STUDIES ON FIRE RETARDANT MILITARY UNIFORMS

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Abstract—Military sector is one of the most textile demanding sector with various special and critical requirements. Application of Nonwovens in the field of Flame Retardancy (FR) Uniforms will not only be cost effective but also can be produced at higher production speeds compared to conventional woven technology. In battlefield solider are exposed to flame threats and thermal radiative, thus it gives need to the use of FR Uniforms in the Military Sector. The following paper discusses the current commercially available FR Military Uniforms and material which it is made of, fibers available for forming FR Military Uniforms and Special FR Finishes for Fire Retardancy of the fabric.

Keywords— Fire Retardancy, FR's, Nonwoven, FR Finishes, Military Uniforms

I. INTRODUCTION

Military is one of the most textile material consuming sector with the most special and critical requirements. Since the army or military forces are subjected to various unpredictable environments at very short notice, the general requirements for military protective textiles are critical and diverse. While the most important requirement of military is to keep the armed forces personnel safe, textiles used in military applications are required to fulfil certain environmental, physical, camouflage and fire-resistant characteristics.^[1] Nonwoven composite fabric has emerged as one of the fastest and economical way of fabric manufacturing. Until now, use of nonwoven composite fabrics in military sector was restricted to niche and special applications, such as shoe interlinings and disposable apparel, due to limitations in its performance. The Fire Resistant (FR) military garments made using FR nonwoven composites have the potential to offer relief from heat stress combined with better economics and higher production speeds. However, there is a need of functional garments with specialty properties and special attributes in the military. The functional properties of current conventional woven uniforms are limited or fixed by the properties of the individual yarns which lie in the twodimensional plane of the fabric or garment. The threedimensional, nonwoven composite fabric offers plenty of possibilities of utilizing various fibers and fiber blends in multiple layers or webs with additive special chemical technologies to impart specific functional characteristics for the intended use. The main utilization of the fire-resistant composite nonwoven garment is to replace the conventional fire-resistant garments made out of very expensive woven fabrics.^[2]

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II. FIRE HAZARDS AND INJURIES IN MILITARY

Thermal radiative and flame threats are hazards that soldiers are frequently exposed to on the battlefield. Air force personnel experience when under attack in aircraft at high altitude or aboard helicopters closer to the ground level altitude where a they encounter particularly hazardous environment in a confined place such as a cockpit. Navy personnel experience when they are subjected to missile attacks in the confinements of the vessel. Military personnel face difficulty in escaping from the aircraft like helicopters and jets flying at high altitudes. In addition to missile attacks, aircraft fire hazards include take off, in-flight, refilling of fuel, landing, and post-crash fires. Post-crash fires from ruptured fuel tanks of damaged aircrafts are also common in aviation environments. Moreover, military aviation fires are fiercer than those encountered in civil aviation, mainly because fuels used for military applications have specifically formulated compositions to meet specific functional and operational needs. The navy submarine environment particularly is a hazardous problem within the navy as vessel safety relies only on a closed cycle air purification system. Once fire breaks out, smoke and toxic fumes may overwhelm the air purification system resulting in fatalities due to inhalation of smoke and toxic gases. This hazard is aggregated by the clothing and textiles in bulk storage. Crew clothing ignition plays a very key role as a major problem inside the submarine since the fire can spread very quickly in an enclosed compartment. A statistical analysis was carried out on the burns sustained in combat explosions in the war in Afghanistan and Iraq (April 2003-April 2005) by USA, revealed that burn injuries are still a persistent threat in military combat environment.[1][2][10]

III. EXISITNG FR MILITARY UNIFORMS

Flame retardant clothing have been available since early in the Second World War. Flame retardant treatments available during this period were only non-durable or temporary treatments using various combinations of ammonium salts of sulphuric, phosphoric acids or hydrochloric to impart flame resistance on woven cotton fabrics mainly. Synthetic flameresistant fibres were developed from 1950s onwards and high-performance FR fabrics comprising inherently FR fibres such as the para- and meta-aramids, semi carbon (oxidised acrylic), polybenzimidazole (PBI), and phenolic (novaloid) appeared from 1960 onwards. There are two major flame

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retardant treatments which are widely used for cotton fiber viz. Proban (Rhodia, formerly Albright and Wilson) and Pyrovatex (Ciba). Proban forms an insoluble polymer in the fiber voids and the interstices of the cotton yarn that is mechanically held in the cellulose fibres and yarns. Pyrovatex process chemically bonds the FR substance to the cellulose fibre. The Proban process uses phosphorus containing tetrakis (hydroxymethyl) phosphonium chloride (THPC) which is further reacted with urea. The product of this reaction is further padded onto cotton fabric and dried. The fabric is then reacted with ammonia in a chamber and finally oxidised with hydrogen peroxide. Pyrovatex process involves application of FR with a crosslinked resin and curing of the fabric at high temperature of 160^oC. Some of the commercial FR materials used in military clothing are as follows: ^{[2][3]}

- 1. Durable FR treatments for 100% cotton^{[2][3]}
- $Proban^{\mathbb{R}[2][3]}$

Proban finished fabrics are known to retain their FR properties for the lifetime of the garment. Fabrics acquire their FR properties from the polymer which is embedded in the fabric through finishing process, which can be only removed using powerful oxidising agents. When exposed to flame, Proban fabrics form an insulating char which stays in place and helps in protecting the wearer. These fabrics have no afterglow, do not smoulder, do not melt and the flame does not spread outside the charred area.

• Indura^{®[2][3]}

Indura[®] is also a Proban processed 100% cotton. Such exceptionally flame retardant phosphonium finished cotton fabrics have been used for NASA flight uniforms which were used in enhanced oxygen atmospheres.

• Antiflame^{®[2][3]}

This is a Pyrovatex processed 100% cotton. The fabric is treated with dialkylphosphonamide flame retardant followed by curing(heat). Chemically bonded flame retardant or Pyrovatex process guarantees flame retardancy for an infinite number of wash cycles as long as the wash and care instructions are followed.

2. Durable FR cotton blends^{[2][3]}

BDU Uniforms (nylon/cotton (50/50))^{[2][3]}

Use of a commercial melamine-formaldehyde product with a trimethylolmelamine in combination with a commercial product Fyroltex HP (Akzo) based on oligomeric phosphate-phosphinate species which imparts high levels of flame retarding performance and laundering durability in the fabric.

Indura Ultra Soft[®](75% cotton/25% nylon warp and a 100% cotton weft)^{[2][3]}

The fabrics are finished with the ammonia curing process and are designed to provide guaranteed flame resistance for the life and increased abrasion resistance of the garment. On expose to thermal flux the nylon blend is completely absorbed by the majority of cotton fibre. Therefore, nylon does not flow or lead to skin contact.

• Valzon[®] (60% FR acrylic fibre and 40% cotton)^{[2][3]}

The FR acrylic fibre is treated with a FR during the fibreforming process. The cotton is not treated for FR but derives its selfextinguishing characteristics in the presence of FR acrylic fibre.

3. Inherently FR synthetic materials^{[2][3]}

- Nomex[®] (Du Pont) and its blends^{[2][3]}
- Nomex[®] is an inherently FR fiber having a meta-aramid chemistry and is predominantly used in military clothing systems to provide protection from flame and intense heat. Nomex has good thermal stability and does not melt with the fiber decomposing between 370-430^oC. When exposed to high heat fluxes, Nomex fiber consolidates and thickens therefore preventing exposure of skin to the incident heat flux and hence preventing second- and third-degree skin burns. Commercial blends of Nomex[®] available for FR fabric are 93% Nomex, 5% Kevlar, and 2% static dissipative fiber, 35% Nomex/65% FR viscose and many more,

Kermel[®] and its blends^{[2][3]}

100% Kermel[®] fabric made from long staple fibres is particularly suitable for the outer layers of multi-layered outfits. The fabric does not melt or burn and maintains its chemical characteristics. For these reasons FR fabric made from Kermel[®] fibre blends is suitable for general combat uniforms in military sector. Due to its intrinsic softness and suppleness , Kermel[®] fibre allows the manufacturing of high-quality fire resistant knits contributing to improved protection against fire hazards. Commercial blends available of FR Kermel[®] fiber are VMC40 (40% kermel, 60% FR viscose), 50% Kermel and 50% flame retardant viscose, 70%. Kermel V70 (70% Kermel: 30% FR viscose).

IV. FIBERS USED IN FR NONWOVENS

Manufacturers of nonwoven products can make fabric out of almost any kind of fibers including traditional textile fibers, as well as newer high performance fibers. The selection of fibers depends on customer requirement, processability, cost, and changes of properties because of consolidation and web formation, and determines the properties of the final nonwoven products. The fibers can be used in the form of staple fiber, filament or even yarn. The fibers used include textile fibers such as polyolefin (PP/PE), polyester, cotton, rayon, nylon, wool, lyocell, modacrylic; and advanced fibers, such as aramid (Nomex ® /Kevlar ®) ; conductive nylon; melamine (heat and fl ame resistant); bi-components (sideby-side, sheath-core, segmented pie, and islands-in-thesea);hollow fibers; Spandex ® fibers: fusible co-PET fiber; nylon 6 support/matrix fiber; chlorofiber; antibacterial fiber; stainless steel; glass micro-fiber; rubber thread: poly(tetrafluoroethylene) (PTFE); and electro spun polymeric nanofibers. Some of the fibers which can be used in composite nonwoven military uniform are: [4][5]

1. Cotton^{[4][5]}

Cotton fiber was used extensively during the early development period of spunlace or nonwoven industry. The first method was bonding the short cotton fibers with resin and latex. Cotton fiber has physical properties like fiber length, resilience and strength which is important particularly to its process-ability. For example, long cotton fiber is suitable for producing nonwovens. The fiber has excellent absorbency and feels comfortable for the skin. The dry and wet strengths are good. Resilience recovery and Dimensional stability are moderate. Due to its excellent comfort properties cotton is used as a blend with FR Nylon 6, FR Nylon 6.6, FR Viscose to achieve Fire Retardancy.

2. *Fire Retardant Viscose*^{[4][5][6]}

A FR viscose fiber is formed by applying a phosphazene derivative, hexaphenoxycyclotriphosphazene (HPTP), to viscose spinning solution. Due to the existence of hydrogen bonds, the orientation of cellulose is accompanied by the orientation of APG molecules and HPTP, which produced villous structure inside the fiber. It can be concluded that the FR agent is compatibly integrated into cellulose. LOI of the FR viscose fiber was significantly increased with the increase of HPTP concentration. As viscose fibers containing 16 % HPTP can achieve an LOI value of 28.6 % (27.5 % after 30 washes, which suggests durable FR), they can survive more than 3 ignitions. The degradation of HPTP made the decomposition of cellulose accelerated. Primary decomposition was moved up by about 20 °C, while secondary decomposition was delayed by around 46 °C. This causes more char content being formed and less weight loss. It is used in blends with other fibers.

3. Polyester^{[4][5]}

They are easily produced from petrochemical sources, inexpensive, and have a desirable range of physical properties. They are lightweight, strong, wrinkle resistant and easily dyeable, and have very good wash wear properties. The FR nonwoven apparel fabric developed by The USA Marine Crops was made at experimental stage using staple polyester with FR Nylon 6, FR Nylon 6.6 and FR Viscose Rayon.

4. FR Nylon 6 and 6.6^{[4][5][7]}

Generally, phosphorus-based compounds are added during the polymerization stage to achieve FR nylon fibers. Magnesium oxide and Red phosphorus addition during the polymerization stage of nylon 6 polymer gives a fiber with good FR and an LOI of 28.5%. The FR additive for addition at the spinning dope stage has to be stable at the melt spinning temperature, so the choice of chemicals becomes limited. The use of a complex compound of an antimony and alkyl phosphonic acid at the spinning dope stage gives FR nylon fiber having an LOI of 29-30%. The addition of chlorinated polyethylene and zinc molybdate in the spinning dope was also found effective. An interesting effect is seen when a brominated pentaerythritol, boric acid, and antimony trioxide combination was added in a spinning dope of nylon 6; the resultant flame-retardant fiber had

an LOI of 29%, but if any of the compound was not added, the LOI was reduced to 25-26%. The high thermal stability required for the flame-retardant additives may be dispensed with using surface finishing, which is supposed to be a more convenient and easier method. In this method, the choice of chemicals becomes wide. The treatment with thiourea-based condensation products is very popular for flame retardancy of nylon effective fabric. The other method is hydroxymethylation of nylon fabric with formaldehyde, followed by treatment with pyrovatex CP. It gives an excellent flame retardancy to nylon and an LOI of 31.4%.

5. Polyamide^{[4][5]}

Synthetic man-made fibers account for the largest part of the raw material used in manufacturing of nonwoven bonded fabrics. Polyamide fibers are the oldest ones that are used in production, and they also increase the serviceability of the product. This improved quality is of importance for various purposes where nonwoven bonded fabrics are subjected to frequent folding as in the case of paper reinforced with synthetic fibers, and where they are subjected to exceptional resistance to abrasion, as is the case with needled floor coverings. The most important values for the physical properties of normal spun polyamide fibers, degrees of luster ,which covers various fiber thickness, and cross-sectional forms. Polyamide fibers are used in blends with other fibers to form FR Nonwoven Fabric.

V. TYPES OF FLAME RETARDANTS FOR NONWOVENS

The mechanism of flame propagation is quite complex, there are various approaches to control it. Accordingly, this opens to a wide choice of materials that can help prevent the start or growth of the burning process in any nonwoven. The choice of the right material depends on the fabric construction and composition as well as the performance requirements in the end application. Since the different FRs may require diverse application methods, and the cost and performance will vary, these also determine their suitability for a specific application and particular product. There are various types of FR's for Nonwovens which are discussed below. ^{[8][9]}

1. Additive and Reactive FR's^{[8][9]}

FR's can be incorporated in the polymer matrix or, in textiles, can be applied onto the material. FR'sthat can be mixed with polymer are called additive and those added by reaction are called reactive FR's. Reactive FR additives form a chemical bond and cannot migrate from the polymer matrix applied on. They are more expensive than additive FR's and their application is particularly used in duroplastics such as polyurethanes and polyesters. Additive FRs can be introduced during polymer forming stage or later. Since these are not chemically bond to polymer, they can be released easily from the polymer matrix. These additives are mainly used in thermoplastics.

2. Inorganic FR 's^{[8][9]}

Some of the most commonly used inorganic FRs include antimony trioxide, aluminum trihydroxide (ATH) and magnesium hydroxide. ATH decomposes at 200°C to aluminum oxide and water. The water becomes a barrier for the flame and prevents the flame from reaching the textile or material surface. It slows the burning by absorbing heat. Magnesium hydroxide can be used for higher processing temperatures because it does not decompose until around 300 °C. Its function in FRs has the same mechanism as that of aluminum trihydroxide (ATH). Calcium carbonate is also used in some applications and on heating is likely to release CO_2 (carbon dioxide), which prevents flame propagation.

3. Halogenated FR's^{[8][9]}

Halogenated FRs are generally divided into two groups, brominated and chlorinated FR's. These compounds are active in the gas phase where they remove hydroxyl radicals and hydrogen. These radicals interfere with the burning process of the material which produces flammable gases. They can reduce the concentration of fire as well as terminate fire. At high temperatures these FR compounds release Chlorine or Bromine which react with combustible gases to give HCl or HBr; they, in turn, remove hydroxyl and hydrogen by reacting with these radicals to produce water. Brominated FR's are usually 50-85% bromine with different properties and are applied as FR coatings on the material. Disadvantages of these halogenated FR compounds are that they produce corrosive gases such as HBr, HCl and emits high levels of fume. Even though they are less expensive and effective, they are considered as environmentally hazardous chemicals. Today non-halogen FR's system are favoured by industrialists and researchers. The most widely used halogenated FRs are chlorinated paraffins hexabromocyclododecane (HBCO), tetrabromobisphenol (TBBPA), polybrominated diphenylethers (PBDEs), and brominated polystyrene.

4. Phosphorous compound FR's^{[8][9]}

These FR's include both organic and inorganic compounds and act primarily in the solid phase and during heating. They produce phosphoric acid which further reacts with the substrate to form a char, forming a carbon layer. In so doing these compounds prevent further supply of flammable gases and oxygen and hence make the progression of flames difficult. Phosphorous compounds are used as halogen-free alternatives and have shown great market acceptance and their further development is very promising. Some of the most important phosphorous compounds are phosphinates and phosphanates used in flexible PU foams for building and automotive applications, phosphate esters commonly used in engineering plastics, red phosphorous ismainly preferred in PA6 and PA6.6 applications, and ammonium polyphosphate one of the most commonly used FRs in textiles.

5. Nitrogen-based FR's^{[8][9]}

Nitrogen-based FRs have various effects on flame. In the condensed phase they form a cross-linked structure by transformation of melamine which inhibits formation of

combustible gases. In the gas phase, they release ammonia or gaseous nitrogen, which acts to dilute flammable gases and thus reduce flame. Nitrogen-based compounds act in synergy with phosphorous based FR's and most of them are based on melamine compounds.

6. Intumescent Coatings^{[8][9]}

Intumescent materials provide a thick fire protection layer by a decomposition process at high temperatures, which causes the material to swell into a thermally stable char layer. The majority of intumescent coatings use ammonium phosphate, zinc borate, organic esters and melamine phosphate as the acid source. Blowing agents are generally nitrogen compounds such as guanidine, urea and melamine. Intumescent coating systems are mostly based on ammonium polyphosphate (acid source) melamine and its derivatives (as blowing agent) and pentaerythritol derivatives are often used as char forming agents. A good intumescent system can expand up to 50 to 200 times the original thickness. Intumescent coatings are effective in reducing heat release rate and flame propagation and thus preventing combustion. As an insulator, the foam layer prevents heat transfer to the polymer and mass transfer from the polymer to the flame. The disadvantages of intumescent systems can be summarized as: poor durability, poor bonding with substrate and aesthetic features, rapid aging, and low resistance to erosion and wear.

VI. CONCLUSION

Inherently Fire Retardant fibers have been used for very long time in the FR Sector, many of them are still expensive. There is a continuous effort to produce less expensive FR fabrics, so that many products can be made out of it at a more affordable price. There will be continuing efforts in the direction of FR fabrics with a different chemistry will be produced to accomplish this goal. Nonwovens because of its higher productions speeds, cost effectiveness and properties have tremendous potential to capture the apparel industry. Nonwovens is and will definitely emerge as a sunrise industry in the near future.

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