10mm to 50mm. Pad can be latex foam, memory foam or layers of material such as cotton, wool or down. Whatever type of mattress pad one chooses, it should fit snugly over the entire sleep set. Further dermatologists recommend using a sleep material that helps keep the skin dry to regulate the body temperature. Natural fibers such as cotton and wool can take perspiration away from the skin and keeps one cooler[11], at a uniform temperature so one need not spend the night taking away the cover, only to chase it down a few hours later. Finally, it is recommended to rotate the sleep set often for a more even wear, sag, and longevity.

2.2.1 Mattress Size

Mattresses sold in the market are available in four different sizes as shown in Table 2. Standardization helps in keeping costs low, and consumers find it easy to choose and buy the coordinates such as sheets, pillows, and pads. The mattress size is determined by the number of people who sleep on the mattress, the size of bedroom, and other furniture in the bedroom[10]. First of all the mattress should be able to fit in the room with a comfortable clearance of about 500mm (20”) on all sides. Length of the new mattress should be slightly (by about 150mm or 6”) longer than the tallest person sleeping on it (Extra longs available as California size). The width of the bed should allow one to place a pillow and stretch elbows in back of the head without touching the adjacent person or extending beyond the mattress edge.

2.2.2 Mattress Pad

Generally mattress pads are placed over the mattress to fulfill one or more purposes such as improving firmness or cushioning comfort, hygiene, flame retardancy, and additional support to the body. Often these pads have protective fabric covers generally made of cotton rich fabrics with anti-soil/ anti-bacterial properties[31]. The pad acts as a barrier or buffer between the mattress and bed sheet, minimizing body soil getting onto the mattress. Sometimes mattress pad are made of several layers or stratified type of construction.

Table 2 Standard Sizes in Mattresses

TYPE		Size (Width x Length)	
		USA & Canada	Europe
TWIN (SINGLE)	inch	39 × 75	36 × 75
	mm	991 × 1905	914 × 1905
FULL (DOUBLE)	inch	54 × 75	54 × 75
	mm	1372 × 1905	1372 × 1905
QUEEN	inch	60 × 80	60 × 75
	mm	1524 × 2032	1524 × 1905
KING	inch	76 × 80	72 × 75
	mm	1930 × 2032	1829 × 1905

A typical pad should snug fit over the mattress just like a fitted sheet rather than just lying freely on top. Pads may be heavily quilted or flat. Some pads are specially tailored to support and soothe body parts such as back and joints Mattress pads are expected to provide comfortable level of cushioning properties that is, pads compress due to body weight, conform to the body's shape and then spring back to their original shape once person gets up. To obtain these properties the pads are made of chosen fibers or specialty foam or feathers that contain trapped air in voids. Specialty pads advertisement[32] show that they exhibit visco-elastic properties: feel harder (more viscous) as well as bouncier (more elastic). Even entire mattress could be made of visco-elastic material. These types of mattresses or pads are quite expensive.

Fiber-based high-loft nonwovens are popularly used for mattress pads; consist of fibers, usually a cotton-rich blend of fibers. Customers look for comfort properties that withstand general conditions of wear and tear, exposure to variations in ambient temperature and humidity. Producing the mattress pads with better quality, for assured performance at ever demanding cost reduction is the primary goal of the manufacturers. This encourages search for new materials and innovative approaches[33] to satisfy the short term and long term needs and customer demands, as a result use of blend of synthetic and natural fibers is growing. Dramatic changes in the level of their acceptance and the diversity of their use are seen, as engineers are gaining control over the necessary design skills and wider adoption making them more cost effective[34]. At the same time due to an increased importance of renewable resources for raw materials and recyclability or biodegradability of the product at the end of the useful life is demanding a shift from petroleum-based synthetics to agro based natural fibers in all mattress applications.

Fiber-based nonwoven webs possess a good blend of strength, lightweight, and flexibility. Generalized tensile properties of nonwoven blend[26] when they are produced from natural fibers such as cotton and binder fibers are shown in the Figure 3. These blends have an important inherent quality that provides excellent z-directional properties[35] that minimizes delaminating problem.

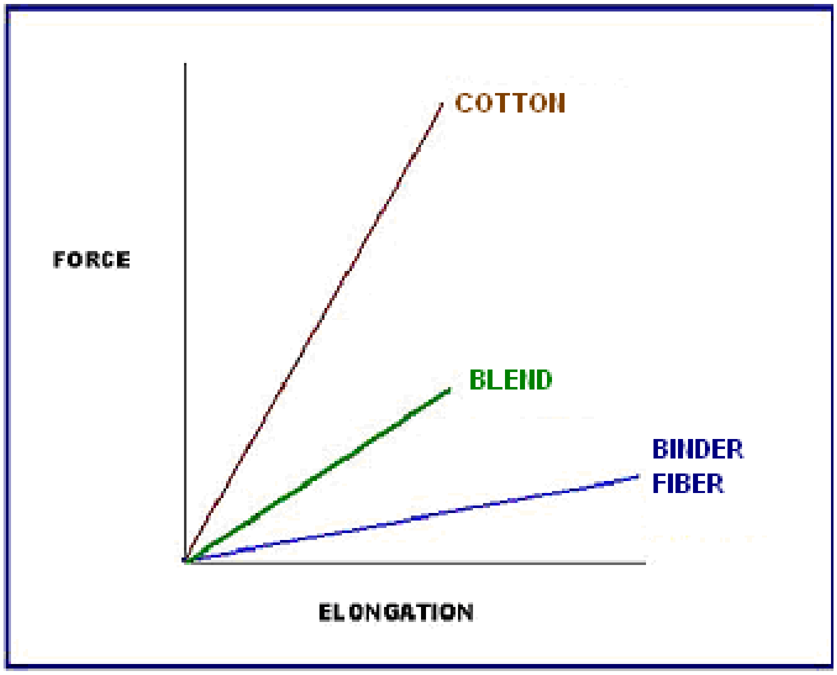


Figure 3 Tensile Properties of Cotton, Binder Fiber, and Blend.[26]

Flammability of a material also depends on its surface to mass ratio[36]. Fibers have a large surface area and hence even a small quantity tends to ignite easier and burn faster than a solid block of the same material. A heavy, tightly woven fabric is more resistant to ignition than a light and fluffy pad or sheer fabric made of the same material. Igniting an edge of a pad or raised surface fibers is usually easier than igniting a flat surface. The edges and raised fibers have a very large exposed surface and they can ignite easily with a very rapid flash of fire across the pad surface.

In some cases, depending upon the nature of fiber material these surface flashes16 may cause the entire fabric to burn, but in others the surface flash may not produce enough heat to ignite the base pad. The orientation of the product also influences its flammability38. An item in a vertical configuration will usually burn faster than the same item in a horizontal position. Thus the products such as curtains, drapes and wall coverings are more involved in fires than the carpet. If a carpet catches fire, the flame usually does not spread rapidly, partly due to the horizontal orientation. However, if a product that is designed to function safely as a floor covering is misused as a wall covering, it may pose an unusual fire hazard because of the combination of vertical orientation and a raised surface. The fibers used in mattress pad construction are classified into three categories: Natural fibers, Manmade or manufactured fibers, and Binder fibers.

2.2.3 Natural Fibers

First fibers known to mankind are the natural fibers that are found in nature or produced from naturally available materials from plant and animal sources[36]. Various types of natural fibers are listed in Figure 4.

Majority of the natural fibers are plant based cellulosic fibers. Among organic fibers, wool and silk are made of protein and are of animal origin. Wool is popularly used in warm clothing, whereas silk is used in expensive garments and gained popularity for its shine and ability in producing bright colors on dyeing.

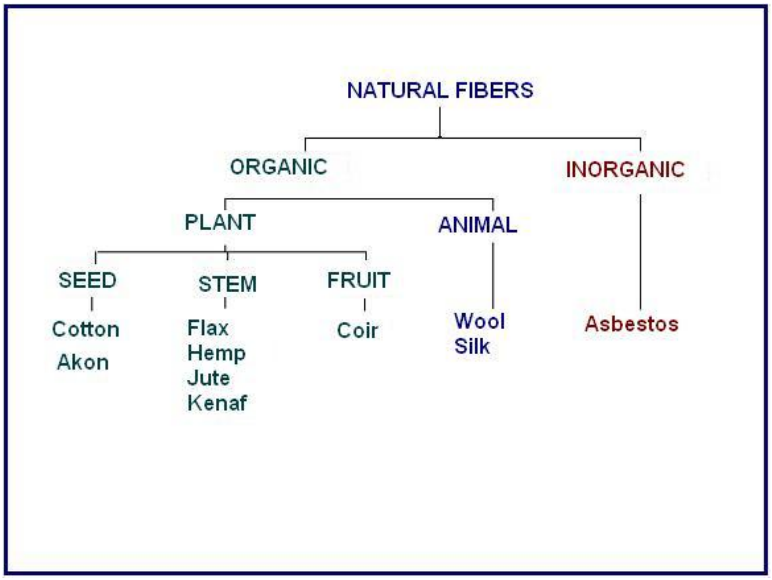


Figure 4 Types of Natural Fibers.

Asbestos is an inorganic natural fiber, which was used as insulation material until 1970. Due to its carcinogenic nature, it is no more used without encapsulation. Among natural fibers, cotton is a durable, breathable fiber with a soft feel and excellent absorbency[16]. In addition, it has superior wet strength, and ability to dry quickly.

Cotton is the most popular natural fiber used in home furnishings. It is agro-based, biodegradable and eco-friendly. Cotton is well known for its excellent absorbency, comfort properties, and natural feel. Cotton is the seed fiber of the plant named: *Gossypium hirsutum*[36].

Other cellulosic natural fibers such as flax, hemp, kenaf are not popular in mattress applications. Flax with properties[36] similar to that of cotton, but with better strength and modulus, is an alternative to cotton. Flax is a bast fiber from the plant, *Linum usitatisimum*. Flax is known to have existed 10,000 years ago[37].

Kenaf[36] is another bast fiber from a cane like plant, *Hibiscus cannabinna*, which grows fast. Compared to cotton and flax, kenaf entered the textile fiber market very recently. Initial interest in kenaf in the United States was as a domestic supply of cordage fiber as a jute substitute in the manufacture of rope, carpet backing, and burlap. Later, kenaf was identified as a very promising fiber source as a substitute for fiberglass and synthetic fiber. Today, kenaf is considered as a commercial crop in USA. Therefore, government encourages the commercial use of the kenaf, but it is found to get brittle and disintegrate while constructing mattress pads.

2.2.4 Manmade Fibers

The natural fibers have some drawbacks: cotton wrinkles, wool shrinks, and silk requires delicate handling. To overcome these drawbacks and to cater to the increased demand in terms of volume due to growing population as well as choice of clothing and ever changing fashion, scientists researched and developed manmade fibers or manufactured fibers[38].

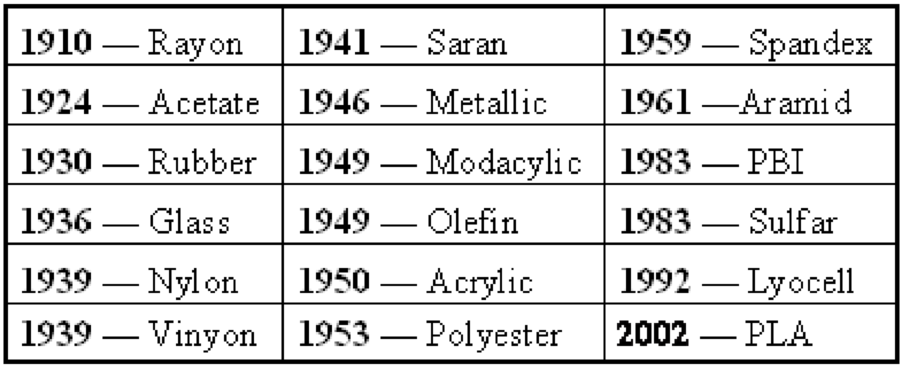
The earliest attempt to create an artificial fiber was in 16th century[17], by Robert Hooke. Later in 18th century, Sir Joseph W. Swan, an English chemist and electrician experimented with forcing a liquid through fine holes into a coagulating bath. His fibers worked like carbon filaments in Edison's Electric Bulb invention. Later he tried to knit a fabric too.

Rayon, an artificial silk is the first fiber produced in commercial scale in 1889. A French chemist Count Hilaire de Chardonnet who researched rayon is now honored as “father of the rayon industry.” Later, American Viscose Company, formed by Samuel Courtaulds and Co., Ltd., began its production of rayon in 1910. In 1893, Arthur D. Little of Boston, invented yet another product: cellulose acetate and developed it as a film. The Celanese Company developed the first commercial textile use of acetate in 1924. Summary of manufactured fibers[38] that are commercially successful are shown in Table 3.

Rayon and acetate had been derived from plant cellulose, and hence known as regenerated fibers[17]. The first synthetic fiber, “a miracle fiber, Nylon” was born in 1931 was invented by Wallace Carothers of the DuPont Company. Nylon is synthesized from petrochemicals and created a revolution in the fiber industry. Later more fibers joined synthetic group: metalized fibers by BASF, modacrylic fiber by Union Carbide, and olefin fiber by Hercules, Inc., wool like acrylic fibers by DuPont, and polyesters by Imperial Chemical Industries in UK and by Dupont in USA. Fabrics made of polyester fiber revolutionized clothing industries with “wash and wear” product performance.

Today the new fibers in the market are targeting properties such as greater comfort, flame resistance, antistatic, anti-bacterial, soil-release, achieve greater whiteness/ dullness or luster, improved dyeability, and better blending qualities. New fibers with varying cross-sectional shapes (round, trilobal, and segmental etc.) and fineness (microfibers and nanofibers) are in the market. All these innovations are to make our life better and comfortable[34]. Cost competitiveness, and eco-friendliness are gaining importance in recent days.

Table 3 Manufactured Fibers with the Year Commercialized



1910 — Rayon	**1941** — Saran	**1959** — Spandex
1924 — Acetate	**1946** — Metallic	**1961** —Aramid
1930 — Rubber	**1949** — Modacylic	**1983** — PBI
1936 — Glass	**1949** — Olefin	**1983** — Sulfar
1939 — Nylon	**1950** — Acrylic	**1992** — Lyocell
1939 — Vinyon	**1953** — Polyester	**2002** — PLA

2.2.5 Thermoplasticity, Thermal Stability, and Flammability

A list of FR fibers along with their trade names is shown in Table 4. Many synthetic fibers are thermoplastic; meaning they melt when heated. In case of fire, the mattress pads made from these fibers tend to melt and shrink away from small flames[16]. But thermoplastic melt can stick to skin that causes severe burn injuries. However, they are usually more difficult to ignite with a match or cigarette lighter. This is another important characteristic in determining the ease of ignition. Non-thermoplastic fibers, such as cotton or rayon, do not melt and may be more susceptible to ignition by small flames. Many times cotton smolders instead of a mere flaming combustion. Hence thermoplastic and non-thermoplastic fiber blends, such as cotton-polyester blends, are prepared which tend to behave more like non-thermoplastics since the non-melting cotton prevents the melting polyester from withdrawing from the flame.

In addition to thermoplasticity, the chemical structure of a fiber also affects the burning behavior. Generally the more carbon and hydrogen that is present in the chemical structure, the more will be the heat of burning. Thus many synthetic fibers such as polypropylene, nylon, and polyesters have a potential to generate more heat due to burning than an equivalent amount of a cellulosic fibers. Moreover to get to a flaming combustion, the synthetic fiber must undergo pyrolysis or thermal breakdown into smaller volatile fragments

Thus if fibers are made of polymers with very high thermal stability, such as aramids then they exhibit improved FR properties. Similarly other fibers, such as the modacrylics and FR polyesters, contain chemical moieties in the backbones functioning as flame-retardants. FR fibers should not get destroyed by the fire easily and possess desirable strength to reinforce the char. If self-extinguishing fibers are weak, then they are blended with the stronger ones. These FR fibers are effectively used in products against fire from small ignition sources; however, they are frequently overwhelmed in larger fires, such as a burning building[3].

Table 4 List of FR Fibers

Generic name	**Trade name**
FR cellulosics	Visil
FR Polyester	Trevira CS
Aramid	Nomex
Modacrylic	Kanecaron
Melamine	Basofil
Novoloid	Kynol
Polyetherimide (PEI)	Ultem
Polyether etherketone (PEEK)	Victrex
Silica Fibers	Omnisil

2.2.6 Smoke Hazards

In case of a typical building or a confined space fires (as shown in Figure 5), often the primary human hazard is products of combustion: smoke and toxic gases[17]. When cellulosic materials burn the only gaseous products formed are CO, CO_2 and water vapor. They can cause suffocation, but the dangerous one is CO, which in addition poisons the bloodstream just like cyanide. Relatively the amount of CO is produced in a fire depend primarily on the shortage of oxygen, and in case of household fires it is almost always true. Like cellulose, polyesters and polyolefins are the type of synthetic fibers that produce only CO, CO_2 and water when burned. Whereas polyamides and acrylics contain nitrogen and they are capable of producing hydrogen cyanide, another toxic gas during burning[3]. Compared with CO, hydrogen cyanide is probably not a major factor, as shown by the studies at the Center for Fire Research of the U.S. National Institute of Standards and Technology that the primary toxic gas in most building fires is CO, regardless of variety of synthetic fiber products used in the building[3]. Thus most popular synthetic fibers usually behave no better, nor worse, than other organic materials.

Many synthetic fibers melt when exposed to heat, and this can be an advantage in preventing ignition by small flames. In case of fire they burn, pieces of the flaming material may drip away; in many cases takes away the fire and the product self-extinguishes. This effect is used in children's sleepwear generally made of 100% FR polyester fiber[2].

2.2.7 Binder Fibers

In order to produce nonwovens from natural fibers, it is generally blended with a thermoplastic binder fiber and through-air thermo-bonded[26]. Conventional binder fibers (Figure 6) are polyolefins, which are not biodegradable, and pose difficulty in disposal at the end of useful life. Thus new biodegradable polymers and fibers are gaining ground. Out of these, a few are easily available in the market.

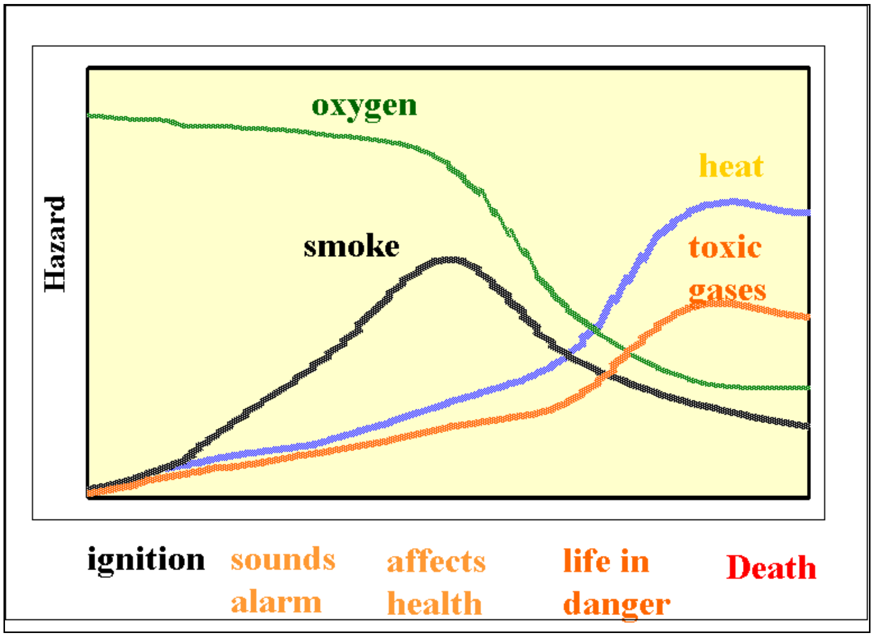


Figure 5 Building Fire Hazards[3].

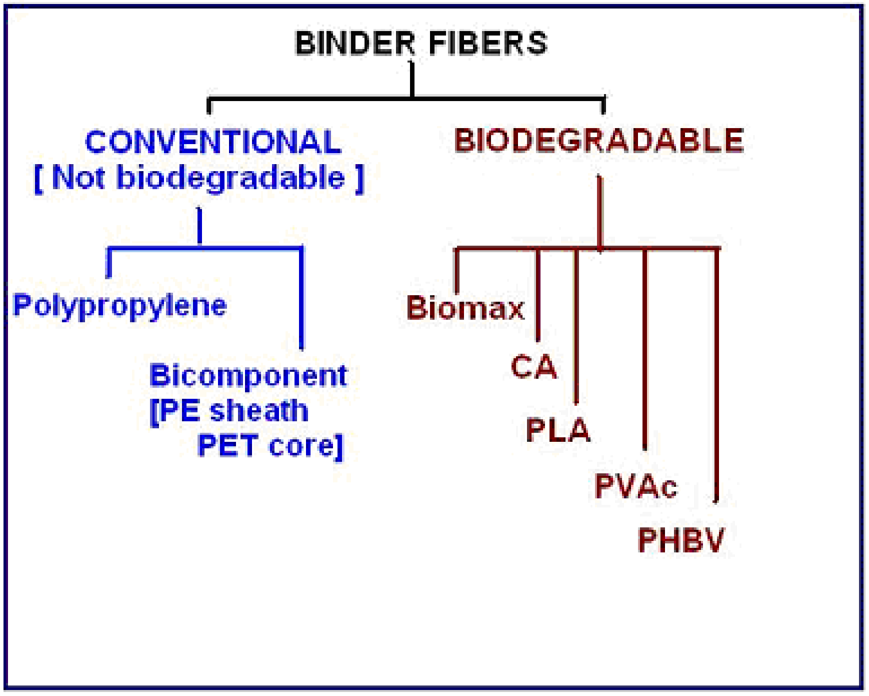


Figure 6 Types of Binder Fiber.

At present, the most common binder fibers are bicomponent fibers containing low melting polyethylene sheath and PET core as shown in Figure 7. Moreover lower the bonding temperature better it is for cotton-based products as it reduces degradation.

Recently bicomponent fibers (recycled PET core and low-melt PET sheath) are popularly used as binder fibers in cotton nonwovens[26]. They are produced in sufficient and large quantities and available at an economical price. Moreover they have lower melting point (80 to110°C) compared with polypropylene fibers (melting point 150°C).

Biodegradable thermoplastic binder fibers are: Plasticised Cellulose Acetate CA, Eastar from Eastman Chemical Company[39], Ecoflex from BASF, Polylactic acid (PLA) from Dow-Cargill[40], Poly hydroxybutyrate valerate (PHBV) from Metabolix[41] and Biomax from Dupont[42]. Generally, these contain chemicals that are tasty to the biodegrading organisms so that the final product biodegrades easily. All these are expensive and have higher melting points. Eastar has a melting point of 120°C, PLA fiber 175°C, and Biomax 200°C. These are employed in applications requiring full biodegradability.

2.3 Fiber Blending

Fiber blending and uniform web formation is crucial in the production of fiber-based nonwovens. Good web formation is characterized by macroscopic and microscopic uniformity of fiber deposition in the pad[43]. A hand mixing and blending fiber is not an easy task. Moreover product varies in uniformity.

In textile mills fiber bales are untied and dropped in the blow room. Blow room operation carries out fiber opening and blending using large quantities of air. In case of mattress pads several fibers are blended that too in a smaller scale for the research work. Sometimes blending step is repeated until product is sufficiently uniform. Passing through the b Our earlier studies[26] on properties of web forming fibers showed that out of many methods carding is the best-suited method for blending fibers for nonwoven pads.

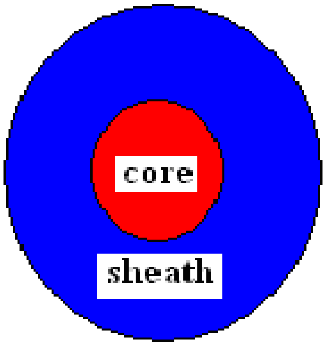


Figure 7 Bicomponent Fiber Cross-section Sketch.

The main objective of carding[43] is to separate small tufts into individual fibers, to begin the process of parallelization and to deliver the fibers in the form of a web. As shown in the Figure 8 the principle of carding is the mechanical action in which the fibers are held by one surface while the other surface combs the fibers causing individual fiber separation. At its center is a large rotating metallic cylinder covered with card clothing. The card clothing is comprised of needles, wires, or fine metallic teeth embedded in a heavy cloth or in a metallic foundation. Alternating rollers and stripper rolls in a roller-top card may cover the top of the cylinder. The fibers are fed by a chute or hopper and condensed into the form of a lap or batting. This is initially opened into small tufts by a licker-in, which feeds the fibers to the cylinder. The needles of the two opposing surfaces of the cylinder and flats or the rollers are inclined in opposite directions and move at different speeds. The main cylinder moves faster than the flats and, due to the opposing needles and difference in speeds, the fiber clumps are pulled and teased apart (Figure 9). In the roller-top card the separation occurs between the worker roller and the cylinder. The stripping roller strips the larger tufts and deposits them back on the cylinder. The web is doffed from the surface of cylinder by a doffer roller[43].

2.4 Bonding Process

Nonwoven pads are made up of fibers where the individual fibers are bonded together. The bonding process replaces the weaving that is used to manufacture traditional woven textiles. By virtue of the varied range of materials and methods available at reasonably low cost the nonwoven products have found their way into many commodity products[35] such as wipes, towels, apparel linings, filter media, and bedding products.

The binder fibers provide the cohesive strength required for structural integrity of the nonwoven fabric. Additional properties such as flexibility, hand (drape), loft (bounce or resiliency), and wet-strength that are quite close to woven fabrics could be obtained by choosing an appropriate binder[43]. These properties are necessary for effective performance, and they enable nonwoven fabrics to compete closely with traditional woven textiles.

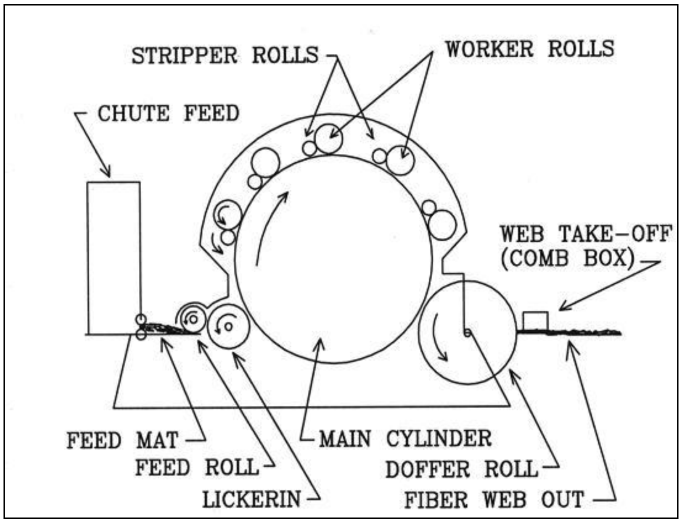


Figure 8 Typical Card[43].

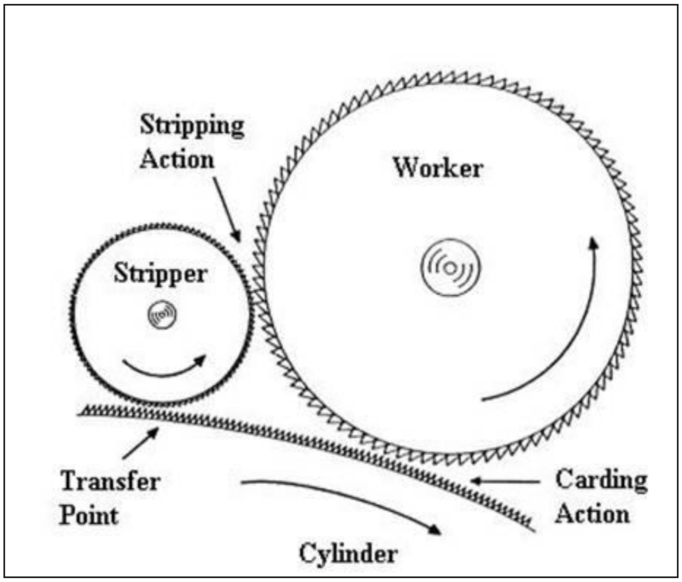


Figure 9 Stripping Action[43].

Bonding operation can be mechanical, thermal, or chemical[44]. Thermal bonding of nonwoven fiber web is an economical and environmentally safe technology, which enhances the product performance. Synthetic fibers of relatively low melting point, such as polyethylene, polypropylene are widely used for the purpose of bonding and known as binder fibers. On applying heat they soften, melt, and fuse together at the contact points of the surfaces of fibers within a web.

The proportion of these bonding fibers within the web can be varied from 10 to 20% to achieve the desired performance properties such as strength, drape, and resilience. A major advantage of thermal bonding is that it creates a nonwoven free of chemicals. Moreover, for fiber-based high-loft and resilient bedding products through air thermal bonding is the most preferred one[16]. Through air thermal bonding takes place as the web is taken on a conveyor through an oven or passed around perforated drums where the heated air is blown through or drawn by a vacuum through the web.

A vertical drum system is significantly compact compared to horizontal configuration[43]. Multiple through-air drum installations are used extensively to serve purposes such as consolidating nonwoven composite structures, drying, and thermal-bonding simultaneously.

Generally bicomponent binder fibers are blended with commodity fibers in the desired proportion and through air bonded into webs. The sheath provides the fusing point while the core preserves the integrity of the nonwoven[43]. Calendaring is another method of thermal bonding where the heat and pressure applied to weld the fiber webs together into high bulk density. Hydroentanglement is yet another process of using fluid forces to lock the fibers together. This is achieved by fine water jets directed through the web, which is supported by a conveyor belt. Entanglement occurs when the water strikes the web and the fibers are deflected. The vigorous agitation within the web causes the fibers to become entangled. Ultra-sonic bonding is one more method, not so common, where the molecules of the fibers held under an embossed roller are excited by high frequency energy generating internal heating, softening and bonding of the fibers.

2.4.1 Bonding Agents

In case of FR treated mattress pads, binder fibers are employed to integrate the web constituent fibers whereas chemical binders are employed as bonding agents to adhere FR chemicals onto the fiber surface within the pad. Normally bonding agent formulation requires adjustments to obtain specific properties, such as flexibility, fire retardancy, drape, loft, and strength. These properties are necessary for effective performance, and they enable nonwoven webs to compete closely with traditional woven textiles.

Basically three factors determine the properties of the nonwoven fabric[45]: fibers, bonding agents, and additives. The fibers are the basic constituents of the nonwoven web. The bonding agent is generally either polymer latex or thermoplastic resin that is incorporated into the web. Additives are sometimes used during the consolidation process to serve specific properties such as color, anti-fungi nature, special surface features, flame retardancy etc.

Bonding agents in the early developmental stages involved modified starches, cellulose derivatives, and natural plant based secretions/gums/glues. After bonding the products exhibited defects such as increased stiffness or poor hand, lower absorbency, and poor launderability43. Moreover the bonding agent became the weak spot in the nonwoven structure that limited its performance. Scientists researched to provide newer bonding agents, which are somewhat expensive but reduce undesirable side effects. The desirable properties of a bonding agent are as follows:

1. Structural integrity without contributing adversely to the stiffness of the pad.
2. The adhesion of the binder to the fiber should be long lasting.
3. Favors some movement of the fibers is necessary obtain flexibility or drape.
4. Good elastic recovery to maintain the original dimensions and shape of the product.
5. Launderability and good weather and UV resistance if used outdoors.
6. Be able to be incorporated with low cost, energy efficient and available processes.

Most bonding agents provide good strength characteristics in nonwovens under dry conditions. The selection of bonding agent is often based on its performance in the end product and cost[13]. Bonding agents are generally made of water dispersible polymers and copolymers. The most popular types of bonding agents used in nonwovens are: acrylics, nitrile elastomers, styrene butadienes, ethylene vinyl acetate copolymers, and polyvinylidene chlorides.

The bonding agent formulation consists of a straight polymer emulsion along with some additives to provide end-use properties. A typical formulation[46] includes the bonding agent consisting of the finely divided and dispersed polymer or copolymer particles, water, and additives such as surfactants, wetting agents, pH modifiers etc. Surfactants are used to stabilize the polymer particles in water during emulsification. Catalysts are sometimes added to functional polymers to provide cross-linking and impart heat and chemical resistance.

Order of addition of chemicals into an agitated vessel and proportion is:

1. Water 50-70%
2. Defoamers 0-0.5%
3. Dispersant 0.1 –1%
4. Bonding agent 30-50%
5. Catalyst 0-1%
6. pH modifier as desired

The bonding agent properties depend on the glass transition temperature (T_g) of the monomer unit selected to form the polymer[46]. Vinyl acetates have higher T_g and will provide greater strength and reduced flexibility compared to acrylics having a lower T_g will provide greater flexibility or softness. Similarly bonding agents contribute the hydrophilic (polar) or hydrophobic (non-polar) nature that affects the water absorbency and wet strength of the final cure-dried product. In general, bonding agents tie the substrate to the active additive.

Acrylics are the best all-around bonding agents, having good colorfastness, dry and wet strength; heat and chemical resistance; durability and a wide range of fabric hand properties. Moreover they are available with glass transition temperatures ranging from minus 40°C for very soft to +105°C very hard nonwoven products.

2.4.2 Method of Application

The process of binder application[45] to a nonwoven pad with structural integrity consists of two steps. These are:

1. Chemical application to the nonwoven pad
2. Curing and Removal of moisture from the binder

The bonding agents may be applied in amounts varying from 0.05 to 50% by four techniques: saturating, spraying, printing, or foaming. They may be applied prior to applying FR chemicals separately or along with FR chemicals at the same time.

2.4.2.1 Saturation Bonding

Saturation bonding is the most popular one, wherein the binder solution encapsulates the fibers in the pad by totally immersing or dipping in a bath or by flooding near the nip point of a set of pressure rolls. Excess solution is squeezed out and removed by the roll pressure. Saturation bonding method is simple and product strength and softness by the choice and amount of binders can be easily controlled.

2.4.2.2 Spray Bonding

In spray bonding, bonding agent dispersion is atomized by air pressure, hydraulic pressure, or centrifugal forces and is applied to the upper surfaces of the pad in fine droplets across the nonwoven web using array of spray nozzles. After spraying, the wet pad is passed through a hot oven to cure or cross-link and remove water by drying. In spray bonding binder chemical is not uniform across the web thickness, and a gradient is formed from the upper to lower surface of the pad. Spray bonding is preferred for high loft pads if the fibers have good absorbency, thus overcome non-uniform pick up.

2.4.2.3 Print Bonding

Print bonding employs existing printing machinery for bonding agent application. Print bonding uses engraved gravure or rotary screen-printing rolls where the pattern and the thickness of the binder coating are controlled. The binder is applied only in predetermined areas. This method is used for applications that require a part of the fabric to be binder-free. Many lightweight nonwovens are also print bonded to minimize bonding agent.

2.4.2.4 Foam Bonding

The process uses air and water as the diluents and carrier for the bonding agent. The air to chemical ratio is about 5. Foam bonding applies the binder at higher binders solids concentration level. Foam bonded nonwovens consume less energy in drying, as less water is used. The formulation includes foam-stabilizing agents to prevent the foam from collapsing during application and drying. The finished product will exhibit greater softness, hand, and resilience. The method poses difficulty in controlling foaming levels.

2.4.3 Cure-Drying

All four methods need Cure-Drying in an oven for drying or curing reactions[43]. Bonding agents follow complex reactions in order to tie additive molecules to the substrate. This is known as curing. Generally the supplier recommends the curing conditions such as concentration, time, and temperature for the specific application. Curing and drying may occur simultaneously. Removal of solvent is considered as drying.

The equipment needs to be designed to minimize binder migration as a result of binder carry over with the evaporating water. The binder concentration will be different at the exposed surface from the bulk. To minimize this, the recommended oven and hot air temperature is between 95-130°C until 50% of the water has been evaporated. After this point, if needed, the temperature can be raised to the recommended temperature to for drying or curing reactions. Higher temperatures and longer durations may have impact on the color of the product.

2.5 FR Treatment

2.5.1 FR Treatment of Synthetic Polymers

Literature available on FR Treatment of Synthetic Polymers is quite vast and it is very useful for studying and interpreting FR treatment of fibrous materials. Flame-retardants (FR) are added to synthetic polymers to impart resistance to combustion, reduce flame spread, suppress smoke formation, and prevent polymer from dripping[13]. As discussed earlier in Section 1, the primary objective is to delay the combustion and save life by providing more time to escape from the fire. A secondary objective is to reduce property damage. FR treatment is given according to their application and also to conform to the regulations and standards. Examples of polymer products that require FR include construction ceiling insulation, roofing and siding, components in mass transit vehicles, television and computer housings, electric wiring cables, and conduits. Combustion takes place when fuel, oxygen, and source of ignition all three factors are present[13]. FR interferes with at least one of these factors. Either FR reacts to shield the polymer by forming a char layer or inert gas layer or undergo a reaction that cools the system. The most commercially viable FR compounds include halogenated types, phosphorus based types, and metallic hydroxides.

2.5.2 Types of Fire Retardants

Halogenated compounds react to stop exothermic processes by trapping high-energy free radicals after they form. From a cost-performance[47] standpoint, halogenated compounds have upper hand. But there have been some health concern, over use of certain halogenated compounds with halogens attached to the carbon backbone, as they persist in the environment, and may accumulate in the tissues of humans and other animals[48]. Hence non-halogenated flame-retardants (NHFR) are gaining importance. NHFRs are broadly divided into two classes[49]:

1. Endothermic type (e.g., the metal hydroxides types)
2. Char formers type (e.g., the phosphorus types)

2.5.2.1 Endothermic Type

Metal hydroxides (Al, Mg) are the most widely used family of FR as it costs low (details in Figure 10) and easily incorporates in polymers[47]. These mineral compounds are incorporated into the polymer such as polyethylene (PE), cross-linked polyethylene (XLPE), thermoplastic elastomers (TPE), polyamides (PA), Polyvinyl chloride (PVC), rubbers, thermosetting resins, and back coatings. Metal hydroxides are environmental friendly, non- corrosive, lower smoke density, inert, do not have effect on pigmentation, and recyclable. Best cost-performance balance is obtained in case of PVC applications[50].

On exposure to heat, the metal hydroxides undergo the endothermic reaction that reduces the temperature of the burning polymer. Aluminum hydroxide or Aluminum trihydrate (ATH) breaks down in the temperature range of 180 to 200°C. As shown in Figure 11 aluminum trihydrate dissociates into aluminum oxide with the release of water. Magnesium hydroxide or Magnesium dihydrate (MDH) acts in a similar way as ATH, but MDH has a higher decomposition temperature of 300°C. Moreover MDH, which is found in nature as well, passes even the most stringent regulatory standards.

Generally these compounds are coated to obtain improved performance. Applications include wiring & cables, injection molding, profiles & pipes, films/flooring/roofing, conveyor belts, construction, insulating foams, electrical & electronics. The drawback of using metal hydroxides in processes like film extrusion is the high loadings of FR required. Loadings can be as high as 65%, a level that will affect the mechanical properties and process-ability of the polymer[47].

2.5.2.2Char Forming Type

Phosphorus compounds are the most popular char forming type of FR. There are several formulations such as organic phosphate esters, phosphates, and inorganic phosphorus salts using organic, inorganic, or elemental phosphorus compounds. Pyrapex is a liquid monomer FR that contains phosphorus and incorporates into the polymer backbone[51].

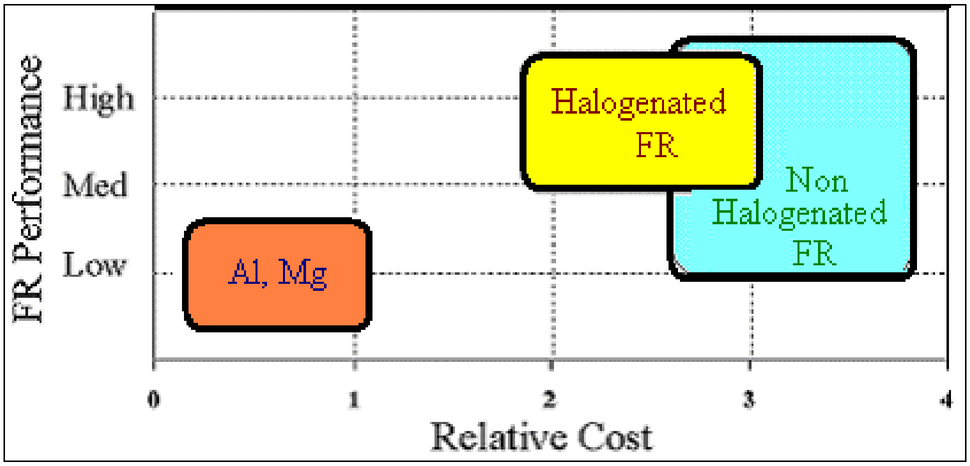


Figure 10 FR Cost –Performance Relation in Polymer Applications[47].

$$2\,Al(OH)_3 \xrightarrow{heat} Al_2O_3 + 3\,H_2O$$

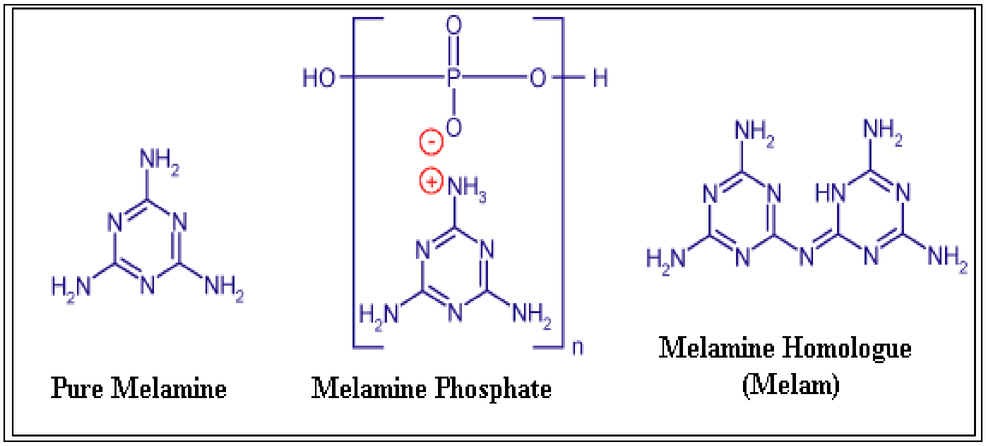
Figure 11 Dissociation of Aluminum Hydroxide

Similarly varieties of phosphorus compounds are used for their FR properties[22], stability, and char forming behavior. In many formulations FR phosphorus attaches itself to the polymer chain. Depending on the structure, they act in various ways to extinguish a flame. For example some terminate active hydrogen and hydroxyl radicals in the vapor phase and others yield phosphoric acids when heated in the fire. These acids promote char formation, which limits further polymer degradation.

Melamine based FR[17] is a small segment in the flame retardant market, but fast expanding. Melamine has excellent ability to act in various modes of FR action. The family of melamines consists of three chemical groups: pure melamine, melamine derivatives, and melamine homologues (typical structures are shown in figure 12). Pure melamine (2,4,6-triamino-1,3,5 triazine) is good UV absorber and heat sink as it absorbs ~2000kJ/mol during melting at 354°C and evaporation.

Other types melt at different temperatures. Melamines are cost effective, have low smoke density and toxicity, low corrosion, safe handling. Presently melamines are used in flexible PU foams, intumescent coatings, polyamides and TPU. Melamine has ability[17] to interfere with all the three components involved in combustion: heat, fuel and oxygen. Initially melamine melts at ~ 350°C at absorbing heat, followed by even larger heat sink effect due to the subsequent decomposition of the melamine vapors.

Melamine is a poor fuel; moreover the product of combustion nitrogen is dilutes the atmosphere. During degradation it releases ammonia, another diluting agent[13]. Melamine contributes to the formation of a char layer in the intumescent process. The char layer acts as a barrier between air and the polymer. Char stability is enhanced by multi-ring structures produced due to self-condensation of melamine. Phosphorus plays synergist role with melamine and increases the char stability through formation of nitrogen-phosphorus substances. Melamine can act as blowing agent for the char to swell up (intumescence effect) and enhance the heat barrier. However there are some health cocerns with the melamine compounds.



Pure Melamine

Melamine Phosphate

Melamine Homologue (Melam)

Figure 12 Three Types of Melamine[15].

2.5.3 Nanoclays, Nanosilicates, and Graphite as FR

Nanoparticles have very high aspect ratio and possess high surface to volume ratio. Well-exfoliated nanoparticles contribute to better mechanical properties of the polymer as well as FR performance. The nanoparticles appear to function by reducing the rate of fuel that is fed into the gas phase. The pores are able to fit a polymeric macromolecule or its decomposition products; thereby trapping or delaying the loss of decomposition products from the condensed phase, and thus slow down burning[13].

The polymer-layered silicate (PLS)[52] exhibits increased modulus and strength, decreased gas permeability, and decreased flammability. New Flame Retardants Consortium[53] has found that silica gel and potassium carbonate reduces the peak heat release rate (HRR) of commodity polymers by up to 70%, with a mass fraction of 5% FR. Polymers reinforced with 2% to 5% of nanoparticles via melt compounding exhibited dramatic improvements in thermo-mechanical properties. So far, nanoclays have shown the broadest commercial viability due to their lower cost of US$5-7/kg, and their utility in common thermoplastics like PP, PET, PE, PS and nylon.

Commercial projects utilize layered nanosilicates[54] Nanoclays[55] and expandable foaming graphite[56], Freeze Flame Nano[57] coating that can be applied on the surface of different woods, plastics and home furnishings consists of PVA, phosphate, and 3% Cloisite (nanoclay). Inclusion of nanoclay has shown to increase the efficiency of known chemistry to enhance the char formation by intumescent action in textiles[58].

While nanoclay adds muscle to plastics, carbon nanotubes impart electrical and thermal conductivity. Carbon nanotubes (with single-wall and multiwall)[59] are a relatively new and their commercial potential has been limited by the high price. Scientists are working on various techniques to reduce cost. Presently nanotubes are employed in high value small volume applications.

2.6 FR Treatment of Fibers and Nonwovens

In case of fabric containing cellulosic fibers, especially the lightweights and raised-surfaced fabrics catch fire easily and the flame spreads fast. This danger fueled the search for FR treatments. As early as 1735, Obadiah Wyld developed a FR mixture[60] of alum, ferrous sulfate, and borax to treat fabrics. Later in 18th century Gay Lussac[61] developed FR treatment using ammonium phosphate. It is interesting to note that both borax and ammonium phosphate are still used for many FR applications.

FR developments are ongoing, while some fabrics failed after washing, since the FR chemical washed out of the fabric. Realizing this, William Perkins developed the first durable FR process known as "Non-flam" in 1912, by treating garments with stannic oxide that withstood two years of use with weekly washing[13].

In 1950s another durable FR, tetrakis (hydroxymethyl) phosphonium salts (THPX) was developed by Albright & Wilson. The US Department of Agriculture Southern Regional Research Center (SRRC), New Orleans, LA conducted detailed research in this field[16]. In fact the most durable fabrics are made up of the self extinguishing FR fibers (such as Nomex and Basofil) which are very expensive.

Blending self-extinguishing FR fibers with FR treated cotton is one option. Other option is to go for chemical treatment, in which case the durability depends upon the strength with which the FR chemical adheres to the fiber surface as well as internal crevices. Moreover the flammability differs widely[62] depending upon the fabric construction (knitted, woven, and nonwoven) and chemical nature of constituent fibers. Some FR finishes are as durable as the fiber itself. Others have lower durability level goes to limited applications. Scientists are developing newer structures with increased durability. Cost remains as an important factor in case of finishing chemicals too. In addition volatiles components cause health concerns.

2.6.1 Non-durable Treatments of Cellulosic Fibers

Non-durable FR treated fibers are most often used for disposable goods such as medical gowns, costumes etc. or for the items that are not washed in water such as mattresses and pillows. Sometimes they are used for curtains and work clothing, in which case they are labeled “dry cleaning only” otherwise FR finishes need to be reapplied after each wash.

Generally FR chemicals[13] such as boric acid, phosphates, metal hydroxides etc. (as shown in Table 5) are dissolved or dispersed in water and then applied by padding or sprayed onto the fibers or fabrics. The fabric is dipped in the solution and then passed through nip rolls to squeeze out the excess solution. Often this dip and nip operation is repeated to obtain more uniform pick up. Wet fabric is then dried in an oven to remove the moisture. Commercial formulations contain wetting agents, swelling agents to assist penetration into the lumen of the cellulose fibers. Recently improvements have been towards semi-durability through additional treatments including proprietary intumescent formulations.

2.6.2 Semi-durable Treatments of Cellulosic Fibers

Semi-durable FR treatments (as shown in Table 6) can withstand a few or occasional water soaking or leaching, but cannot survive multiple laundering. Semi-durable treatments are acceptable in a few applications such as upholstery, curtains, and protective garments. According to BS-5852 standard[17], semi-durable FR fabrics cannot withstand water beyond 30 minutes at 40°C.

First semi-durable FR treatment on cotton was produced in 1940 by slow phosphorylation of cotton in presence of urea. Later a co-reactant, dicyandiamide was added to enhance FR properties. However these fabrics failed in hard water. Another popular method to obtain semi-durable FR cotton is by treating it with boric acid and urea. Presently popular semi-durable FR is Pyrovatim PBS (by Huntsman) that contains salts of polyethyleneimine with aminoalkylphosphonic acids[58].

Table 5 Non Durable FR Chemicals

Sl.Nu.	**Name**
1	Boric acid
2	Ammonium phosphate
3	Diammonium phosphate
4	Ammonium polyphosphate (low DP)
5	Ammonium bromide
6	Ammonium sulfamate
7	Diguanidine hydrogen phosphate
8	Aluminum trihydrate (ATH)
9	Magnesium hydroxide
10	Calcium carbonate
11	Gypsum

Table 6 Semi- Durable FR Chemicals

FR Chemical	**Trade Name**
Phosphoric acid and urea	
Phosphoric acid, urea, and dicyandiamide	
Cyanoguanidine with organic phosphonic acid	Flovan CGN
Salts of polyethyleneimine with aminoalkylphosphonic acid	Pyrovatim PBS
Back coatings	
Coated ammonium polyphosphate	Exolit AP-462
Coated ammonium polyphosphate	FR CROS 487
Melamine coated ammonium polyphosphate	FR CROS 489
Acrylic latex coated ammonium polyphosphate	Antiblaze CU
Acrylic latex coated ammonium polyphosphate	Fyrol 51
Ammonium polyphosphate, pentaerythritol, and melamine	Akro Fireguard
Ammonium phosphate, melamine cyanurate, ATH, and an acrylic binder.	
Aluminum trihydrate (ATH)/ Mg hydroxide/ Calcium carbonate/ gypsum with Styrene Butadiene latex	

Back-coating[13] is one more method of semi-durable FR treatment on one face of the fabric; it is quite popularly used in carpets. Generally phosphorus compounds; fillers such as metal hydroxides, calcium carbonates etc; and char promoters such as pentaerythritol are employed in back-coatings. Often bonding is carried out by latex such as styrene–butadiene rubber to obtain an off-white appearance.

Greater wash-durability is achieved through resin coated ammonium polyphosphates, developed as eco-friendly replacements for the bromides. Furthermore these coatings develop intumescence effect to form a foamy barrier when exposed to a flame. The intumescent foam[63] fills up the gaps between fibers of the fire-exposed fabric. Fabrics containing both cellulosic fibers and melamine fibers have shown synergistic results in FR behavior.

2.6.3 Durable Treatments of Cellulosic Fibers

Among the treatments shown in Table 7, the most popular durable finish for cellulosic fibers, in use for about 50 years, continues to be based on tetrakis (hydroxymethyl) phosphonium salts (THPX), as they are cost effective. The basic research was carried out at the Southern Regional Research Laboratory of US Department of Agriculture, in New Orleans[16]. As shown in Figure 13, the reaction between formaldehyde and phosphine takes place in the presence of acid (either hydrochloric or sulfuric).

Traces of formaldehyde present in THPX could develop volatile carcinogenic bis(chloromethyl) ether in the work area. Hence it is necessary to have proper personal protection equipments while handling THPX.

Abundant literature is available on the methods to react these phosphonium salts, with ureas, melamines, etc. with cellulose. Popular one is Proban[64] process wherein THPX is reacted with urea, applied onto cotton, dried and then cured (at 160 to 180ºC) to develop cross links with gaseous ammonia.

Table 7 Durable FR used in Cellulosic Materials

FRChemical	Binder Chemical	Remark
Tetrakis(hydroxymethyl) phosphonium salt [Proban Process]	Ureas, melamines/NH3, H2O2	Tensile Strength Loss
N-Methylol dimethylphosphono propionamide,[Pyrovatex CP]	trimethylolmelamine [Aerotex M-3], dimethyloldihydroxyethyleneurea (DMDHEU) [Freerez 900] Cat: H3PO4 and MgCl2	Yellowing, Tensile Strength Loss, Semi-durable
Same as above	DMDHEU, dimethylurea/glyoxal, MgCl2	Softer
Same as above	dimethylurea/glyoxal, MgCl2	Softer
hydroxy-functional organophosphorus oligomer [Fyroltex]	1,2,3,4-butanetetracarboxylic acid, NaH2PO2	Tensile Strength Loss
Cyclic methylphosphonate FR (Antiblaze 19) [Thermosol]	NH3, hexabromocyclododecane	Yellowing, Tensile Strength Loss
methylphosphonoamidic acid (Firestop)	Ammonium chloride, melamine formaldehyde	Softer
Organophosphorus compounds	Acrylic monomers grafting Fe2/H2O2 redox	Add-on high (38%)
Phosphoric acid	Grafting 2,3-epoxypropyl methacrylate (GMA), ethylene diamine	Durability not known
Encapsulated acid and base	Resin coated	Eco-friendly
Diammonium phosphate	Chitosan, Citric acid, butanetetracarboxylic acid, and sodium hypophosphite	Eco-friendly

$$\boxed{4\mathrm{CH_2}(=\mathrm{O}) + \mathrm{PH_3} + \mathrm{HX} \rightarrow (\mathrm{HOCH_2})_4\mathrm{P}^{+}\mathrm{X}^{-} \quad \text{where} \quad \mathrm{X}^{-} = \mathrm{Cl}^{-} \text{ or } 1/2\mathrm{SO}_4^{-}}$$

Figure 13 THPX Formula[16]

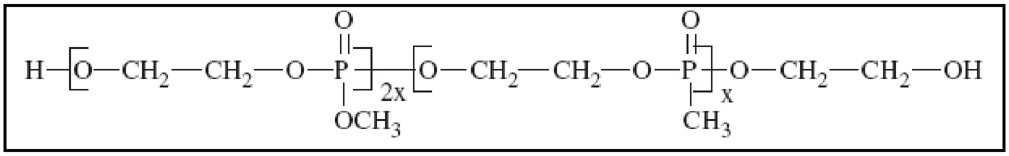
Final treatment is with hydrogen peroxide to form a finished structure: N-CH_2-P (=O)-, a stable phosphine oxide structure with no hydrolysable links. As a result, it can withstand 100 launderings with alkaline detergent. This process used on cotton goods for sleepwear, military uniforms, nursing homes. Newer Versions of THPX employ chemicals[58] such as cyclic methylphosphonate (Antiblaze 19 by Albemarle), hydrogenated C16–18-tallow alkylamine, etc.

2.6.4 Other Durable Finishes for Cotton

Akzo Nobel's Fyrol 51 or Fyroltex HP, is an oligomeric alcohol-terminated methylphosphonatephosphate, has the structure as shown in Figure 14. Firestop Ltd introduced "Noflam" a phosphorus-chlorine based product (a mixture of ammonium salt of methylphosphonoamidic acid and ammonium chloride) shown in Figure 15. Although the product is water soluble, if cured with melamine–formaldehyde resin and urea, it survives multiple launderings. Acrylic monomers as a reactive binders work well with organophosphorus compounds to bond to cotton cellulose through grafting[65] processes using the Fe_2_/H_2O_2 redox system. The results have shown that FR treatment is durable, survive 50 washes. However this durability is obtained at add-on levels higher than 38%.

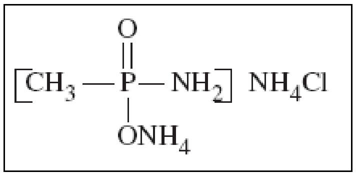
2.6.5 Thermosol FR Treatment of Polyester Fabric

An early version of thermosol[17] used tris(dibromopropyl) phosphate, but after 1970 it was discontinued due to carcinogenic nature. Today Rhodia's Antiblaze 19 or Amgard CU, or Special Materials' SMC 688 all contain liquid phosphates as shown in Figure 16. Chemtura's CD-75PM thermosol treatment, which uses hexabromocyclododecane applied as emulsion, and cured at 190ºC passed the NFPA-701 flammability test after multiple launderings. Brominated FR such as hexabromocyclododecane, Decabromodiphenyl ether, and antimony oxide are all under toxicity and eco-scrutiny[48].



$$H-\left[O-CH_2-CH_2-O-\overset{\overset{O}{\|}}{\underset{\underset{OCH_3}{|}}{P}}\right]_{2x}-\left[O-CH_2-CH_2-O-\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{P}}\right]_{x}-O-CH_2-CH_2-OH$$

Figure 14 Fyroltex Formula[58].



$$\left[CH_3-\overset{\overset{O}{\|}}{\underset{\underset{ONH_4}{|}}{P}}-NH_2\right]\ NH_4Cl$$

Figure 15 Noflam Formula[17].

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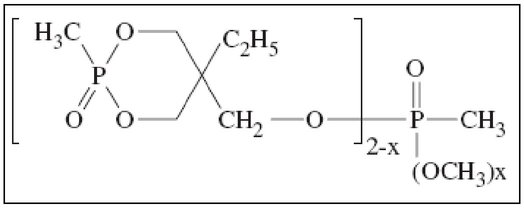


Figure 16 Liquid Phosphate Formula[17].

2.6.6 Recent Techniques to Obtain Durable FR

The health and environment legislation awareness is pushing manufacturers to develop eco-friendly FR fabrics with competitive cost. Addition of chitosan[66] during the phosphorylation process as a source of nitrogen has synergistic effect with phosphorus. Chitosan was dissolved in a citric acid solution and added to a phosphorylation bath containing diammonium phosphate, butanetetracarboxylic acid, and sodium hypophosphite.

A novel method to obtain durable FR characteristics is through encapsulated[67] FR deposition onto the fabric, and then thermo-bonded to the fabric. FR performance is enhanced by the layered structures wherein one coating holds an acid, while the other holds a base (CaCO3), which, when exposed to flame, will react to release CO2 gas; and also foam up to generate an intumescent-type FR action.

It is economical to incorporate of FR chemicals while production of regenerated cellulosic fibers by the wet extrusion process. Visil fibers[17] treated this way with polysilicic acid retard flame by both endothermic reaction (water release) and char formation. Daiwabo's Corona fiber uses sodium silicate in the viscose dope and applies a magnesium salt on as spun fiber[62].

2.7 FR Mechanism

Combustion involves three key factors: fuel, oxygen, and a source of ignition. Under favorable conditions the fire begins and the FR incorporated in the product interferes with at least one of these factors (as shown in the Figure 17). There are two types of FR actions: Physical actions and Chemical actions[13]. To obtain success in fire retardancy char formation, stability and structure integrity of char plays an important role. Generally, self-extinguishing fibers provide reinforcement and the product of pyrolysis form film-like structures between fibers.

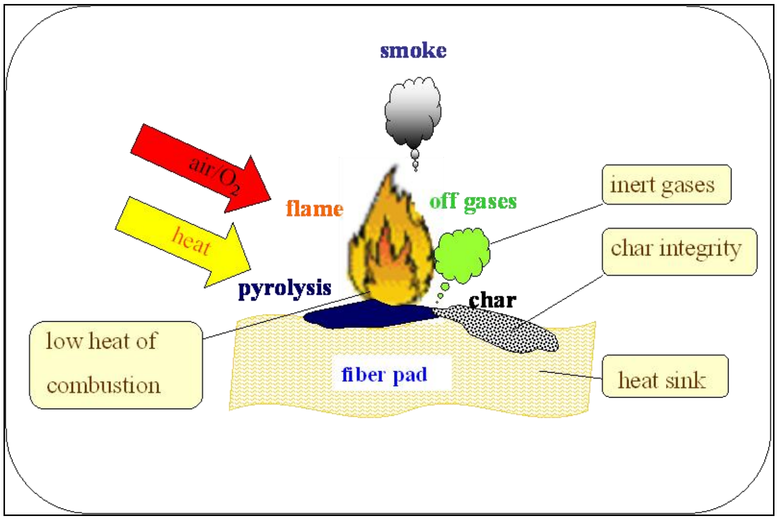


Figure 17 Schematic of FR Mechanism[15]

2.7.1 Physical Actions

1. Physical dilution: The FR can act as a thermal sink, increasing the heat capacity of the product or bring the fuel content to a level below the lower limit of flammability. Example: Inert fillers such as talc, clay, glass fibers.
2. Inert gas dilution: The FR decomposes to produce large volumes of noncombustible gases during combustion. These gases dilute the oxygen supply to the flame or dilute the fuel concentration below the flammability limit. Example: Metal hydroxides, and metal carbonates release H2O, CO2 respectively.
3. Thermal quenching**:** Endothermic reaction of the FR results in thermal quenching. Example: Metal hydroxides and metal carbonates.
4. Protective coatings**:** FR forms a protective char layer that acts as a barrier, reduces the heat transfer from the flame to the combusting material. Example: Intumescent systems.

2.7.2 Chemical Interactions

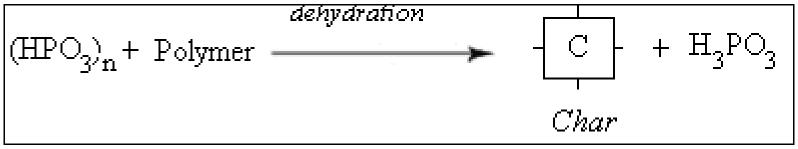
1. Gas Phase Reaction: FR interferes in the free radical mechanism of combustion to stop or suppress the exothermic reactions. This cools down the system. Example: Bromine compounds.
2. Solid Phase Reaction: FR reacts to form an inert or carbonaceous layer on the polymer surface. Example: Phosphorus compounds.

2.7.3 Char Forming Type Reaction

While burning, the oxidation reaction takes place, which is an exothermic reaction that favors propagation of combustion. Pyrolysis (endothermic reaction) sets in later at higher temperatures works as FR. Phosphorus compounds are the most popular char[68] forming type of FR. Depending on the structure; they act in various ways to extinguish a flame. During combustion the phosphorus is converted into phosphoric acid (Figure 18), which extracts water from the degrading product causing it to char (Figure 19 and Figure 20). This results in a protective char layer that shields the base material from burning.

$$(NH_4\text{-}PO_3)_n \xrightarrow{>250\ ^\circ C} (HPO_3)_n + n\,NH_3$$

Figure 18 Dissociation of Phosphate Compound



$$(HPO_3)_n + \text{Polymer} \xrightarrow{\textit{dehydration}} \underset{\textit{Char}}{\boxed{C}} + H_3PO_3$$

Figure 19 Phosphate Char Formation.

$$\text{Cellulose} \rightarrow 6n\,C\,(\text{carbon}) + 5n\,H_2O\,(\text{water})$$

Figure 20 Cellulose Dehydration.

Ammonium polyphosphate (APP) along with polyol exhibits a chemical effect in the condensed phase known as "Intumescence" where in the gaseous products swell the molten mixture several times into foamy char (insulating layer) through a cross-linking reaction. An ideal intumescent expands 100 times its original thickness. It requires a careful selection of the components and the processes to achieve this. Usually a synergist (such as pentaerithritol, melamines etc.) is added to accelerate the process. There are many proprietary intumescent formulations in the market[15].

2.7.4 Durable FR Mechanism in Cellulose

On heating slowly at the temperatures <300°C Cotton goes through various processes such as dehydration (Figure 21), rearrangement, formation of carboxyl and carbonyl groups, evolution of oxides of carbon and formation of carbonaceous char[69]. At temperatures >300°C, cotton degrades fast to form tars and carbonaceous residue (Figure 22) releasing a variety of volatile fragments. The tar contains levoglucose and other polymeric materials, at temperatures above 600°C; it forms oxides of carbon (Figure 22).

Phosphorus compounds offer resistance to combustion by lowering the decomposition temperature of cellulose that favors dehydration as opposed to depolymerization, thus reducing the formation of combustible volatile fuel compounds. The tar formed would be heavy. Phosphate and polyphosphate complexes lead to higher char yields; a glassy film formation[70], acts as a surface barrier to oxidation and hence makes the sample become self-extinguishing.

Chitosan cellulose phosphate[66] treated fabrics exhibit better FR properties due to the synergistic effect and the steps followed are:

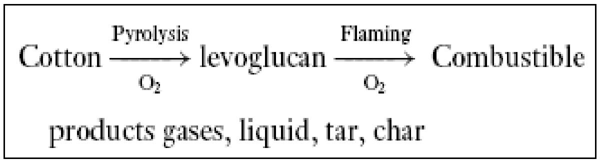
1. Phosphates reduce the heat releases by increasing the CO/CO_2 ratio that reduces afterglow propagation.
2. DAP decomposes into ammonia and phosphoric acid (Figure 22), which speeds up cellulose dehydration

3. Phosphoric acid forms a glassy film barrier between the fabric and air preventing flame propagation.
4. Phosphate derivatives inhibit afterglow reactions by preventing levoglucan the formation
5. Chitosan plays a complex synergetic role to enhance FR performance.

2.8 Model Development

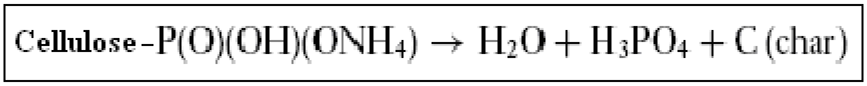
Several types of FR models are available in the literature. Probably combining a few chosen models discussed below one could develop a model for FR pads:

2.8.1 Correlation between Limited Oxygen Index (LOI) and Phosphorus Content: Limited Oxygen Index (LOI) is measurement of the minimum oxygen concentration that will support flaming combustion of a material (details of LOI are in section 2.9.2.1, section 3.5.1, and Appendix 2) Yong et al[71] discussed the correlation between LOI and phosphorus (P) content in a FR treated cotton fabric. In this experiment, the combination of a hydroxyl functional organophosphorus FR agent and melamine formaldehyde was used for FR treatment of cotton fabrics.



$$\text{Cotton} \xrightarrow[O_2]{\text{Pyrolysis}} \text{levoglucan} \xrightarrow[O_2]{\text{Flaming}} \text{Combustible products gases, liquid, tar, char}$$

Figure 21 Cellulose Pyrolysis and Combustion.



$$\text{Cellulose-}P(O)(OH)(ONH_4) \rightarrow H_2O + H_3PO_4 + C\,(\text{char})$$

Figure 22 Cellulose Phosphate Char Formation.

Melamine formaldehyde was used as a binder between FR chemical and cellulose. It also plays a synergistic role to enhance FR performance by providing nitrogen to phosphorus during combustion. Phosphorus concentration on the fabric was analyzed by inductively coupled plasma atomic emission spectroscopy. The correlation between LOI and the phosphorus content on the treated fabric has been discussed. A statistical model was developed to predict the LOI of the treated cotton fabric based on the phosphorus and melamine formaldehyde concentrations. LOI of the cotton treated with 16% P and 6% Melamine with different pH values, cured at 165°C for 2.5 min, and after different numbers of laundering cycles as a function of concentration P on the fabric.

Correlation Equation is: $LOI = 17.77 + 4.57\,P + 0.39\,M$

Figure 23 shows actual relation between LOI and %P. A linear least square estimated regression function exists between LOI and P. As shown in Figure 24, the model can be used to predict LOI of a treated fabric sample based on the phosphorus concentrations on the fabric determined by atomic emission spectroscopy and the melamine formaldehyde concentration in the finish solutions.

2.8.2 Correlation with Char Formation:

Formation of Intumescent char is quite important in the FR polymers. Char provides a spatial buffer between the combustible material and the heat source. In addition char acts as a thermal barrier. Referring both to the mechanism by which char is formed and the mechanism by which volatile products escapes to the surroundings, a simple model of pyrolysis of char-forming polymers is developed and discussed[72]. The physical situation that is considered is the essentially one-dimensional case of a horizontal specimen of material, insulated along its vertical sides, subject to an external heat flux and surface heat losses, such as in the cone calorimeter. Moreover it is assumed that the kinetic mechanism of the char-forming process is expressed as a series of n first-order steps in the general form: **Char formation rate = Km;** where m is the vector $(m1, m2\ldots mn)^T$ and K is a matrix of Arrhenius rate terms.

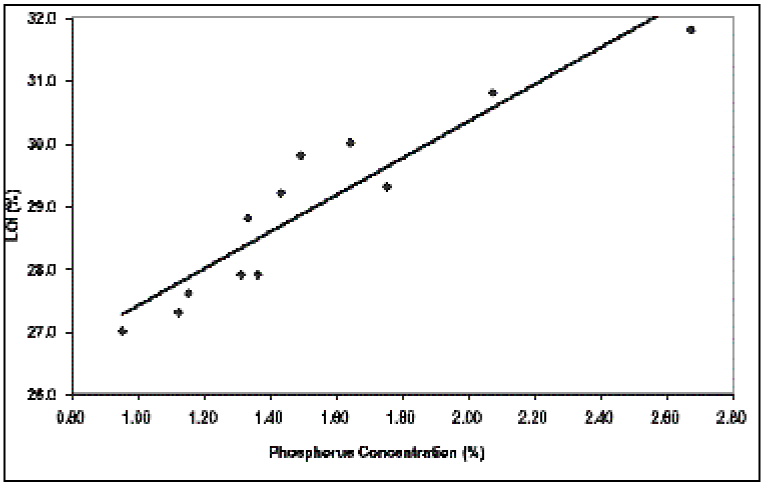


Figure 23 LOI vs P%

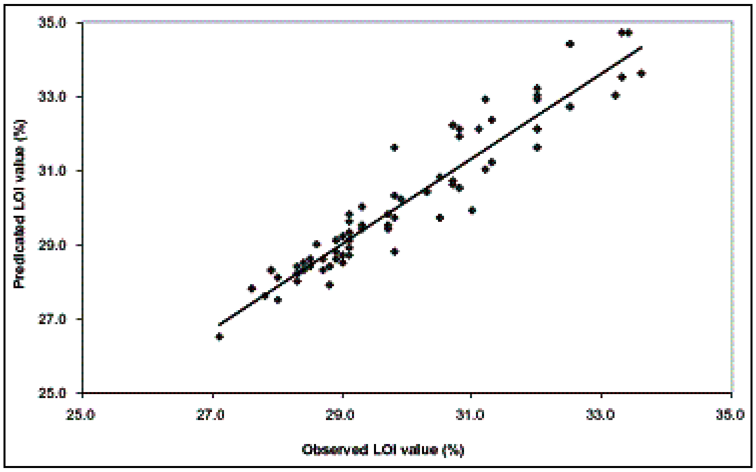


Figure 24 LOI Values Predicated vs. Observed.

2.8.3 Effect of Increased Heating Rates on Char Formation:

A mathematical model developed to predict the behavior of an intumescent flame retardant within a rigid textile fiber reinforced composite during exposure to heat. An empirical data showing the enhancement of char formation, at temperatures >400°C has been developed[73]. The intumescent based on melamine phosphate is dispersed on the surface of a FR cellulosic fiber (Visil, Sateri, Finland). Polysilicic acid present in the fiber reacts with the phosphate or polyphosphate components of the intumescent to form a FR char-bonded structure. Moreover additional layers with glass fabric in the composite structure have shown to promote enhanced char formation. In order to model the thermal decomposition of a cellulose and intumescent mixture, several different decomposition schemes, involving competitive and successive reactions, have been considered.

TGA mass loss showed at least three waves of overlapping reactions. A simple, reduced kinetic scheme has been compared with a temperature dependent scheme to determine the effect of increased heating rates on the yield of solid residue.

2.9 FR Tests, and Regulations

Flammability regulations are developed by various agencies such as the U.S. Consumer Product Safety Commission (CPSC), California Bureau of Home Furnishings, and National Fire Protection Agency that can be broadly classified into two categories: For Polymer Products[68] and Fibrous materials.

2.9.1 Flammability Testing Regulations for Polymer Products

UL-94 vertical burning test: this provides a relative flammability and dripping behavior of polymer used in electrical equipments, and appliances. It addresses such end-use characteristics as ease of ignition, flame spread, fuel contribution, intensity of burning, and products of combustion. Test method comprises of a sample (bar) measuring 125 x 12.5 mm, and 3 mm thick is mounted vertically in an enclosure with no draft. A burner is placed beneath the sample for 10 seconds and the duration of flaming is timed. Any dripping that ignites surgical cotton placed 305mm below the bar is noted.

The test has several sub-classifications as follows:

   a. *94 V-0*—No specimen has flaming combustion for more than 10 seconds after each ignition. Specimens do not burn up to the holding clamp, drip and ignite the cotton, or have glowing combustion persisting for 30 seconds after the second removal of the test flame.
   b. *94 V-1*—No specimen shall have flaming combustion for over 30 seconds after each ignition. Specimens do not burn up to the holding clamp, drip and ignite the cotton, or have an afterglow of more than 60 seconds.
   c. *94 V-2*—This involves the same criteria as V-1, except that specimens are allowed to drip and ignite the dry surgical cotton below the specimen.

2. Limiting oxygen index (LOI) is covered under ASTM D2863 and it is defined as the minimum concentration of oxygen expressed as volume percent in a mixture of oxygen and nitrogen that just supports flaming combustion of a material initially at room temperature.
3. UL-181 is used for air-duct and air-connector systems. It is based on National Fire Protection Association standards for air conditioning and ventilating systems.
4. UL-214 addresses flame propagation in fabrics and films. Standard specimens 70 x 250 mm are cut both in machine and transverse directions (five of each) for the small-flame test (flame height: 38mm), and 125 x 750 to 2100 mm for the large flame test (280 mm high). The bottom of the specimen is ignited for 12 seconds and the flame is removed. The length of the charred material is measured.
5. E-84 looks at surface burning behavior of building materials on exposed surfaces such as walls and ceilings. It determines relative burning behavior by observing spread along the specimen. Flame spread and smoke density data are reported.
6. Motor Vehicle Safety Standard 302 specifies burn-resistance requirements for materials in passenger compartments. This U.S. federal standard requires that a specimen 100 x 356 mm in the thickness used in a vehicle (thickness over 12.7 mm are reduced to 12.7 mm) should not burn or transmit a flame front across its surface at a rate of more than 100 mm/min.

2.9.2 Flammability Testing Regulations for Fibrous Materials

There are several flammability tests developed by many agencies over the years. The most popular tests for fibrous materials are:

1. Limited Oxygen Index (LOI)
2. Vertical Flammability Test
3. Small Open Flame Test (TB604 or 16 CFR Part 1634)

2.9.2.1 Limited Oxygen Index (LOI)

LOI is measurement of the minimum oxygen concentration that will support flaming combustion. This is preliminary test used at the early stages of research. As shown in the Figure 25, according to ASTM D2863[2], the test specimens (50mm width, 150mm length) are burned in a precisely controlled atmosphere of nitrogen and oxygen. LOI tests are repeated five or more times until the results are concordant. Typical LOI values available from the literature are shown in Table 8.

2.9.2.2 Vertical Flammability Test for Fabrics

(Federal Test Method Standard 191A Method 5903)[2]: Tests a fabric's ability to self-extinguish when exposed to flame. As shown in Figure 26 a 35mm flame is exposed to the bottom edge of a specimen with exposed area 305mm x 50mm for 12 seconds. Sample is considered to pass the test passed if the char length is <5 inch (as an average for ten specimens).

2.9.2.3 Small Open Flame Test[2] (TB604 or 16 CFR Part 1634):

This test method describes a laboratory scale test for samples of over the bed materials such as bedspreads, comforters, pillows, and mattress pads etc. A pad (or pillow) sample placed inside two cover fabrics is ignited with a small open flame (flame height 35mm) and is allowed to burn for over 6 minutes. The specimen passes the test if weight loss does not exceed 25% of original weight and there is no flash over. A barrier pad sample is considered to pass the test if the flame does not create a void of more than 50mm in diameter.

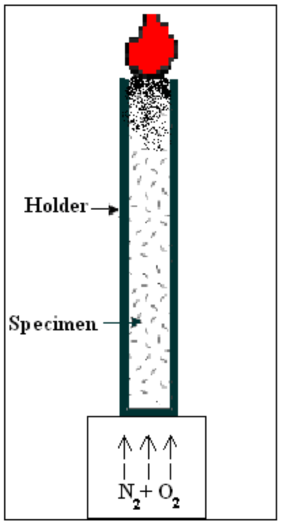


Figure 25 LOI Test Set Up.

Table 8 Typical LOI Values for FR Fibers

Fiber	**LOI**
Cotton	18~21
Acrylic	18~20
FR polyester	28
Kanecaron	28~38
Modacrylic	25~32
Polyester	20~23.5
Polypropylene	18~20
Polyvinyl	35~40
Rayon	18~20

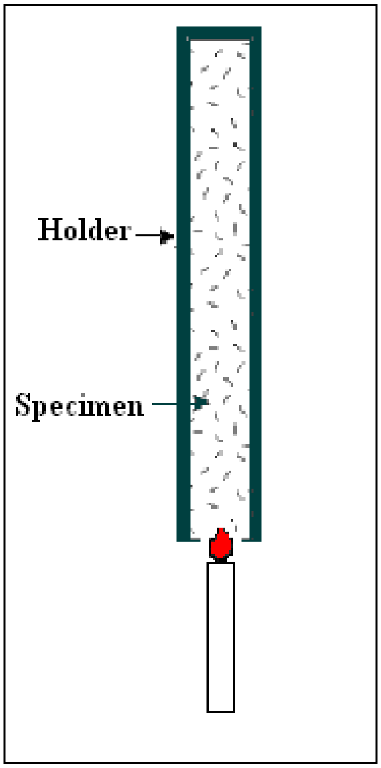


Figure 26 Vertical Flame Test Set Up.

There are several flammability tests (compiled in Table 9&10) evolved and developed by many agencies over the years. Many of these tests were first introduced in California State, which is facing a large number of fire incidents. Manufacturers are encouraged to employ innovative methods to develop FR properties and meet the standard tests.

Later these test methods are refined over years, entered in the Federal Register in Chapter 16 of Code of Federal Regulations and then enforced across the nation. Thus one can expect small differences between California (CA) Technical Bulletins and corresponding Code of Federal Regulations (CFR).

2.10 Challenges Involved in FR Treatment

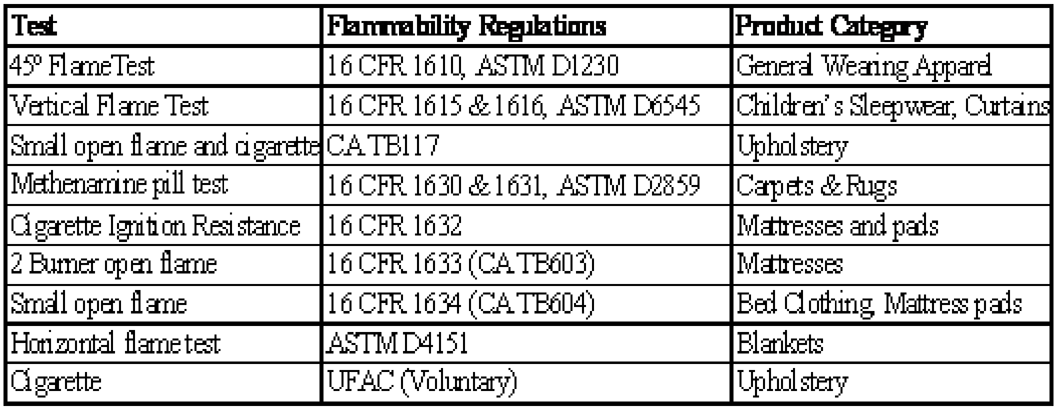
In case of synthetic FR polymers the effect on mechanical properties depends upon the polymer, additive, and the processing steps[74]. In majority situations effect of FR are summarized below:

- Polymer viscosity increases, and heat distortion temperature (HDT) increases.
- The tensile strength decreases, and the elongation at break reduces.
- Impact strength drops drastically at higher level of FR loading.

In case of the nonwoven pads containing cellulosic fibers as well as synrthetic fibers, while imparting FR properties some structural changes occur affecting some of the desirable properties. Challenge is how to minimize the detrimental effects.

Changes in the mechanical properties due to FR treatment are inevitable because of the structural changes introduced by the process and the stresses built within the fibers. Strong acidic reagents would reduce the strength of the cotton fabrics. Generally, the higher the concentration in the formulation, the larger will be the number of links between the reagents and the fibers. Blending of self-extinguishing FR fibers would compensate the loss, to a certain extent.

Table 9 Flammability Tests and Regulations



Test	**Flammability Regulations**	**Product Category**
45º FlameTest	16 CFR 1610, ASTM D1230	General Wearing Apparel
Vertical Flame Test	16 CFR 1615 & 1616, ASTM D6545	Children’s Sleepwear, Curtains
Small open flame and cigarette	CA TB117	Upholstery
Methenamine pill test	16 CFR 1630 & 1631, ASTM D2859	Carpets & Rugs
Cigarette Ignition Resistance	16 CFR 1632	Mattresses and pads
2 Burner open flame	16 CFR 1633 (CA TB603)	Mattresses
Small open flame	16 CFR 1634 (CA TB604)	Bed Clothing, Mattress pads
Horizontal flame test	ASTM D4151	Blankets
Cigarette	UFAC (Voluntary)	Upholstery

Table 10 Evolutions of FR Patents and Regulations for Fiber Products

Year	MILESTONES	DETAILS
1735	First FR patent - Obadiah Wyld (Britain)	Alum, sulfate, and borax treatment
1912	First Durable FR - William Henry Perkins	Stannic oxide Non-Flam process
1953	First Flammable Fabrics Act introduced	By the Federal Trade Commission
1954	16 CFR1 Part 1610	Clothing Textiles - flame spread time >4 s
1971	16 CFR1 Part 1630	Extended to Carpets and Rugs
1972	Consumer Product Safety Commission	New Safety Commission formed
1973	16 CFR1 Part 1632 (Cigarette Ignition)	Mattresses and Mattress Pads
1974	16 CFR Part 1616	Children's Sleepwear
1986	Sleep Product Safety Council (SPSC)	For research on flammability
1990	SPSC Addresses mattress fires	Ignited by open flame sources
1992	CA Technical Bulletin TB 129	Mattresses in Public Buildings
1997	National Association of State Fire Marshals	Open flames on bedclothes
2000	Bill introduced in California	Large Open Flame Test on Mattresses
2005	CA Technical Bulletin TB 603 enforced	Large Open Flame Test CA only
2006	California Technical Bulletin TB 604	Small Open Flame Test (Draft)
2007	16 CFR1 Part 1633 (Large Open Flame)	Mattresses Test all across USA
2009	16 CFR1 Part 1634 (Small Open Flame)	Over the Mattress products all across USA

The loss in breaking and tear strength of the finished fabrics would be can be improved by optimizing the rigid links. Generally tear strength loss is due to poor fiber elongation, decreased mobility of reacted structures in the cellulosic fibers. Allowing longer polymer chain formation would decrease the stress within the fibers, thus improving the flexibility and mobility. If finished fabrics are subjected to thermal curing for a long time that will scorch the fabrics and degrade polymer chains. Therefore, curing time and temperature would be optimized with respect to strength and color. Yellowing of the finished fabrics could be due to the number of double bonds present in the reactants. Sometimes the unsaturated monomers polymerize to form a polymer having fewer unsaturated bonds. Fewer the double bonds in the finish formulation, higher would be the whiteness index of the finished fabrics.

Reduction in air permeability of the fabric due to deposits of the chemicals needed to impart FR properties would be compensated at the fabric preparation stage. Moreover softening chemicals would be used to preserve the soft handle of the fabric. Dye-ability of the fabric would change after FR treatment and hence suitable HPHT dyes or reactive dyes would be required.

2.11 Focus of This Research

The most important requirement is low cost, which is absolutely essential in manufacturing any product. Moreover, the attempt is to make use of existing machinery and minimize buying expensive new machinery in the process. Based on our experience and the literature available focus of this research is on developing cotton-based nonwoven pads with FR properties by blending cotton with other commercially available fibers, binders, and followed by chemical treatments; offering a cost-effective recipe to meet the upcoming flammability standards. Furthermore the research explores the opportunities in taking advantage of possible synergistic effects to achieve maximum performance at low cost.

3.0 EXPERIMENTS

Research was carried out by acquiring samples of cotton, FR fibers, binder fibers; FR chemicals, bonding agents, etc. from available sources within the institution as well as from the industries and organizations that can contribute to, and take advantage of this project. Some of the chemicals such as dispersing agents were bought from standard laboratory chemical suppliers. Experiments were carried out to produce FR nonwoven pads with cotton as the major component.

3.1 Fibers Used in Construction of Mattress Pads

Cotton, Cellulosic FR, Binder Fibers, and Synthetic FR1 have adequate convolutions, crimps, or twists that assist in web formation. Cellulosic FR fibers have longitudinal grooves. Synthetic FR1 fibers have oval cross-section, smooth surface, and diameters vary from fiber to fiber. Synthetic FR2 fiber is smaller in diameter than Synthetic FR1, has round cross-section, smooth surface, and very low number of twists that poses difficulty in carding. Moreover Synthetic FR2 is brittle, breaks easily due to the mechanical forces involved in the carding operations. Binder fibers have bicomponent core-sheath cross-section with smooth surface. SEM pictures of these fibers are shown in Appendix 5.

3.1.1 Cotton

Cotton used in the research is from the commercial lot obtained from SRRC-USDA. It is gray (unbleached) cotton, mechanically cleaned thus practically free of undesired contaminants such as leaves, twigs, stones, seeds, seed-parts etc. It was supplied in the form of sliver packed in a bag. Naturally, cotton does not melt, but yellows above 185°C and then degrades[36] at > 290°C. Cotton has convoluted surface that helps in carding or web formation.

3.1.2 Cellulosic FR Fiber

Cellulosic FR fiber used in the research is from the commercial lot obtained from a mattress manufacturer. While regenerating cellulose during the fiber manufacture, it has been treated with polysilicic acid and some proprietary additives to impart FR properties. The fiber properties are suitable for carding. In fact, it is a specifically tailored form of rayon which has chemicals embedded in the fiber for applications such as technical textiles, furnishing textiles, insulation and fire barriers.

3.1.3 Synthetic FR Fibers

Synthetic FR1 is ivory white colored melamine fiber obtained from the manufacturer that is suitable for carding/nonwovens. It is manufactured through a patented melamine technology[75] and the product quality is specifically tailored to FR mattress pad application. The fibers have oval cross-section, diameters vary, but surface is smooth. It has good heat stability, low flammability, high wear performance, solvent resistance and ultraviolet resistance. In addition it meets all known environmental regulations with regard to processing and use. It has low thermal conductivity, excellent heat dimensional stability and that it does not shrink or melt or drip when exposed to flame. Synthetic FR2 is a silica fiber obtained from its manufacturer that is suitable for carding/nonwovens. The patented technology[76] is more eco-friendly than glass fibers. These fibers possess high break strengths, a few twists, and compatible to all bonding agents. These fibers have round cross-section, diameters are quite uniform, and surface is quite smooth. It shrinks a little, does not melt or drip when exposed to flame.

3.1.4 Binder Fiber

Commercial grade bicomponent fiber with low-melt polyester sheath and PET core is obtained from a mattress manufacturer. Moreover, our experience shows that pads containing these bicomponent fibers as binder fibers exhibit superior FR performance (pad is more cohesive) when exposed to flame than the pads produced with polyolefin based bicomponent binder fibers. Generally, bicomponent binder fibers are blended with commodity fibers in the desired proportion by carding process and through air bonded in a conventional oven to form a nonwoven pad. The sheath provides the fusing point while the core preserves the integrity of the nonwoven. Low melt bicomponent fibers[26] having sheath melting at ~80°C and core melting at ~250°C is used as binder fibers. Cross-sectional view is shown in Figure 7 in Section 2.3.6. Moreover, the pads containing these fibers can withstand safe ironing and laundering conditions.

3.2 Fiber Blending and Fabrication of Nonwoven Pad

Experiments were carried out to produce dry-laid nonwoven pads using the fibers with cotton as the major component fiber. These fibers were mixed in the desired proportion and fed to SDS Atlas card (Figure 27) to prepare a web of blended fibers (~305mm wide webs). The blend is passed through carding once more to improve the uniformity throughout the product. The process conditions for through air bonding were optimized to impart sufficient strength for further handling, loftiness and appearance. Table 11 shows the various combinations of fibers used to produce the webs. For each combination 8 rolls (~305mm wide x 1200mm in length) were prepared. All nonwoven pads produced are for standard mattress pads having a target basis weight ~300g/m^2 (~1oz/ft^2) and thickness range ~15mm (~½").

3.3 FR Treatment

The nonwoven pads with a width of ~305mm, a basis weight of ~300g/m^2 and a thickness of ~15mm were prepared in control and two combinations and used in all experiments. Early trials with the spray on chemicals onto the pad followed by cure-dry were not successful. It resulted in a non-uniform pad with spray side rich with the chemicals, formed a stiff layer and peeled away from the rest of the pad. Hence further experiments were carried out in the Mathis Laboratory Equipment for dipping, coating, padding, hot air assisted curing, and drying.

Figure 27 SDS Atlas Card.

Table 11 Details of Fiber Blend

	Control	**Combination I**	**Combination II**
% Binder Fiber	15	15	15
% Cotton	85	50	50
% Cellulosic FR	0	20	20
% Synthetic FR 1*	0	15	0
% Synthetic FR 2*	0	0	15

** FR fiber1 is melamine fiber and FR fiber 2 is silica fiber.*

FR chemicals such as boric acid, phosphates, silicates, and nanoclays are applied to the blended fiber web as a solution or dispersion in water in the presence of a necessary dispersing agent, and bonding or bonding agent.

Pad was passed through the trough slowly at 0.5m/min to get sufficient residence time to imbibe chemicals into the fiber web and then passed through press rolls at 0.5bar pressure and dried at 125°C. The treatment (passing the pad through dip-nip operation) repeated twice to improve uniformity and optimum pick up. Figure 28 shows Two Roll Padder Type VFM and Oven/Dryer Type KTF-S and Figure 29 shows the schematics of the same. The trough contained freshly prepared dispersion of FR chemicals. Components were added one after another with at least 2 minutes agitation before next component addition. For a typical 20% dispersion, the order of addition of chemicals into an agitated vessel and proportion is:

• Distilled Water	79.6%
• Dispersant (Triton X-100)	0.2%
• FR chemical	20.0%
• Bonding agent	0.2%

The process conditions were optimized to obtain sufficient adherence without appreciable change in loftiness and appearance.

3.3.1 Selection of Bonding Agent

The bonding agents (1%, 5%, and 10% based on the FR Chemical) such as Rhoplex[46], Eccogard[47], and Seyco-Rez[50] PFF were added and mixed in the slurry just before the application. Experiment was conducted with a mixture of 3% FR Chemical 1 & 4%FR Chemical 2, and 3% FR Chemical 3 (containing nanoclay Cloisite 20A). Calculated amount of solution/slurry was weighed and incorporated into the nonwoven web using Mathis equipment through the dip, squeeze (0.5bar pressure) three times, and cure-dried at 125°C. Treated web evaluated for integrity and ability to bond FR chemicals.

Figure 28 Mathis Padder, Thermobonding Oven.

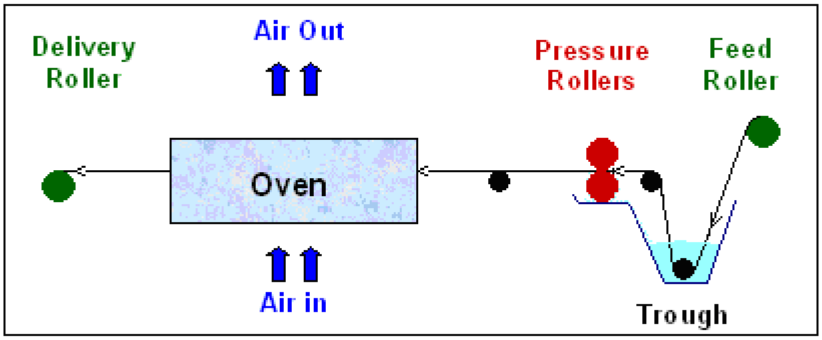


Figure 29 Schematic of the Dip Nip and Cure-Dry Equipment.

Table 12 Details of FR Chemical Treatment

	Control	Set 1	Set 2	Set 3	Set 4
% FR Chemical 1**	0	5	10	15	20
% FR Chemical 2**	0	5	10	15	20

***FR chemical 1 is Boron compound and FR chemical 2 is Phosphorus compound.*

Rhoplex[46] TR-520 is recommended for high loft nonwovens to obtain resilient, durable bonding of FR additives maintaining good strength and durability. It is an aqueous, salt tolerant all-acrylic emulsion with low formaldehyde (<0.6%). Rhoplex has excellent resistance to yellowing at high temperatures. Its outstanding mechanical stability and self-thickening nature ensures even binder distribution and penetration. FR chemicals can be loaded to 100% level.

Eccogard[47] BV 200 is recommended for a soft non-combustible precatalyzed bonding agent for non-woven products to impart soft hand, flame retardancy, solvent resistance and greatly increase tensile and compressive strength. It is water soluble and compatible with many FR chemicals. Seyco-Rez[50] PFF is a buffered, precatalyzed, modified glyoxal-based bonding agent, which provides extremely low formaldehyde (<0.3%) release in pre-cure and FR finishing while retaining good physical properties during on fabric.

3.3.2 FR Chemical Treatment Process Details

FR treatment was carried using chosen bonding agent at different levels of FR Chemicals as show in the Table 12. Dispersion agent[16], Triton X-100 (1% based on the additive) was added while preparing a solution/slurry of chemicals in distilled water. Bonding agent (1% based on the additive) was added at the end just before feeding into the trough to minimize agglomeration.

To understand the morphology SEM pictures were taken after bonding, after FR treatment, and after the burning (char) test. Also EDS graphs were taken for the same samples to confirm and identify the FR chemicals. FR treated pads were tested for flammability tests LOI and Small open flame test TB604. LOI test was used for preliminary screening, whereas small open flame test was used for selected samples as a confirmatory test.

3.4 CHARACTERIZATION METHODS

The samples produced in the experiments were tested for physical properties and structure only after conditioning the samples for at least 24 hours under standard laboratory conditions, which is 21°C ± 1°C and 65% ± 10% relative humidity.

3.4.1 Fiber Properties

The most important characteristics of a fiber that influence their processability in a card are fiber linear density or fineness, staple length, crimps or twists, tensile strength and fiber finish. Generally the fiber supplier applies the proprietary finish. These properties are taken from the literature and supplier's catalogs. Scanning Electron Microscope pictures of the fibers were taken (Appendix 5) to visualize the crimps, shape of the twists and convolutions.

3.4.2 Differential Scanning Calorimetry

Differential Scanning Calorimetry of the polymers and fibers was carried out in a Mettler DSC821. The sample was placed in a 40-microliter volume standard aluminum crucibles with lid. In order to vent the air trapped three holes were made on the lid using a pin. Nitrogen at 200 milliliter per minute was used as the carrier gas in all the samples. Heating rate of 10°C per min was used while running the DSC. DSC scans were used to get an idea about the melting behavior of various binder fibers.

3.4.3 Basis Weight

Basis weight was measured according to ASTM D3776-96. Pad samples were cut into rectangular pieces of 305mm x 305mm (12"x 12") size and weighed. Basis weight is expressed as grams per square meter.

3.4.4 Thickness of the Pad

Thickness of the pads measured according to TB604 Annex D: In order to measure the thickness of the test specimens uniformly and consistently, the sample is set on a horizontal table and a square platen is placed on the specimen. The distance between the platen and table surface is measured in mm. The square platen has dimensions 305 mm X 305 mm (12" X 12") and thickness ~3mm (1/8"). It was constructed of Plexiglas board with a handle to lift and position the plate. The total weight of the thickness measurement plate is 325(±25) grams. Average of 16 readings (four readings from four sides) were taken for evaluation.

3.4.5 Scanning Electron Microscopy & Energy Dispersive X-ray Spectrum

The Scanning Electron Microscope (SEM) photographs were obtained using Leo 1525 surface scanning electron microscope in back scatter mode with Gemini column at system vacuum of about 1.3×10^{-5}torr and at an acceleration voltage ~5kV. SPI Module sputter coater was used to coat the samples with gold for 5 seconds at 20mA plasma current to reduce charging while scanning. SEM pictures were taken to understand the morphology. Pictures were taken at the desired magnification focusing on various fibers, fiber-to-fiber bond points, adhered additives, etc. After the burn tests the char was observed for the structural integrity and intumescent (swelling) behavior. Further, the same samples were analyzed for Energy Dispersive X-ray Spectrum (EDS or EDAX) to identify the elements (Al, P, Si, etc.) present in the sample. The EDS does not detect Boron, since it is outside the detection range.

3.4.6 Tensile Properties

Tensile test was conducted according to IST 110.4 (ASTM D5035-95) using Six-Station United Tensile Tester as shown in Figure 30. Specimen size used was 25mm (1") and gage distance 75mm (3"). Extension rate was 305mm per minute. Average of five readings reported. Sample dimensions such as thickness and basis weight were measured before cutting the specimen.

Figure 30 United Tensile Tester.

3.5 FLAMMABILITY TESTS & MODEL

All samples were subjected to flammability tests only after conditioning the samples for at least 24 hours under standard laboratory conditions, which is 21°C ±1°C and 65% ± 10% relative humidity.

3.5.1 Limited Oxygen Index (LOI)

Samples were tested for Limiting Oxygen Index (LOI) levels using the General Electric Flammability Tester (Figure 31) according to ASTM D2863[2] method (details in Appendix 1). LOI is the minimum concentration of oxygen that will just support flaming combustion in a flowing mixture of oxygen and nitrogen. A specimen is positioned vertically in a transparent test column and a mixture of oxygen and nitrogen is flown upward through the column. The specimen is ignited at the top with a flame. The oxygen concentration is adjusted until the specimen just supports (flame) combustion. Nitrogen flow is kept constant and oxygen flow is varied in increments of about 0.5%. Certain flow rate that supports a flaming combustion is arrived at and the concentration reported is the volume percent. A 50mm wide, 150mm long rectangular specimen is used for the test. LOI tests are repeated five or more times until the results are concordant.

Classification[77] based on LOI values showed in Table 13. Cotton has LOI value of 19 that indicating it a flammable one. Where as Cellulosic FR is slow burning since its LOI is 26. Synthetic FR fiber 1 and 2 both are self-extinguishing since LOI values are more than 28. With 100% pure oxygen FR fiber 2 (Si) did not burn at all, whereas FR fiber 1 did burn with a bright golden glow. In case of real fire oxygen does not increase, instead depletes.

Similar classification[77] was used for pads. In fact it is convenient to make a pad using carded web, cut the specimen to the required size, and then test LOI. In this research the control pad is constructed out of cotton and binder fiber (15%) using carded web, which is through-air thermal bonded.

Figure 31 General Electric LOI Tester.

Table 13 FR Classification Based on LOI

LOI Value	Type
LOI < 21	Flammable
LOI = 21	Marginally Stable
21< LOI < 100	Intrinsically Non-flammable
21< LOI < 28	Slow Burning
28< LOI < 100	Self-Extinguishing

3.5.2 Small Open Flame Test (TB604)

Sample pads before and after treating with FR chemical [only chemical 2 was chosen and used based on LOI test results detailed later in section 4.6.1] were tested according to California Technical Bulletin 604[2] or 16 CFR Part 1634[1] laboratory scale flammability test for samples of filling materials of bedding products such as mattress pads (Figures 32 &33), comforters, pillows (Figure 34), and mattress pads etc. 305mmx305mm sample pads were covered with two layers of fabrics (Test details are in Appendix 2).

This test is a laboratory scale flammability test for samples of filling materials of bedding products (comforters, pillows, and mattress pads etc.) weighing up to 450grams (1 pound). In this test the sample is ignited with a small open flame and allowed to burn for over 6minutes. The specimen passes the test if weight loss does not exceed 25% or creates a void less than 50mm (2”) in diameter. Test fails if flash over (bursting into flame) occurs anytime in those 6 minutes. After the burn test the charred samples were conditioned, then weighed, and thickness was measured for evaluation.

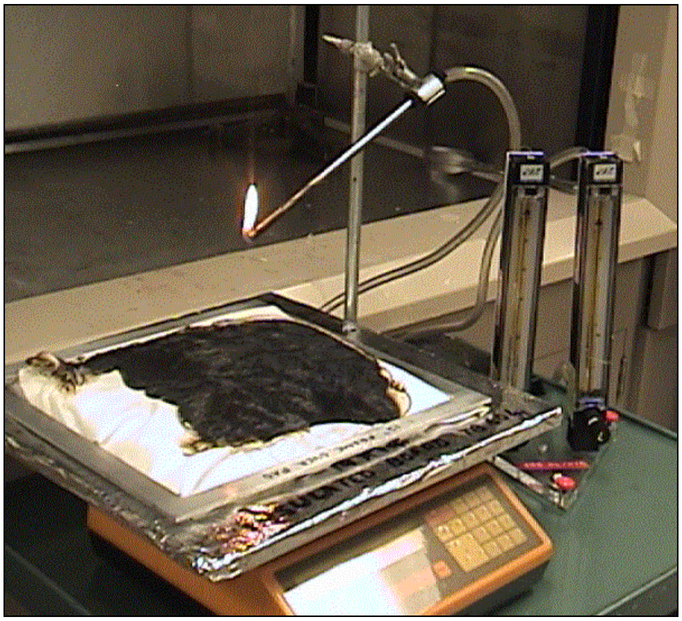


Figure 32 Small Open Flame Test Set Up.

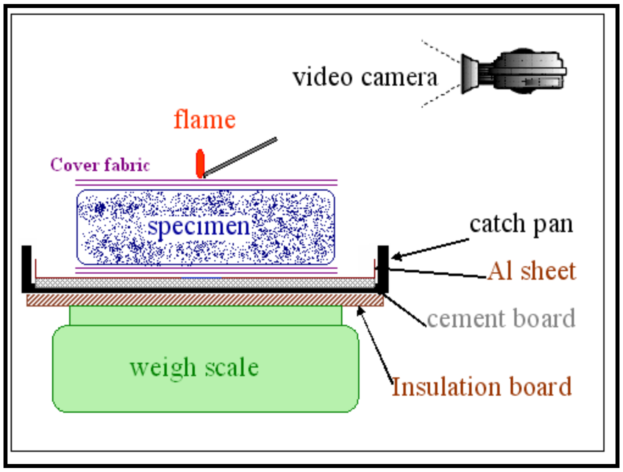


Figure 33 Small Open Flame Test for Mattress Pads.

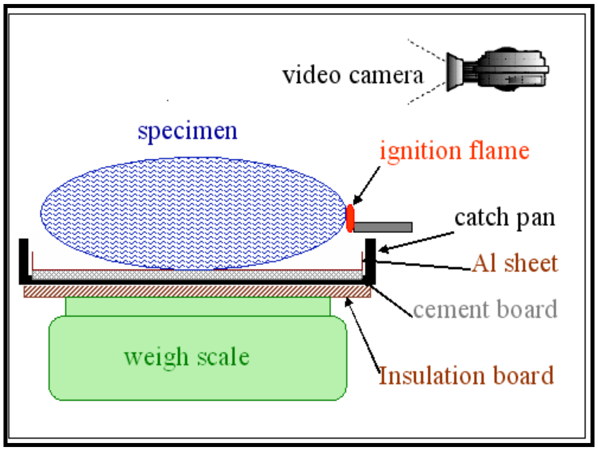


Figure 34 Small Open Flame Test for Pillows.

3.5.3 FR Model Development

Using the data obtained from LOI tests and Small Open Flame TB604 tests FR Model was developed. Excel and JMP 7 Statistical[78] software was used to analyze the experimental data and then develop the model.

3.5.3.1 Model for LOI

We have LOI values measured for fibers and pads of varying composition before and after FR chemical treatment. LOI values were correlated with the FR content (for both FR Chemical 1 & 2), and the relation was compared with the literature data.

3.5.3.2 Model for Small Open Flame Test

While conducting the Small Open Flame Test (TB604) tests (for all samples) data collected for every 15seconds on following parameters:

1. Weight of the sample pad
2. Char area
3. Temperature at the pad center (temperature sensor located under the pad)

After the test the charred specimen thickness, total charred area etc. measured. If abundant air or oxygen supply is available the heat of combustion of cellulose[79] is 12.6 kJ/g. In case of open flame test initially cellulose burns to evolve volatiles; at the same time char is formed. FR chemicals promote char formation and self-extinguishing FR fibers support the char and hold it in place.

It is assumed that the oxygen available is only at the upper surface. In case of control pad (does not have self-extinguishing FR fibers) the char crumbles, oxygen is available from sides as well as upper surface and flame spreads fast across the specimen. The endothermic effect due to volatile formation is estimated to be about 0.538 kJ/g and char formation leads to an estimated exothermic effect of about 2 kJ/g of char formed[80]. Char formation favors flame retardancy.

According to the test procedure, the top surface of the test specimen is subjected to a 35mm high butane gas flame oriented at 30° with respect to horizontal line. The tip of the burner is placed at the center of the top surface for 20 seconds, and then the burner is removed. This way the ignition is initiated. Flame propagates and FR activities take place simultaneously. As shown in Figure 35, the schematics of the small open flame test where flame size diminishes as the flame travels from the center to periphery, simultaneously developing the char on the pad surface. Flame travel speed, time to extinguish the flame is related to the composition of the pad.

Following parameters are of importance to understand the 1-dimensional model:

1. Width of the pad, W
2. Diameter (equivalent) of the charred area, B
3. Weight of the pad before and after char, Mi, and Mc
4. Temperature (sensor located at the center)

Pad dimensions (square with side W=305mm or 12”) and initial weight (Mi) measured before the test. Instantaneous data on char size, pad weight, and temperature was gathered from the video recordings and then was plotted against time in X-axis. Char area is calculated from the measurements of char width (usually a circle with equivalent diameter B). After the test sample weight (Mc) is taken. % Weight loss and % Charred area calculated using formula in Figures 36, and 37.

Using the experimental data empirical equations were developed to correlate charred area and weight loss with the composition of pad. The weight loss is expected to be due to the combustion hindered by the FR activities. Temperature (sensor was located at the center of the pad between the pad and bottom cloth) data was plotted to understand initiation, propagation, and termination steps involved in the burn test. In fact temperature sensed is a contribution of the net heat generated in the system and the thermal conductivity of the char. Generally char is a poor conductor; hence the temperature is expected to drop as the flame travels away from the sensing point.

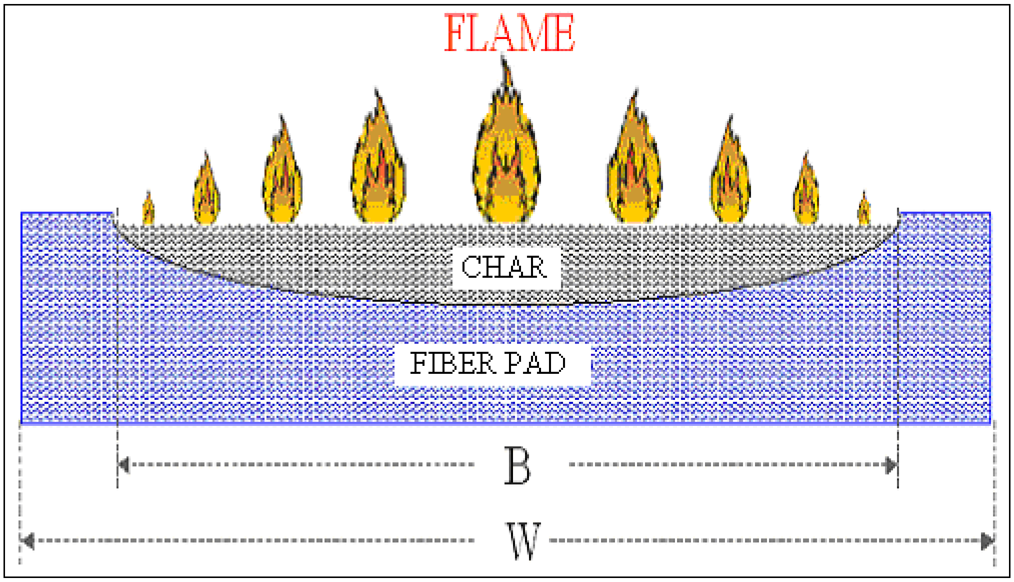


Figure 35 Schematics of Small Open Flame Test.

% Weight loss = 100*(Initial wt- wt after the test)/ Initial wt = 100* (Mi-Mc)/Mi

Figure 36 Weight Loss Calculation.

% Charred area = 100*(Initial area- area charred) / Initial area $= 100^* (W^2 - 0.25\pi B^2) / W^2$

Figure 37 Charred Area Calculation

4.0 RESULTS AND DISCUSSIONS

4.1 Fiber Properties and Web formation

The important characteristics of a fiber that influence their processability in a card are fiber linear density or fineness, staple length, crimps or twists, tensile strength and fiber finish. Generally the supplier applies the proprietary finish on fiber. These properties are taken from the literature and supplier's catalogs and summarized in the Table 14. Important parameter for FR is the LOI values of the fibers used. As desired the FR fibers have higher LOI values. If cotton has LOI 19, cellulosic FR has LOI 26, and synthetic FR fibers have LOI more than 32. Thus overall blend should have a resultant LOI higher than cotton. Staple size, length, and finish play important roll at carding stage.

All fibers except Synthetic FR2 (Silica) fiber ran well in the card when fed in the blended (hand mixed) form, and withstood repeated carding operations. Synthetic FR2 fiber was blending well, but breaks into pieces and about 10% of the fiber was lost in the carding (falls out). About 10% extra fiber was added in the feed blend to compensated this loss.

Cellulosic FR, Binder Fibers, and Synthetic FR1 have adequate convolutions, crimps, or twists that assist in web formation. SEM pictures of these fibers are shown in Appendix 5. Cellulosic FR fibers have longitudinal grooves. Synthetic FR1 fibers have oval cross-section, smooth surface, and diameters vary from fiber to fiber. Synthetic FR2 fiber is smaller in diameter than Synthetic FR1, has round cross-section, smooth surface, and very low number twists that poses difficulty in carding. Moreover Synthetic FR2 is brittle, breaks easily due to the mechanical forces involved in the carding operations. Binder fibers have bicomponent core-sheath cross-section with smooth surface.

DSC scan of binder fiber is shown in Figure 38. Since it has two components, it exhibited two melting peaks. First peak is at ~80°C corresponds to low melting sheath of low melt PET (a copolymer with a structure quite close to PET) and second one at ~250°C corresponds to homopolymer PET core.

Table 14 Fiber Properties

Fiber	**Cotton**	**Cellulosic FR**	**Synthetic FR1**	**Synthetic FR2**	**Binder Fiber**
Structure	Natural	Regenerated	Melamine	Silica	Bico
Linear Density dtex	0.8-2.8	1.7	3.0 var	3.0	4.4
Staple length mm	25-41	41-51	50 var	~75	~50
Cross-section Shape	Kidney	Non-circular	Oval	Round	Round
Crimps	Convolutions	Low	Low	Twisted	Medium
Specific Gravity.	1.27	1.62	1.40	1.70	1.36
Break Tenacity g/dtex	2.5-4.9	1.6-2.4	0.8-2.2	6.9	1.8-2.5
Breaking Elongn %	3-9	16-26	18	<2	~25
Moisture %	7	6	2	3.5	0.5
LOI	18-21	26	32	>38	~20
Melting Point °C	Nil	Nil	Nil	Nil	80 (sheath) 250 (core)

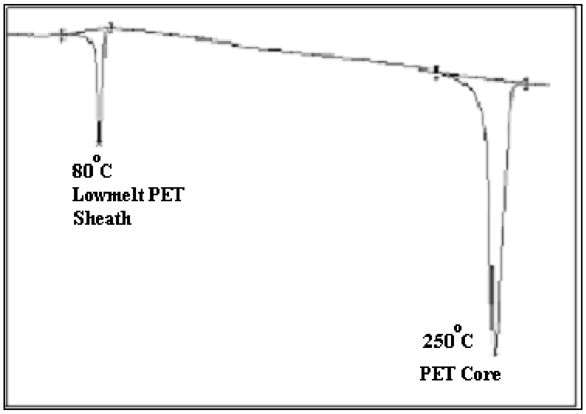


Figure 38 DSC Scan of Bicomponent Fiber

4.2 Thermal Bonding of Nonwoven Pads

To determine the optimum bonding temperature for the webs, bonding studies were carried out at a range of temperatures from 160 to 180°C at 5°C intervals. The cotton-rich nonwoven webs containing 15% low melt binder fibers achieved optimum thermo-bonding at the hot air temperature of 175°C and residence time of 3 minutes in the oven, and possess sufficient strength for further handling. As shown in Table 15, at 170°C and below bonding was not adequate, and above 175°C web turned yellow with a char smell indicating degradation of cotton. These optimum conditions were used in further studies.

4.2.1 Structure of the Pad

The SEM picture of the pad (Figure 39) after thermal bonding shows binder fiber integrating the web of fibers at the crossover points. Binder fibers show melting and bonding of the adjacent fiber at the contacted surface. Convoluted fibers are cotton, fibers with smooth surface are synthetic fibers, and fibers with grooves on the surface are cellulosic FR (More pictures are in Appendix 6).

EDS graphs of the bonded nonwoven pads are shown in Appendix 7. All pads show C and O that is present in cellulose. The sample was gold sputter coated to reduce charging while taking SEM pictures. Hence Au shows up in all graphs. EDS graph of Combination I (Cotton +binder +Cellulosic FR +Synthetic FR1) shows up Si present in the constituent cellulosic FR. Combination II (Cotton +binder +Cellulosic FR +Synthetic FR2) EDS graph shows up Si at higher level due to the presence of Silica fibers (Synthetic FR2). Trace amount of Al present in cellulosic FR also shows up in the graph. Neither Al nor Si are identified in the control pad made of mere cotton and binder fibers.

Table 15 Through-Air Bonding of Webs

Air Temp in °C	Bonding Time in Min	Bonding	Web Color
160	3	Poor	Normal
165	3	Poor	Normal
170	3	Medium	Normal
175	**3**	Good	Normal
180	3	Good	Yellow
180	10	Good	Yellow

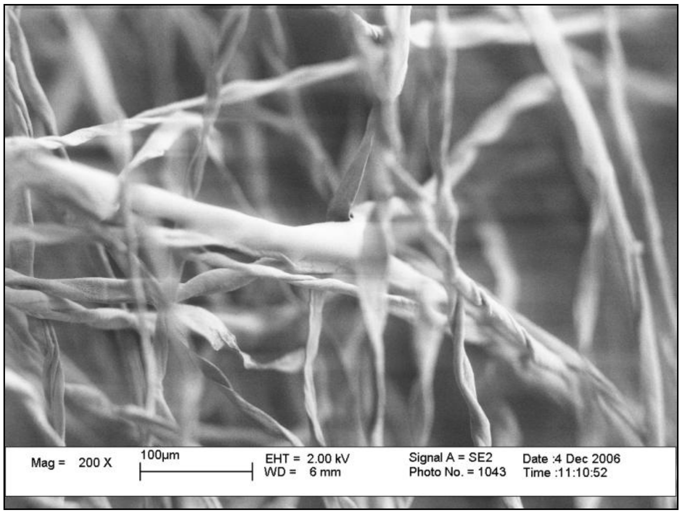


Figure 39 SEM Picture of the Pad Bonded at 175°C.

4.3 Selection of Bonding Agent

In all trials the pad was passed through the trough slowly at 0.5m/min to get sufficient residence time to imbibe chemicals into the fiber web and then passed through press rolls at 0.5bar pressure and cure-dried at 125°C for 10minutes. The treatment (passing the pad through dip-nip operation) repeated twice to obtain thorough soaking.

In the Mathis equipment the trough was filled with freshly prepared dispersion of FR chemicals. For 10% dispersion, the order of addition of chemicals into an agitated vessel and proportion was:

• Distilled Water	88.9%
• Dispersant (Triton X-100)	0.1%
• FR chemical	10.0%
• Bonding agent	1% & 5%

Experiment was conducted with the mixture of FR Chemical 1 (3%), FR Chemical 2 (4%), and FR Chemical 3 (3%) containing nanoclay Cloisite 20A. Total FR Chemicals targeted pick up was 10%. As shown in the Table 16 Bonding agent, Rhoplex worked the best for FR chemicals. The chemical pick up or add-on is close to the desired level, and the treated product has soft feel at 1% level of bonding agent. The SEM picture of FR treated nonwovens clearly shows the presence of constituent fibers (Figure 40) and additives adhering onto their surface (inset picture at magnification 5000 shows good adherence, more SEM Pictures in Appendix 3). There were no loose or unattached FR particles detected.

EDS graphs of the FR treated nonwoven pads are in Appendix 9. Boron present in pad due to treatment with FRchemical1 is not detected since it is out of range of EDS. Phosphorus in EDS graph indicates presence of FRchemical2 in the pad. Al indicates presence of nanoclays FRchemical3 in the pad. When the pad is treated with all FRchemicals (1, 2, and 3) EDS graph showed Al, Si, and P.

Table 16 Pads Treated with Various Bonding Agents

Bonding Agent	%	% Pick up	Bonding	Feel	Particles
Eccogard	1	3.8	Poor	Soft	Loose
Eccogard	5	4.1	Poor	Soft	Loose
Seyco	1	2.3	Poor	Soft	Loose
Seyco	5	2.8	Poor	Soft	Loose
Rhoplex	1	9.6	Good	Soft	Adhered
Rhoplex	5	9.7	Good	Hard	Adhered

Target pick up is 10%

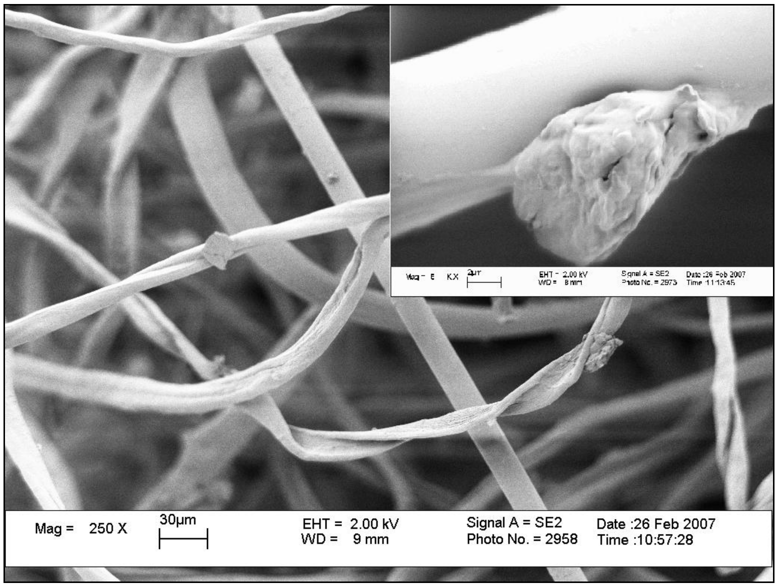


Figure 40 SEM Picture of FR Chemical Treated Nonwoven.

4.4 Characteristics of the Char

The SEM picture of the char (Figure 41) obtained after burning shows a reinforcing grid of self-extinguishing FR fibers undestroyed by the fire. These FR fibers support the char formed out of Cellulosic fibers. The FR additive residues are still present on the fiber surface and strengthen the char. The film structure is formed out of pyrolysis of thermoplastic binder fibers and cellulose (forms tar). Broken fibers are charred cellulose. More SEM pictures are in Appendix 10.

The EDS graphs (Figure 42) confirmed presence of P (from FR Chemical 2), Si (small amount from Cellulosic FR and large amount Synthetic FR2). Trace Al may be from cellulosic FR or FRChemical3 (nanoclay). The char containing FR Chemical 2 exhibited improved structural integrity; whereas the char containing FR Chemical 1 was fluffy and loose (More pictures are in Appendix 11).

4.5 Mechanical Properties

Tensile test results along with the thickness and basis weight of the samples are presented in Table 17. Blending with FR fiber 1 tensile peak force increased from 3 to 5N, where as blending with FR fiber 2 reduced the tensile force to 2.7N. FR fiber 1 reinforced the pad. Probably this is due to low crimps and smooth surface of FR fiber 2 that reduced inter fiber grip. Elongation increased marginally in case of FR fiber blends. FR chemical treated pads exhibited higher tensile force, increased by 1N, at the same time elongation dropped from 50% to less than 10%. This indicates FR chemicals strengthened the pad. Combination I exhibited highest tensile force. Combination II and III have similar strength but later one has higher elongation. This is because of lower degree of adhesion among fibers. In case of Combination III since bonding is done after depositing FR chemicals onto fiber adhesion is poor. After the FR chemical treatment, basis weight of the pad increased by about 12%; and thickness reduced from 13 to 10mm or less. In case of Combination III pad thickness did not change, this indicates thickness reduces during cure-dry process.

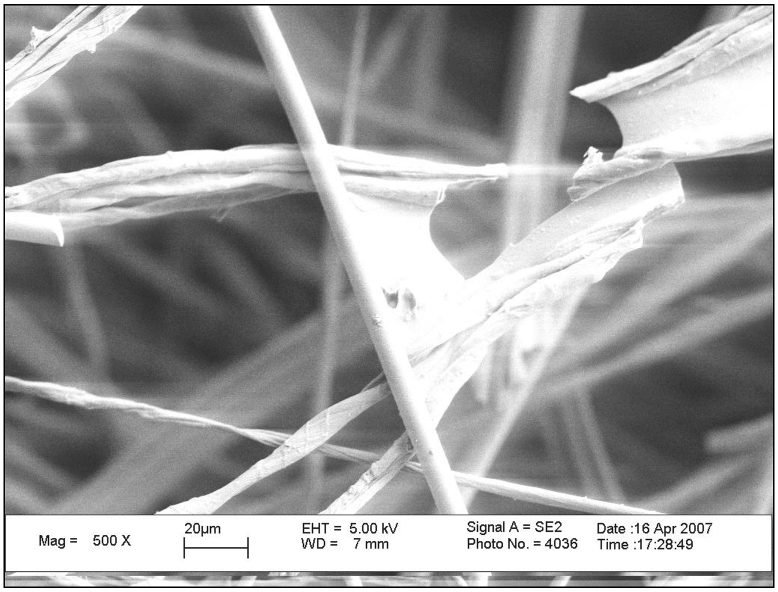


Figure 41 SEM Pictures of the Char.

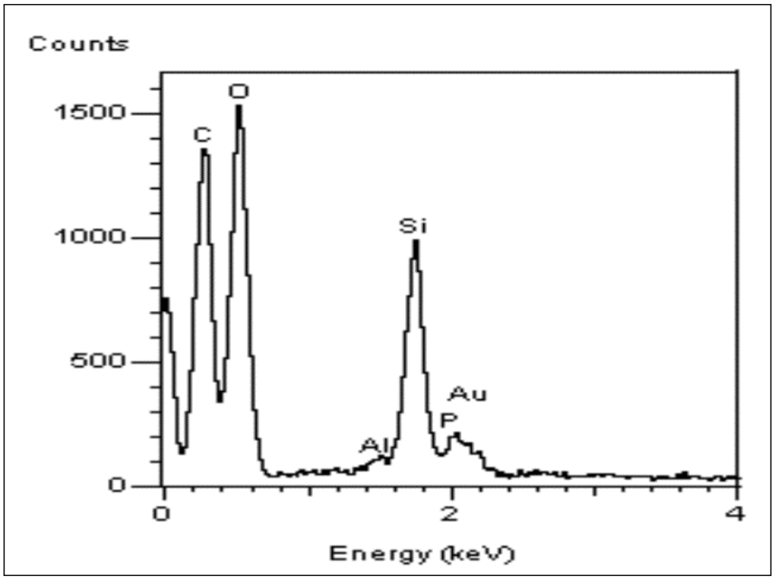


Figure 42 Typical EDS Graph of FR Chemical Treated Pad.

Table 17 Mechanical Properties of Mattress Pad Samples

	Basis weight	**Thickness**	**Tensile Test**	
			Peak Force	**Elongation**
Unit	**g/m^2**	**mm**	**N**	**%**
Control	338	13	3.18	53
Combination I	323	13	4.98	56
Combination II	296	13	2.65	58
Control+FRC_2	387	10	4.68	73
Combination I+FRC_2	393	9.5	8.82	6
Combination II+FRC_2	349	9.5	5.43	9
Combination III *	378	13	5.44	24

** Fibers are treated with FR chemicals before fabricating the pad.*

4.6 Flammability Test Results

4.6.1 Limited Oxygen Index (LOI)

Flame retardancy of the nonwoven shows a marginal improvement by blending cotton with FR fibers. The LOI value increased from 19 for cotton to 22 for the blend (combination I or II). LOI results (Figure 43) indicate superior performance of FR Chemical 2 compared to FR Chemical 1. Hence for later tests only FR chemical 2 was used. LOI >28 is self-extinguishing (see Table 13, section 3.5.1) and generally classified as FR. This is achieved by incorporation of ~10% FR Chemical 2. Nonwovens containing a mixture of FR Chemical 1 & FR Chemical 2 did not show up or correlate with LOI values. In all samples if the fiber is self-extinguishing and does not melt or burn at all, then it can function as a char-reinforcing grid.

4.6.2 Small Open Flame Test Response

FR treated mattress pad samples were subjected to Small Open Flame Test (TB604). Pad passes the test if the flame does not create a void of more than 50mm in diameter and or loss in weight is not more than 25%. During the test char formed on the sample pad (shown in the Figure 44 and more pictures are in Appendix 12.) but none of the samples developed void or hole at the center. Other side of the sample did not char and had slight change in color. Test results are compiled in Table 18.

FR chemical treated samples of combination II & I only passed the test. This demonstrates that the product of this research would be a suitable candidate to comply with the latest open flame standard. All others failed because of loss in weight was more than 25% due the combustion. During the test the flame traveled across the control (cotton + binder fiber) pad. Scorching and smoldering was predominant due to the presence of cotton. Flame spread was slower in case of Combination I & II (have FR fibers in addition to cotton). Flame spread further slowed down in presence of FR chemicals.

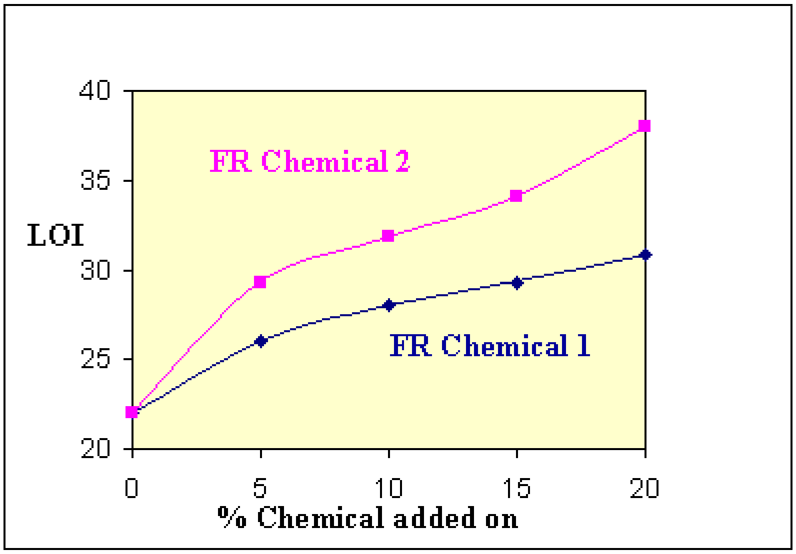


Figure 43 LOI of Chemical Treated Pad (Combination I)

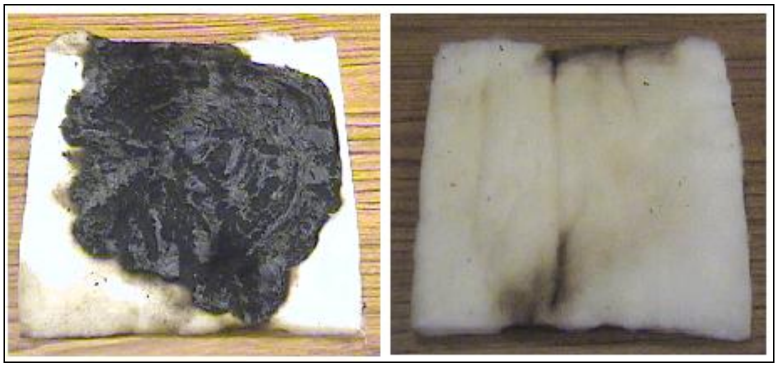


Figure 44 Sample Pad after the TB604 Test

(Char on the fireside and change in color on other side)

Table 18 Small Open Flame Test Results

ID	Flame extinguished	% Char area	% Weight Loss	Void at Center	Result
Control	No	100	56	No	Fail
Combination I	No	100	49	No	Fail
Combination II	No	100	39	No	Fail
Control +FRC$_2$	Yes	69	34	No	Fail
Combination I +FRC$_2$	Yes	34	10	No	Pass
Combination II +FRC$_2$	Yes	19	11	No	Pass
Combination III*	Yes	94	36	No	Fail

** Combination II with fibers FR treated before bonding*

In case of FR chemical treated pads the flame slowed down drastically, and extinguished (indicated by % charred area less than 100 in Table 18) before reaching the periphery. In case of Combination III, the constituent fibers are treated with FR chemicals before constructing the pad. The pad appeared fluffy, with lower degree of bonding. The sample failed the test because of loss in weight of more than 25%. Flame extinguished just before reaching the periphery. Charred area was 94%. Probably the FR chemicals on the surface of the fibers hindered thermo bonding, provided more voids, and increased passage of air favoring combustion.

4.7 FR Model Results

4.7.1 FR Property Relation to FR Chemical Concentration in the Pad

LOI data for various pad samples was statistically analyzed. The results show (Figure 45) a strong positive linear relationship with the concentration of FR present in the pad as shown by Regression Coefficient $R^2>0.9$ and p value 0.0001. FR Chemical 2 influences LOI more than FR Chemical 1 as shown by the increased slope of the line. Figures 46 and 47 represent the linear relationship between LOI and % FR Chemicals. Figures 48 and 49 show the linear relation between LOI and % FR chemical (drawn in Blue) with the 95% confidence interval (drawn in Red).

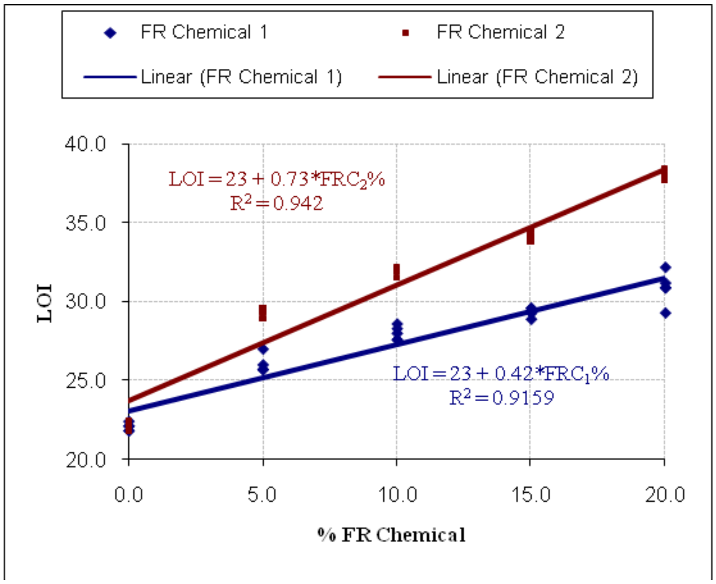


Figure 45 LOI vs % FR Chemical 1 and 2 Compared.

$$\boxed{LOI = 23 + 0.42 * FRChemical1\%}$$

Figure 46 LOI and FR Chemical 1 Relationship.

$$\boxed{LOI = 23 + 0.73 * FRChemical2\%}$$

Figure 47 LOI and FR Chemical 2 Relationship.

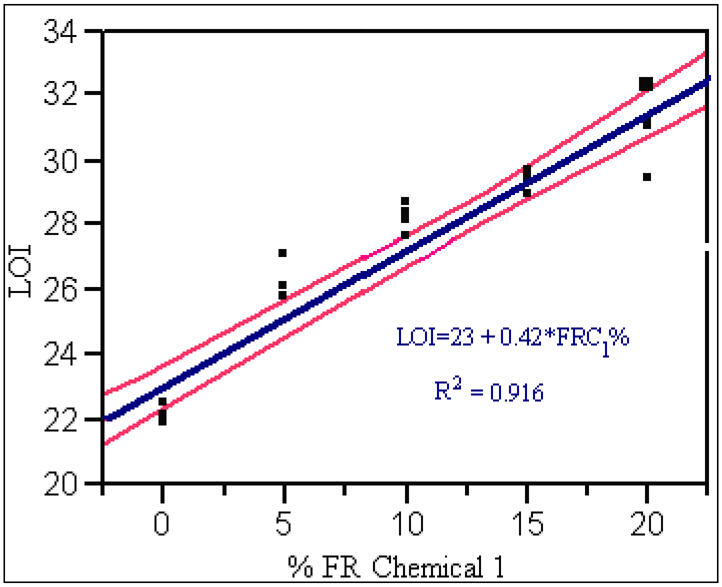


Figure 48 LOI vs % FR Chemical 1 with 95%Confidence Interval.

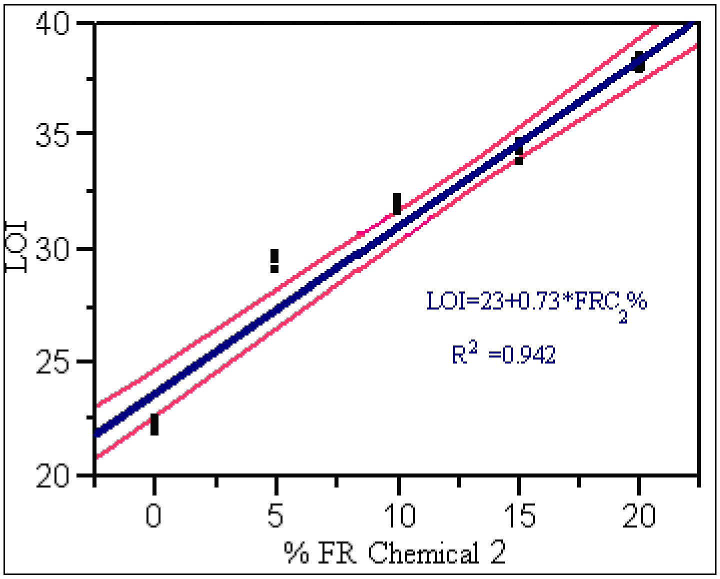


Figure 49 LOI vs % FR Chemical 2 with 95%Confidence Interval.

4.7.2 Small Open Flame Test

4.7.2.1 Burn Time

As seen from Table 18, Control (untreated pad) burnt in 3minutes, faster than all other samples. Flame spread over entire surface leaving behind 100% charred surface. FR fibers slowed down flame spread marginally, as in case of Combination II and I. Further incorporation of FR chemicals into the pad slowed down combustion and extinguished the flame before the flame could reach the periphery. It can be concluded that FR chemical treatment is required to extinguish the flame (within 6 minutes as specified for the test). None of the samples developed hole at the center, and hence passed the test using this criteria.

4.7.2.1 Pad Weight Loss

As seen from Figure 50, FR Chemical treated pads exhibited lower rate of weight loss compared to untreated ones. This is because chemicals promote char formation, thus hinder combustion, and ultimately extinguish the flame. Figure 51 was derived empirically to provide relation between weight loss and composition.

4.7.2.2 Charred area

As seen from Figure 52, in the absence of FR chemicals the charred area was 100%. After FR Chemical treatment charred area reduced. Charred area was substantially reduced when both FR fibers and FR chemicals are present in the pad. Figure 53 was derived empirically to provide relation between charred area (CA) and composition.

4.7.2.3 Base temperature

As seen from Figure 54, base temp rises to a peak and drops thereafter. Higher the FR content lower would be the peak value. In presence of FR chemicals the peak temperature drops in general, but not consistent, thus relation between the peak value and composition could not be derived easily.

Weight loss $\Delta W = (1-0.07Wp)*\{(0.50Wc+0.95Wb+0.45Wv)-0.50(W_1+1.2W_2)\}$

Wc = *% Cotton in pad*
Wb = *% Binder fiber in pad*
W1 = *% FR fiber1 in pad*
W2 = *% FR fiber2 in pad*
Wv = *% FR cellulosic in pad*
Wp = *% FR Chemicals in pad*

Figure 50 Weight loss and Composition Relationship.

Charred area $CA = Wc+Wb+W_1+W_2+Wv - 0.5Wp(0.83W_1+1.05W_2)$

Figure 51 Charred Area and Composition Relationship.

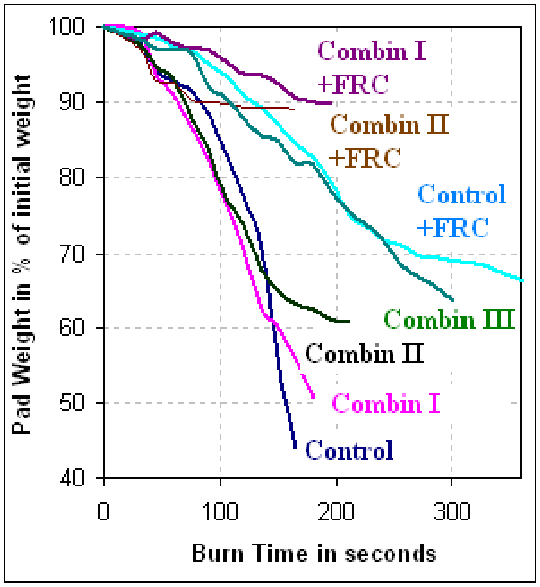


Figure 52 Pad Weight vs Burn Time.

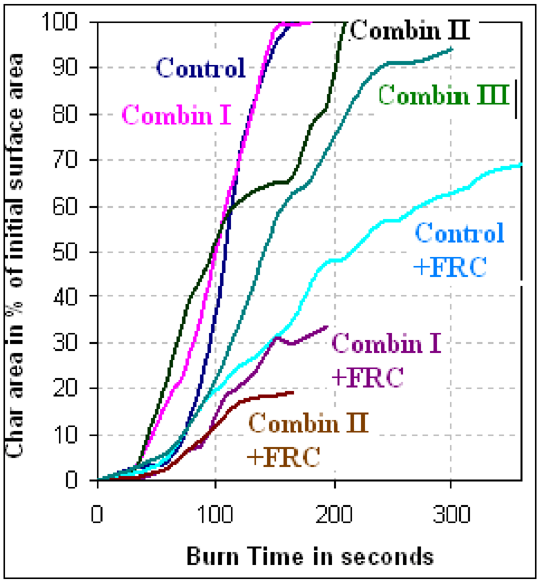


Figure 53 Char Area vs Burn Time.

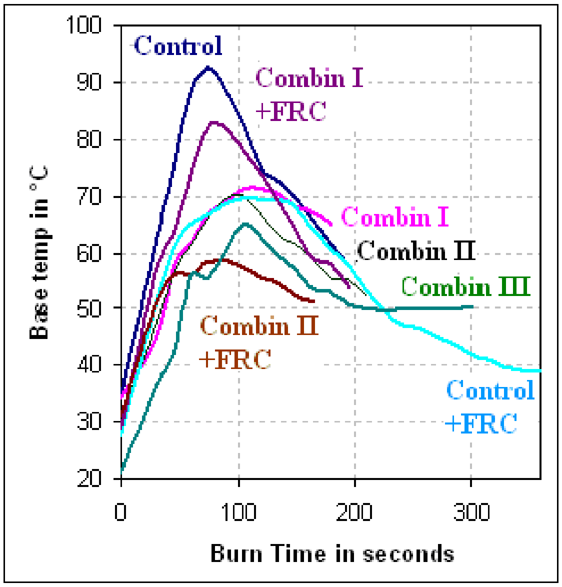


Figure 54 Base Temperature at the Center vs Burn Time.

4.8 Mechanism

FR Chemical treated Combination II&I have passed the LOI and Small Open Flame tests. The relevance of all four types of mechanisms (section 2.7) is discussed here.

Physical dilution: The FR fibers (cellulosic FR & synthetic FR) and chemicals present in the pad (FR chemical 2) act as a thermal sink, to bring down the fuel content and reduce thermal conductivity.

Inert gas dilution: The FR chemicals decompose to produce large volumes of noncombustible gases during combustion. These gases dilute the oxygen supply to the flame and dilute the fuel. FR chemical 2 dissociates to release ammonia (Figure 18 in section 2.7.3) that dilutes combustion mixture to slow down combustion. Even cellulose degradation releases water vapor (Figure 20 in section 2.7.4).

Thermal quenching**:** Pyrolysis of thermoplastic binder fibers and cellulose (Figure 20 to 6 in section 2.7.6) are endothermic reactions that result in thermal quenching.

Protective coatings**:** FR chemical 2 (Phosphorus compound) forms a protective char layer (Figure 22 in section 2.7.4) that acts as a barrier, and reduces the heat transfer from the flame to the combusting material. When flame is applied to the mattress pad, initially burning occurs where in fibers react with air or the oxidation reaction takes place, which is an exothermic reaction that favors propagation of combustion even after removal of the flame. In a minute or two, the pyrolysis (endothermic reaction) occurs. Later due to the FR phenomenon, temperature drops and slowly flame extinguishes. During combustion, the phosphorus is converted into phosphoric acid (as shown in Figure 18, Section 2.7.3), which extracts water from the degrading product producing char (as shown in Figure 19, Section 2.7.3) that shields the base material from burning. Evolving gaseous products of combustion swell up the char surrounded by molten polymer providing an Intumescent effect, slowing down combustion drastically.

Self-extinguishing FR Fibers present in the web, which do not melt or burn easily, provide structural integrity by reinforcing the char. Without self-extinguishing FR Fibers (as in case of FR chemical treated Control pad) the char would crumble and expose the fuel to air that favors propagation of flame and failed the test. Synthetic FR fiber 2 (silica) does withstand flame better than Synthetic FR fiber 1.

4.9 Cost Evaluation

The most important requirement is low cost, which is absolutely essential in manufacturing any product. We have developed FR mattress pads that pass the test and comply with the flammability regulations. Cost of the mattress pad was estimated based on the cost of FR fibers and FR chemicals (Table 19) relative to cotton (Relative cost of cotton =1, at cotton price $0.60 per lb). While procuring the fibers and chemicals the commercial price data was gathered from the supplier. In fact the samples were taken out of bulk package. In all calculations handling cost is not included and it is expected to be same for selected fiber.

By blending cotton with FR fibers (20% Cellulosic FR and 15% synthetic FR), the LOI value increases from 19 for cotton to 22 (Table 20) and cost of the product is $2.77 per lb with synthetic FR1 fiber vs. $1.77 per lb with synthetic FR2 fiber.

Flame retardancy is further improved by FR chemical treatment. LOI results (Table 21) indicate further increase in LOI from 22 to 38 as the chemical loading increased up to 20%. Moreover, the results show superior performance of FR chemical 2 compared to FR chemical 1. Generally LOI >28 is classified as FR, and LOI of ~32 is desirable for most of the mattress applications. Although unit cost of FR Chemical 2 ($1.94 per lb) costs more than FR chemical 1($1.30per lb), quantity needed to obtain LOI=32 is ~10% FR chemical 2, and add-on cost is $0.23 per lb of web. This cost is lower than ~20% FR chemical 1 with add-on cost $0.33 per lb of web to obtain the same LOI (=32).

Table 19 FR Fibers and Chemicals Relative Cost

	Relative cost		**Relative cost**
FR Fibers		**FR Chemicals**	
Aramids	18.92	Phosphorus compound	1.93
Acrylic (oxidized)	7.57	Boron compound	1.30
FR Cellulose	1.33	Citric acid	1.58
Ceramic	809.63	Magnesium compound	0.52
Glass	2.27	Urea	0.87
Melamine	12.11	**Others**	
PBI	136.20	Binder Fiber	1.25
PBO	98.37	Dispersant	31.48
PEEK	113.50	Bonding Chemical	19.17
FR Polyester	2.50		
Silica Fiber	5.00		

Table 20 Cost of Cotton -FR Pad

	Control	**Combination I**	**Combination II**
Relative Cost per lb	1.04	2.77	1.70
LOI	19	22	22
% Binder Fiber	15	15	15
% Cotton	85	50	50
% Cellulosic FR	0	20	20
% Synthetic FR 1*	0	15	0
% Synthetic FR 2*	0	0	15

** FR fiber1 is melamine fiber and FR fiber 2 is silica fiber.*

Table 21 FR Chemical Treatment Cost

	Control	**Set 1**	**Set 2**	**Set 3**	**Set 4**
% FR Chemical 1**	0	5	10	15	20
Add on relative cost $/lb	0	0.08	0.16	0.25	0.33
LOI	22	26	28	29	32
% FR Chemical 2**	0	5	10	15	20
Add on relative cost $/lb	0	0.11	0.23	0.34	0.46
LOI	22	29	32	34	38

*** FR chemical1 is Boron compound and FR chemical 2 is Phosphorus compound*

5.0 CONCLUSIONS

Commercially available cotton, cellulosic FR fiber, and synthetic FR fiber 1 and synthetic FR fiber 2 were chosen as a feedstock; these fibers along with low melt binder fiber in the desired proportion were processed in the card to obtain intimate blend of the fibers. Cotton, cellulosic FR fiber, synthetic FR fiber 1 (melamine) fiber, processed well in the card, and withstood repeated carding operations to achieve a uniform web. Whereas the synthetic FR fiber 2 (silica) was blending well to form the web, but found breaking into pieces losing about 10% of the fiber as fall out, and to compensate for this loss, extra fiber was added in the feed blend.

The carded webs achieved optimum thermo-bonding at the hot air temperature of 175°C and residence time of 3 minutes in the oven, and the product (pad) possessed sufficient strength for further handling. Analysis of the SEM picture of the pad after thermal bonding showed binder fiber integrating the web of fibers at the crossover points. Binder fibers show melting and bonding the adjacent fiber at the contacted surface. EDS graphs showed up presence of elements Al, Si, etc. corresponding to the constituent fibers.

Among the three bonding agents tried, Rhoplex worked the best for bonding FR chemicals. The chemical pick up or add-on was up to the desired level, and the treated product had soft feel. In order to incorporate the FR chemicals, the bonded pad was passed through a trough slowly to get sufficient residence time to imbibe chemicals into the fiber web and then passed through press rolls to squeeze out excess solution and cure-dried in the oven. The trough was filled with freshly prepared dispersion of FR chemicals in water containing a dispersant (Triton X-100), and bonding agent Rhoplex.

The SEM picture of FR chemical treated pad clearly showed the presence of constituent fibers, and additives adhering onto their surface, and there were no loose or unattached FR particles detected. EDS graph showed presence of Al, Si, P, etc. corresponding to the constituents. Presence of Boron in the pad is not detected since it is out of range of EDS.

The SEM picture obtained after the LOI burn test showed a reinforcing grid of self-extinguishing FR fibers undestroyed by the fire. These FR fibers supported the char formed out of cellulosic fibers. The char containing FR Chemical 2 exhibited improved structural integrity, whereas the char containing FR Chemical 1 was fluffy and loose. EDS graph showed presence of Al, Si, P, etc. corresponding to the constituents indicating that the FR additive residues are present in the char.

FR chemical treated pads exhibited higher tensile strength, at the same time elongation dropped to about 10%, which is acceptable for the application. Combination I exhibited highest tensile force. Combination II and III have similar strength but later one has higher elongation. This is because of lower degree of adhesion among fibers. In case of Combination III bonding was done after depositing FR chemicals onto fiber, hence adhesion is poor. After the FR chemical treatment basis weight of the pad increased by about 12%; and thickness reduced from 13 to 10mm, as expected. In case of Combination III pad thickness did not change, this indicates thickness reduces during cure-dry process.

Flame retardancy of the nonwoven showed a marginal improvement by blending cotton with FR fibers, as shown by increase in the LOI value from 19 for cotton to 22 for the blend (combination I or II). LOI further enhanced by incorporation of FR Chemicals. LOI results indicate superior performance of FR Chemical 2 compared to FR Chemical 1. Further, the mattress pad samples were subjected to Small open flame test, TB604. Only FR Chemical treated Combination II & I sample pads passed LOI as well as small open flame test. In these samples flame extinguished within test specified duration (6 minutes), developing char on the upper surface, and had about 10% (less than 25% required to pass the test) loss in weight due to the burn test. The char formed on the sample pad was intact with no voids or holes created by the fire. Other side of the sample did not char and had slight change in color.

Statistical analysis of LOI data obtained for various pad samples was used to develop FR models. Analysis showed a strong positive linear relationship with the concentration of FR chemicals present in the pad indicated by the regression coefficient $R^2 > 0.9$; p-value based on t-test $0.0001 < 0.05$ at 95% confidence level. FR Chemical 2 influences LOI more than FR Chemical 1 as shown by the increased slope of the line. Analysis of Small Open Flame test results showed that FR Chemical treated pads exhibited lower rate of weight loss compared to untreated ones and this is because FR chemicals promote char formation, thus hinder combustion, ultimately extinguished the flame. After FR Chemical treatment charred area reduced, and it was substantially when both FR fibers and FR chemicals were present in the pad. Empirical equation was developed to establish relation between weight loss and composition. Similarly another equation was developed to establish relation between charred area and pad composition.

The relevance of four types of mechanisms was observed in the FR Chemical treated Combination II&I samples which passed the LOI and Small Open Flame tests. Both cellulosic FR & synthetic FR and the FR chemical 2 present in the pad acted as a thermal sink, to bring down the fuel content and reduce thermal conductivity. The FR chemicals decompose to produce large volumes of noncombustible gases during combustion. FR chemical 2 dissociates to release ammonia that dilutes combustion mixture to slow down combustion. Even cellulose degradation releases water vapor. Pyrolysis of thermoplastic binder fibers and cellulose are endothermic reactions resulting in thermal quenching. FR chemical 2 (Phosphorus compound) forms a protective char layer that acts as a barrier, reduces the heat transfer from the flame to the combusting material, and as a result, the temperature drops and slowly flame extinguishes. During combustion FR chemical 2 is converted into phosphoric acid, which extracts water from the degrading product producing char that shields the base material from burning. Evolving gaseous products of combustion swell up the char surrounded by molten polymer providing an intumescent effect, slowing down combustion drastically. Self-extinguishing FR Fibers present in the web provide structural integrity by reinforcing the char. Without self-extinguishing FR Fibers (as in case of FR chemical treated control pad) the char would crumble and expose the fuel to air that favors propagation of flame and failed the test.

In the pad construction synthetic FR fiber 1 (silica) found to be cheaper than Synthetic FR fiber 2 (melamine) to obtain the same FR properties. Similarly FR chemical 2 (Phosphorus) found to be cheaper than FR chemical 1 (Boron) to obtain the same level of enhancement of FR properties to pass the flammability tests.

Finally, a cost effective recipe for constructing mattress pads that passes the latest flammability tests was developed. As planned, these nonwoven pads were produced by blending cotton with other commercially available fibers, binders, and followed by chemical treatments that take advantages of various synergistic effects to achieve maximum performance at low cost. The product of this research is a good candidate for mattress pads as well as other products such as upholstered furniture, mattress ticking, and pillows, which are required to comply with the open flame standards.

6.0 FUTURE DIRECTIONS

Focus of this research has been to develop cotton-based nonwoven mattress pads with FR properties by blending cotton with other commercially available fibers, binders; followed by chemical treatments to explore synergistic effects, and achieve enhanced FR performance, and offer a cost-effective recipe to meet the upcoming flammability standards. Future work is towards commercialization of product of this research product, which is good candidate for cotton-based products such as mattress pads, mattress ticking, upholstered furniture, and pillows, etc.

Recommendations:

1. Contact manufacturers who are interested in this research product.
2. Tailor the recipe that makes use of existing machinery and minimize buying expensive new machinery in the process.
3. Tune the recipe focusing on the most important requirement, low cost, which is absolutely essential in manufacturing any product.
4. Simultaneously develop recipes for more durable FR fabrics.
5. Develop recipes for fire protective garments in military applications.

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APPENDICES

APPENDIX 1

Abbreviations

ABS	Acrylonitrile butadiene styrene
APP	Ammonium polyphosphate
ATH	Aluminum trihydrate
FR	Flame retardant
HDPE	High density polyethylene
HDT	Heat distortion temperature
HIPS	High impact polystyrene
HRR	Heat release rate
LLDPE	Very low density polyethylene
MDH	Magnesium dihydrate
MPE	Melt processible elastomers
NHFR	Non-halogenated flame retardant
PA	Polyamide
PC	Polycarbonate
PE	Polyethylene
PE	Polyethylene
PET	Polyethylene terephthalate
PLS	Polymer layered silicate
PP	Polypropylene
PPA	Polymer performance additives
PPO	Polyphenylene oxide
PU	Polyurethane
PVC	Polyvinyl chloride
TPE	Thermoplastic elastomer
TPU	Thermoplastic polyurethane
UV	Ultra violet
XLPE	Cross linked polyethylene

APPENDIX 2

Limited Oxygen Index (LOI) Test Procedure

Scope: To determine the minimum concentration of oxygen in an oxygen/nitrogen mixture that will support a flaming combustion in a specimen according to ASTM D2863 is a method.

Test Procedure: The test sample is positioned vertically in a glass chimney, and an oxygen/nitrogen environment is established with a flow from the bottom of the chimney. The top edge of the test sample is ignited, and the oxygen concentration in the flow is decreased until the flame is no longer supported. For nonwoven pads the sample size is 150 mm long by 50 mm wide. Results for different materials should only be compared if the testing was done on samples of similar size.

Conditioning: Condition the samples in the laboratory conditions for 24hours which is 21°C ±1°C and 65% ± 10% relative humidity.

Steps

1. Cut the sample pad into 50mm x 150mm (2” x 6”) rectangular pieces.
2. Select an initial concentration of oxygen to be used. Try to ignite a test specimen in air, and note the burning behavior. If the specimen burns rapidly, select an initial concentration of about 18% oxygen; if the test specimen burns gently or unsteadily, select an initial oxygen concentration of about 21%; if the specimen does not continue to burn in air, select an initial concentration of at least 25%, depending upon the difficulty of ignition or the period of burning before extinguishing in air.
3. Record the oxygen concentration used as the volume percent measured by an oxygen analyzer according to the calibration chart.
4. Ensure that the test chimney is vertical. Verify that the temperature at the lower end of the chimney is in the range 21-25°C.

5. Mount a specimen vertically in the center of the chimney so that the top of the specimen is at least 100 mm below the open top of the chimney and the lowest exposed part of the specimen is at least 100 mm above the top of the gas distribution device at the base of the chimney.
6. Set the gas mixing and flow controls so that an oxygen/nitrogen mixture containing the desired concentration of oxygen, is flowing through the chimney at a rate 38 to 42mm/s. Let the gas flow purge the chimney for at least 30s prior to ignition of each specimen, and maintain the flow without change during ignition and combustion of each specimen.
7. For fiber pad specimen (Types II) use top surface ignition procedure
8. For top surface ignition, the igniter is used to initiate burning only on the top surface of the upper end of the specimen.
9. Apply the lowest visible part of the flame to the top of the specimen using a sweeping motion, if necessary, to cover the whole surface, but taking care not to maintain the flame against the vertical faces or edges of the specimen. Continue to apply the flame for up to 30s, removing it every 5s, just briefly, to observe whether or not the entire top surface of the specimen is burning on its own.
10. Consider the specimen to be ignited once the specimen is burning on its own.
11. Remove the igniter once the specimen is ignited.
12. Commence measurement of the period and distance of burning once the specimen is ignited.
13. Record the Burning Behavior of Individual Test Specimens: dripping, charring, erratic burning, glowing combustion, or after-glow etc.
14. If burning ceases, but spontaneous re-ignition occurs within 1s, continue the observation and measurements.
15. Mark X if flame continues, or mark O if extinguishes or fails to support the flame.
16. Extinguish the specimen, if necessary, by allowing only nitrogen to flow through the chimney.
17. Remove the specimen and clean, as necessary, any surfaces within the chimney or on the igniter that have become contaminated, for example with soot.

18. Allow the chimney to cool to laboratory temperature of 21 to 25°C, or replace it with another so conditioned one.
19. Install the next specimen. Select the oxygen concentration to be used for testing the next test specimen as follows:

    * Decrease the oxygen concentration if the burning behavior of the preceding specimen gave an "X" response.

    * Increase the oxygen concentration if the preceding specimen gave an "O" response.
20. Repeat until LOI values narrow down to 1 unit range for consecutively 5 specimen

Note: Oxygen Index, in percent, is calculated from the final oxygen concentrations tested. The test results relate only to the behavior of the test specimens under the conditions of this test method and the results must not be used to infer the fire hazards of the material in other forms or under other fire conditions.

APPENDIX 3

Small Open Flame Test (TB604) Procedure

(For Mattress Pads, Option A)

Conditioning: Remove the samples from the covers for conditioning. Condition the samples in the laboratory conditions for 24hours which is 21°C ±1°C and 65% ± 10% relative humidity.

1. Cut the sample pad into 305mm x 305mm (12” x 12”) piece, weigh, and record.
2. Place thickness-measuring plate over the sample, measure the thickness, record.
3. Cut four 305mm x 305mm pieces of standard sheeting fabric.
4. Place two sheets of the fabric horizontally on the test platform. Fully smooth out the sheets such that there are no folds or air gaps in between or under the sheets. Place the sample piece on top of the fabrics.
5. Place two sheets of the fabric on top of the sample piece.
6. Place the top square metal frame over the top sheeting.
7. Mark the center point on the top sheeting.
8. Turn on the video recording
9. Subject the top surface of the test specimen to a 35mm high butane gas flame oriented at 30° with respect to horizontal line. Place the tip of the burner at the center of the top surface for 20s, and then remove the flame.
10. Continue the test until all traces of flaming and smoldering have ceased.
11. Record observations regarding penetration of the flame through the specimen.

PASS/FAIL Criteria

The specimen fails to meet standard if either of the following conditions is reached:

1. The flame burns through the bottom sheet fabric and creates a void in the sheet.
2. The flame creates a void of greater than 51 mm (2”) in any direction in the pad material.

TEST REPORT

- Name and address of the test laboratory
- Date and time
- Operators names
- Test material ID and details (Thickness, weight)
- Any changes in the test method
- Behavior of the specimen in response to the application of the burner:
    1. Extended smoldering combustion
    2. Penetration of the flame through the pad and bottom fabric sheet.
- Record void size in pad and bottom fabric sheet.
- Remove the pad after test and weigh, calculate % weight loss.

State Results PASS or FAIL

APPENDIX 4

Fibrous Raw Material Suppliers for Mattresses

Advance Fiber Tech. Corp.
Atlanta Attachment Company
Atlantic Thread & Supply Co., Inc.
Basofil Solutions
Big Sky Bedding Consulting
Brookwood Companies Inc.
Coats North America
Freudenberg Nonwovens
Glo Tex International, Inc.
Intertek Testing Services N.A., Inc.
Jones Fiber Products, Inc.
Leggett & Platt Fiber Division
Milliken & Company
Performance Fabric & Fibers
Sateri, Inc.
SGS Consumer Testing
Springs Global U.S., Inc.
SSM Industries, Inc.
The Felters Group
The Warm Company
Tietex International
Vita Nonwovens
Western Nonwovens, Inc.
Wm. T. Burnett & Co.

APPENDIX 5

SEM Pictures of Fibers

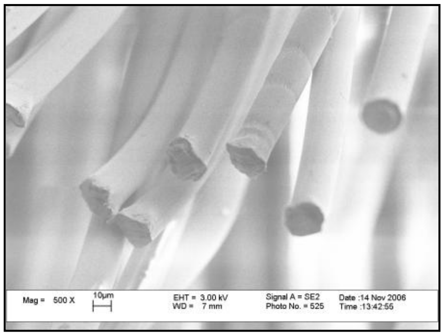


Figure A5.1 Binder Fibers

At magnification 500

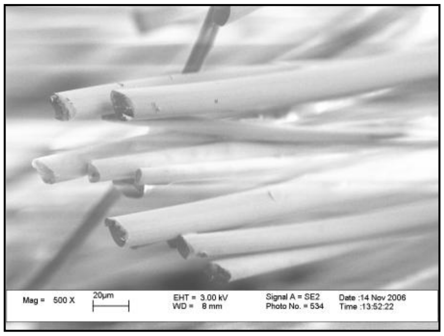


Figure A5.3 Melamine Fibers

At magnification 500

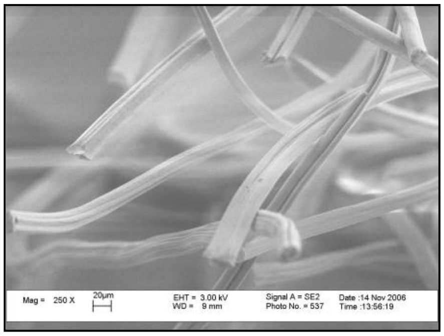


Figure A5.2 Cellulosic FR Fibers

At Magnification 250

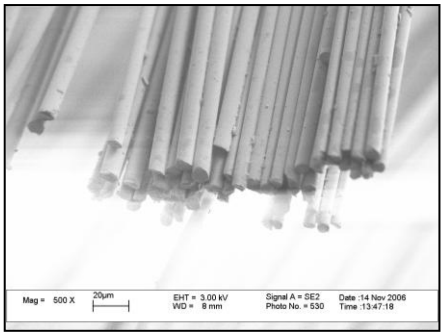


Figure A5.4 Silica Fibers

At magnification 500

APPENDIX 6

SEM Pictures of Nonwoven Pads

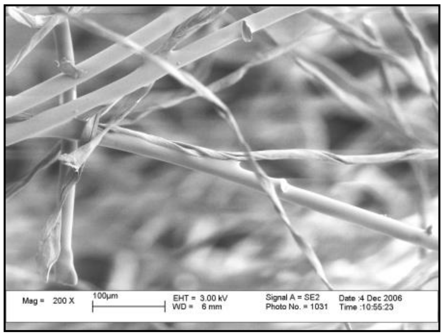


Figure A6.1 Bonded at 160°C

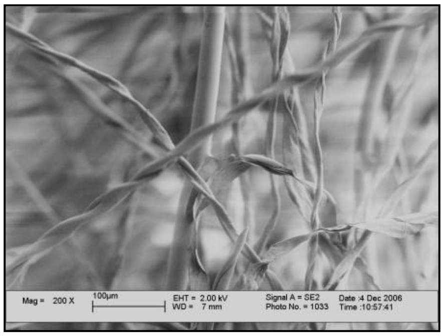


Figure A6.2 Bonded at 165 °C

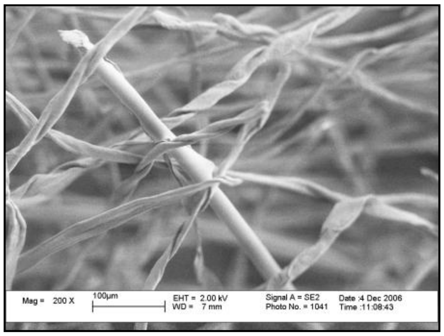


Figure A6.3 Bonded at 170 °C

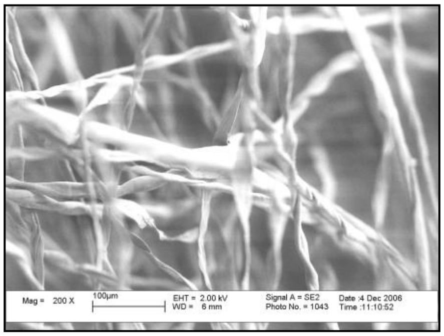


Figure A6.4 Bonded at 175 °C

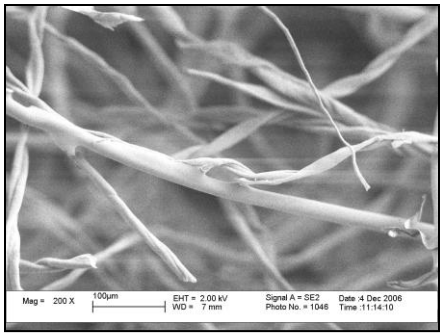


Figure A6.5 Bonded at 180 °C

APPENDIX 7

EDS Graphs of Nonwoven Pads

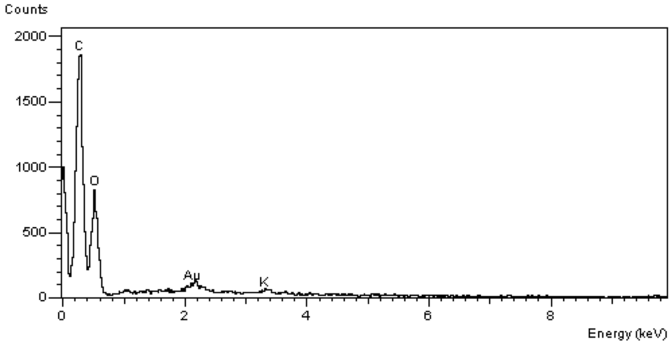


Figure A7.1 Cotton+Binder Pad (Control)

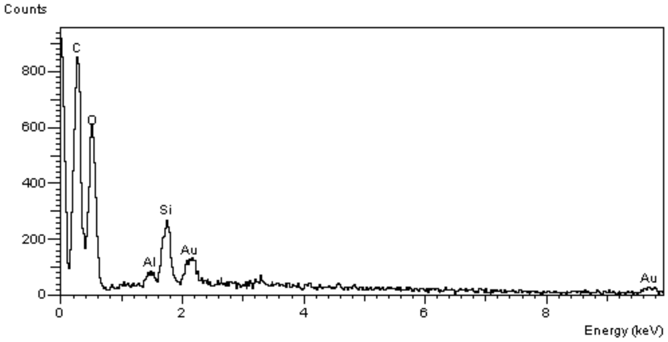


Figure A7.2 Cotton+Binder+Cellulosic FR +Synthetic FR1 Pad (Combination I)

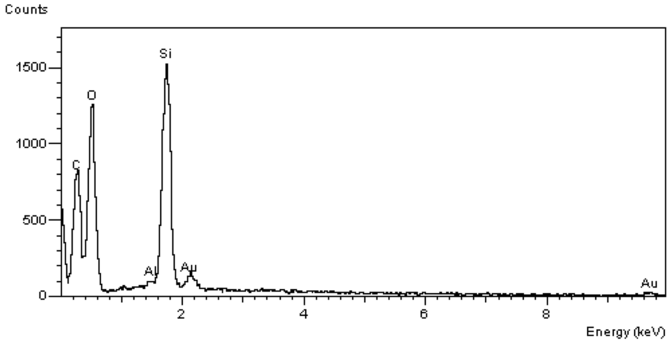


Figure A7.3 Cotton+Binder +Cellulosic FR +Synthetic FR2 Pad (Combination II)

APPENDIX 8

SEM Pictures of FR Treated Pads

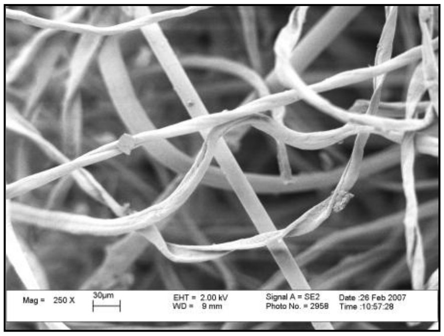


Figure A8.1 Combination I with FR Chemical 2 at Magn.250

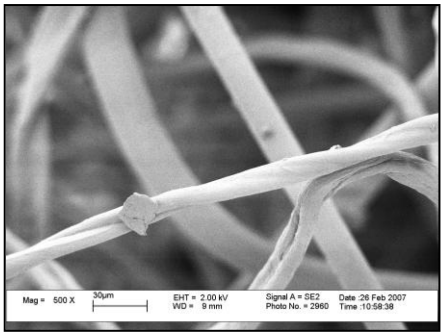


Figure A8.2 Combination I with FR Chemical 2 at Magn.500

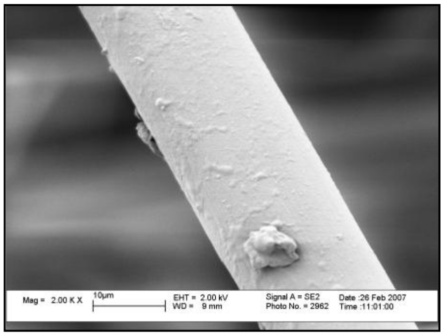


Figure A8.3 Combination I with FR Chemical 2 at Magn.2000

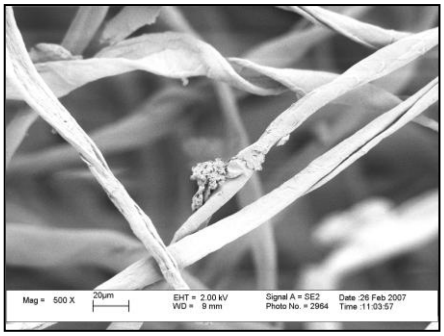


Figure A8.4 Control with FR Chemicals 2 at Magn.250

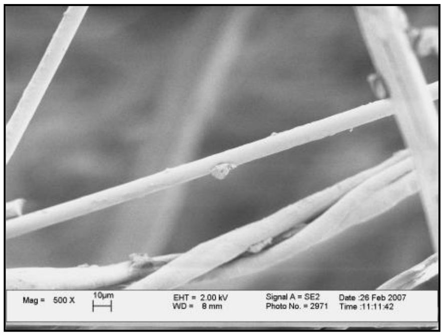


Figure A8.5 Combination II with FR Chemical 2 at Magn.500

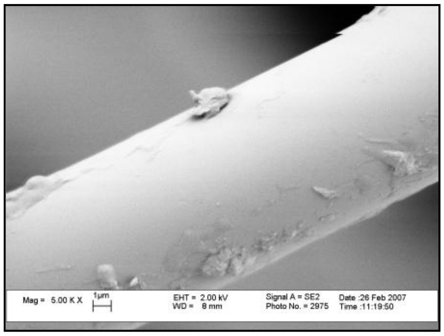


Figure A8.6 Combination II with FR Chemical 2 at Magn.5000

APPENDIX 9

EDS Graph of FR Treated Pads

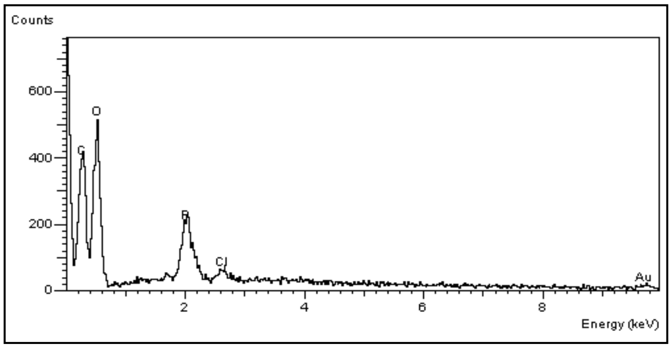


Figure A9.1 Cotton-Binder Control Pad with FR Chemicals 2 (*P*)

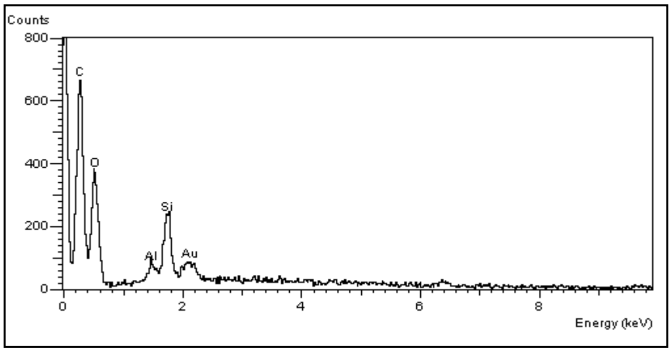


Figure A9.2 Cotton+Binder+Cellulosic FR+Synthetic FR1 Pad (Combination I) with FR Chemicals 3 (Nano clay)

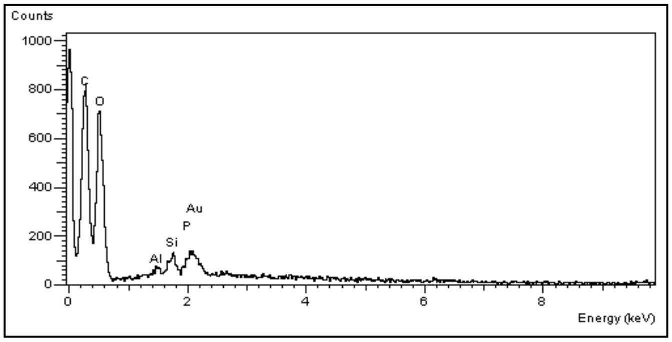


Figure A9.3 Cotton+Binder with FR Chemicals1,2,3

APPENDIX 10

SEM Pictures of Char

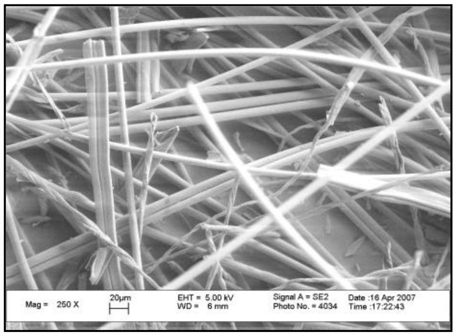


Figure A10.1 Char of Cotton and Cellulosic FR & Synthetic FR2

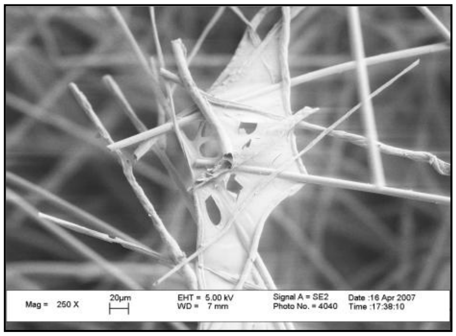


Figure A10.4 Char of CombinationII and FR Chemicals 1,2

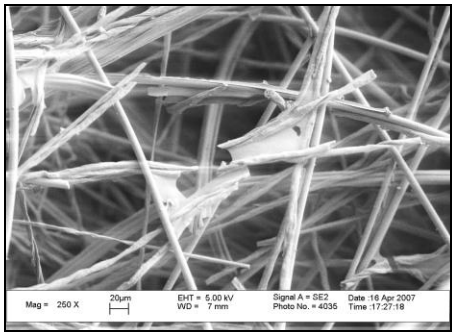


Figure A10.2 Char of Combination II

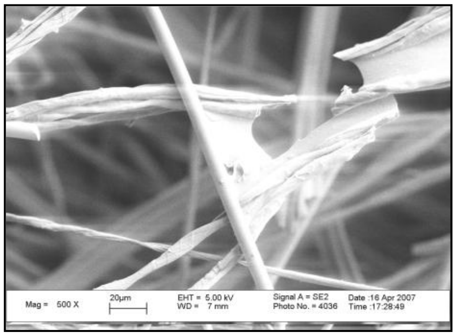


Figure A10.5 is Figure 2 at Magnification 500

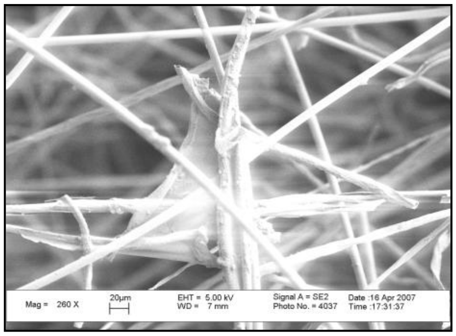


Figure A10.3 Char of Combination II and FR Chemicals 2

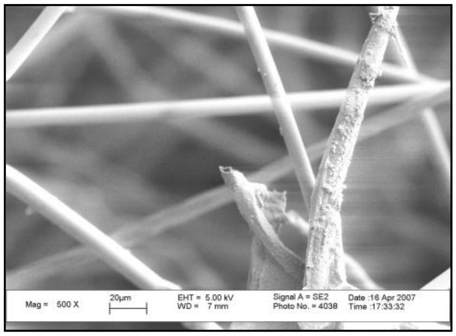


Figure A10.6 is Figure 3 at Magnification 500

APPENDIX 11

EDS Graph of Char

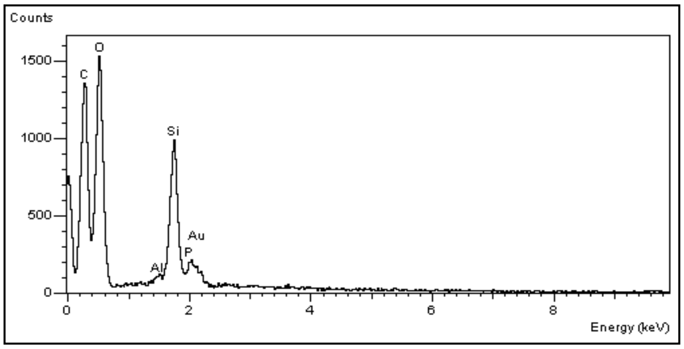


Figure A11.1 Combination II Char with
P from FR chemicals 2, Si from Synthetic FR2

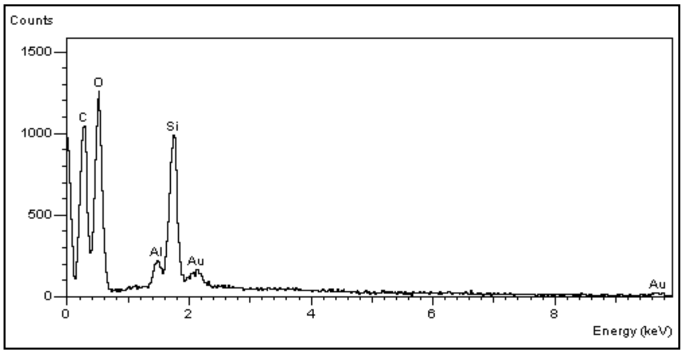


Figure A11.2 Combination II Char with Al from
FR Chemicals 3 (Nanoclay), Si from Synthetic FR2

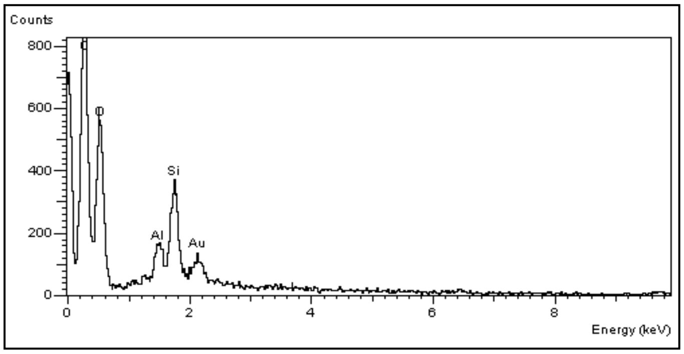
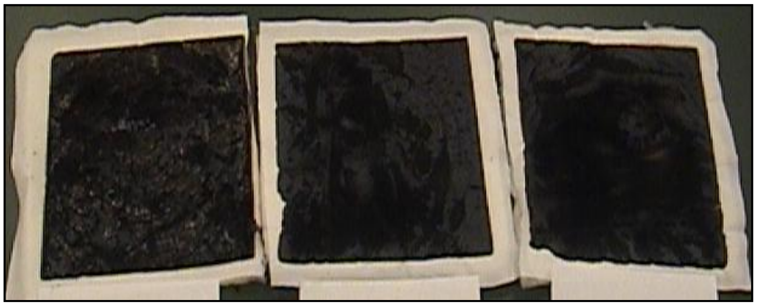


Figure A11.3 Combination I Char with Al from FR
Chemicals3, Si from cellulosic FR

APPENDIX 12

Pad Pictures after TB604 Test

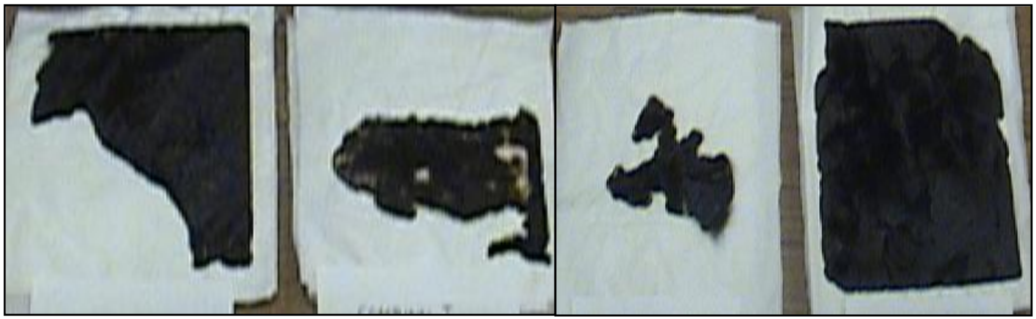


Control Combination I Combination II

Fig A12.1 Fireside

Control Combination I Combination II

Fig A12.2 Back



Control Combination I Combination II Combination III

A12.3 After Incorporating FR chemicals

VITA

Manjeshwar Ganesha Kamath was born in India. He went to Karnataka Regional Engineering College (also known as National Institute of Technology, Karnataka), India and graduated in 1978 with B.S. in Chemical Engineering. He worked in polymer industries in India as well as USA. He migrated to USA in 1996, obtained Professional Engineer License of State of Tennessee in 2000. He joined the University of Tennessee at Knoxville in 2003 and, graduated in 2004 with M.S. in Polymer Engineering.

He has more than 25 years of industrial experience in developing extrusion grade synthetic polymers, specialty fibers, filament yarn, film, bottles, bicomponent fiber, flame retardant fiber, low melt binders, and cotton based nonwoven pads for mattresses. He has also published about 5 book chapters, 5 posters and 20 papers on fibers, polymers, and nonwovens in the recent seven years. Moreover he authored dozens of proprietary technical papers while doing research activities in the industries. Presently employed at Ticona (Celanese) Polymers, Shelby, North Carolina, and concurrently enrolled in Ph.D. program at the University of Tennessee, Knoxville.

He wrote this thesis and graduated in Summer 2009.