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IMPROVING THE FLAME RETARDANT PROPERTIES OF COTTON FABRICS WITH BORON COMPOUNDS

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ABSTRACT

Cotton is an important raw material for the world and Turkish textile sector. The flame-retardant properties of cotton fabrics are rather weak and need to be improved. Boron compounds are intended to be used to improve these properties of cotton fabrics. In this review, flame retardant materials containing boron compounds and their usability in textiles are investigated and summarized.

Keywords: flame retardant, cotton, boron, boric acid

ÖZET

Pamuk, dünya ve Türk tekstil sektörü için önemli bir hammaddedir. Pamuklu kumaşların güç tutuşurluk (alev geciktirici) özellikleri oldukça zayıftır ve geliştirilmesi gerekmektedir. Bor bileşiklerinin pamuklu kumaşların bu özelliklerini geliştirmek için kullanılması amaçlanmıştır. Bu derleme çalışmada, bor bileşiklerini içeren güç tutuşur malzemeler ve bunların tekstilde kullanılabilirliği araştırılmış ve incelenmiştir.

Keywords: Güç tutuşurluk, pamuk, bor, borik asit

1. INTRODUCTION

Textile is the most important material in our daily life. Along with the rapid development of science and technology, wearable, comfortable, and smart functional textiles are becoming necessary (Holme, 2007; E.W.T. Ngal et al., 2014). Cotton is an excellent natural material with a wide range of textile applications in different production areas (Hou et al., 2012) However, carbon (C), oxygen (O), hydrogen (H) content of cotton fiber is combustible and poses a great risk. Therefore industrial and academic studies are focused on reducing of cotton ignitability by changing thermal properties. (Horrocks, 2011; Alongi&G.Malucelli, 2015; A.Abou-Okeil et al, 2013). Indeed, reduction of burning and ignition tendency in textile materials has been known and recognized since man's recorded history. The flame resistant materials such as asbestos were used in Roman times. After 16th century, it is possible to see a number of patents on flame-retardant textiles (Tomasino, 1992). Nowadays, with increasing industrialization, collective settlement areas and developing technology increase the fire risks and this causes the use of flame protective textiles (Ömeroğulları&Kut, 2012). Therefore, demands for flame retardant textile fabrics have grown steadily over the last decades (Xie et al., 2013). To recognize the mechanism of flame

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retardancy in textiles, it is necessary to understand the combustion process and the flame process (Dehabadi, 2012).

Our country has 72% of boron reserves in the world. It accounts for 32% of world production (Bozacı,, 2018).Boron has a superior property such as high ignition temperature and flame retardant effect of boron has been the subject of many studies. Zinc borate, boric acid and fluoroborate are the most commonly used flame retardant boron compounds (Gürü et al., 2010). Boron compounds are environmentally friendly when used as flame retardants. They do not cause toxic gas release and have low volatility value. Boron flame retardants cause the formation of a glass protection layer that acts as a barrier for polymer chain oxidation. They cover the burning material, cut off the contact with oxygen and repress the burning, as well. Using boron compounds as a flame retardant in textiles is increasing day after day (Yılmaz Aydın et al.,2016)

2. COMBUSTION THEORY

When solid materials are heated, some chemical and physical changes can occur at certain temperatures depending on the chemical structure of these materials. Thermoplastic polymers soften and then melt. At some higher temperature both non-thermoplastic and thermoplastic solids are chemically degraded (pyrolyze) (Figure 1). Chemical changes begin and then continue throughout the burning temperature when combustion occurs (Tomasino, 1992; W.D.Schindler&P.J.Hauser, 2004). Combustion; is an exothermic reaction that requires heat, oxygen and appropriate fuel components. When remaining conditions are ignored, the combustion is self-catalyzed and continues until oxygen, fuel, or heat is consumed (Ömerogulları & Kut, 2012).

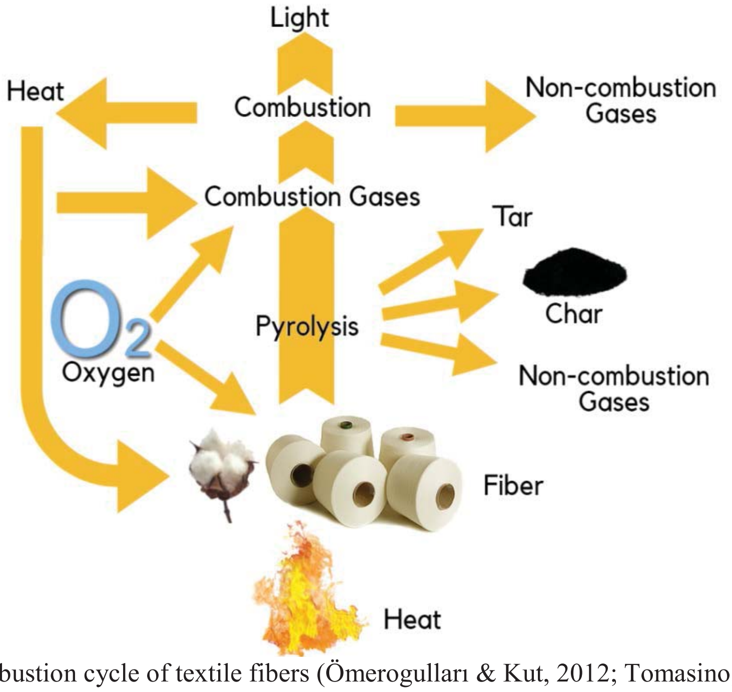

Figure 1. Combustion cycle of textile fibers (Ömerogulları & Kut, 2012; Tomasino, 2012; Dehabadi, 2012; Schindler & Hauser, 2004)

In textiles, combustion behavior is influenced by factors such as fiber type and fiber mixtures as well as the structure of the ignition source and the impact time to the fabric, fabric orientation, ignition point (edge of fabric), ambient temperature, relative humidity, air flow rate and fabric structure. Moreover, studies on the effect of yarn structure and geometry on burning behavior indicate that different yarn twisting methods cause different combustion resistances in yarns (Ömeroğulları & Kut, 2012; Horrocks ve Price, 2001). Additionally, the other important factor in combustion is the Limiting Oxygen Index (L.O.I.) which indicates the amount of the oxygen needed in order to burn (Tomasino, 1992; Bellini et al.,2001). The percentage of oxygen in the air is around 21% (Bellini et al., 2001). The higher LOI exhibits better flame-retardant property. All fibers with lower LOI will burn easily (Tomasino, 1992; Bellini et al., 2001). The LOI of the main textile fibers are given below (Table 1). As seen on table cotton is among the most flammable fibers (Kilinc, 2013).

Table 1. L.O.I. of the main textile fibers (Tomasino, 1992; Bellini et al., 2001; Kilinc, 2013).

L.O.I. of the main textile fibers

Fibers	***LOI (%)***
Wool	25
Cotton	18
Polyester	20-21
Polyamide	20-21
Acrylic	18-20
Modacrylic	22-30

Cotton fibers are pure cellulose form which is the most abundant polymer in nature. Approximately 90% of cotton fibers are made of cellulose (Gordon &. Hsie, 2007). Cellulose $(C_6H_{10}O_5)_n$ is a linear polymer of molecules consisting of building blocks of glucose anhydrite units. These units are organic compounds which are linked to each other by 1-4 ~ glucosidic bonds (int 7, 2017). The cellulosic molecule is a ribbon-like structure of six-membered rings with hydroxyl groups (Figure 2).

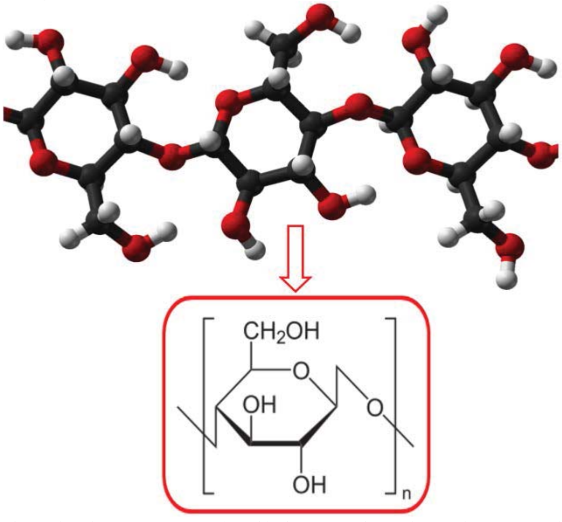

Figure 2. Chemical structure of cellulose (Alongi et al., 2011; int 2, 2017)

The covalently bound chain molecule is cured with internal hydrogen bonds parallel to the oxygen bridges between the rings. Under tensile stress, the molecule has a high modulus and high strength (Klemm et al., 2004). The chemical reactions and heating effects of cotton cellulose depend on the activity of the multi-molecular structure and the hydroxyl groups C_2, C_3 and C_6 (Alongi et al., 2011).

The new Flame Retardants FR usually use the chemical surface of the cotton for covalent bonding. The covalent bond should not alter the physical properties of the cotton (Battegazzore et al., 2014). Esterification reactions are occurred in the cotton fibers during the best finishing operations. Particularly flame retardant processes (usually phosphorylation reactions) take place in this route (Davies & Horrocks, 1986). Cellulose is easily damaged by oxidizing agents such as dichromates, hypochlorites, chlorinated and perchloric acids, peroxides, tetraoxides (Gordon & Hsie, 2007)

Three types of volatile chemicals are generated when cellulosic fibers are heated at pyrolysis temperature such as flammable volatiles (alcohols, aldehydes and alkanes), flammable gases (carbon monoxide, ethylene and methane) and non-flammable gases (carbon dioxide and water vapor) (Figure 3) (Tomasino, 1192; Bellini et al., 2001). Formation of levoglucosan is the significant thermal degradation mechanisms for cellulosic fibers. Levoglucosan and its unblanced pyrolysis products are high degree of flammable materials. The flame retardants for cellulosic fibers can hinder the formation of these materials (Dehabadi, 2012; Schindler & Hauser, 2004).

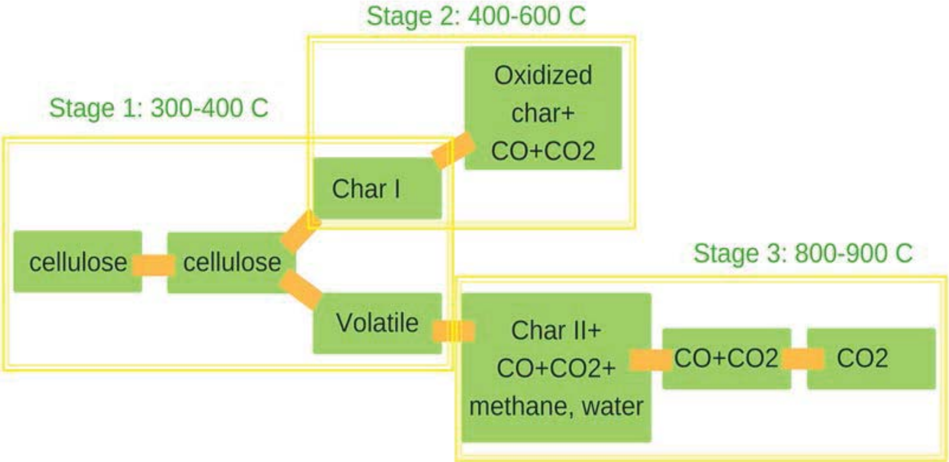

Figure 3 Scheme of cotton cellulose thermal degradation upon heating (Alongi & Malucelli, 2015).

3. FLAME RETARDANTS FOR CELLULOSIC FIBERS

Resistant combustion chemicals are generally based on the six elements. These are phosphrous, antimony, chlorine, boron and nitrogen Kalın, 2008). The most important commercial flammability substances can be classified into three categories. The first category includes flame retardants based on phosphorous (condensed phase mechanism) and halogens (gas phase mechanism). The second category includes synergistic retardancy enhancers. These type of flame retardants have lower flame retarding effects by themselves, but greatly enhance the flame retardancy of first category flame retardants (nitrogen with phosphorous and antimony with halogens). And the last category includes adjunctive flame retardants that show their activity through physical effects (borates, alumina trihydrate, calcium carbonate and intumescents) (Ömeroğulları & Kut, 2012; Schindler & Hauser, 2004).

Conventional flame retardants for cotton fabrics contain halogen and phosphorus. Using of halogen-based flame retardants to reduce the flammability of cotton is one of the most effective ways to reduce the fire hazard. However, various toxic and corrosive gases are formed with using these flame retardants during thermal decomposition. In recent years, intensive efforts have been made to develop halogen-free flame retardants (Lessan et al., 2011; Lu & Ian, 2002).

One of the most important burning mechanism of cellulose fibers is levoglucosan formation and the flame retardants inhibit this formation. Esterification and cross linking of cellulose fibers with phosphoric acid decreases the levoglucosan formation and catalyzes the carbonation and dehydration of cellulose. This mechanism acts as efficient flame retardant (Gürü et al., 2010; Schindler & Hauser, 2004). In one study, researchers investigated the effect of the sol-gelate phosphate based flame retardant coating on the flame retardancy, hardness and strength of polyacrylonitrile fabrics (Yaman, 2009). It has been noted that some compounds containing phosphorus, silicon boron, nitrogen, and other elements might be used as a flame retardant additive. Boric acid and borate salts were used as effective nonflammable additives (Lu & Ian, 2002).

In another study, phosphorous compounds were applied to the cotton fabrics by sol-gel method. Cone calorimeter, vertical burn test, horizontal burn test, thermogravimetric analysis tests were applied to the fabrics. Vertical flammability test results of the samples are given on Figure 4 (Alongi et al., 2011).

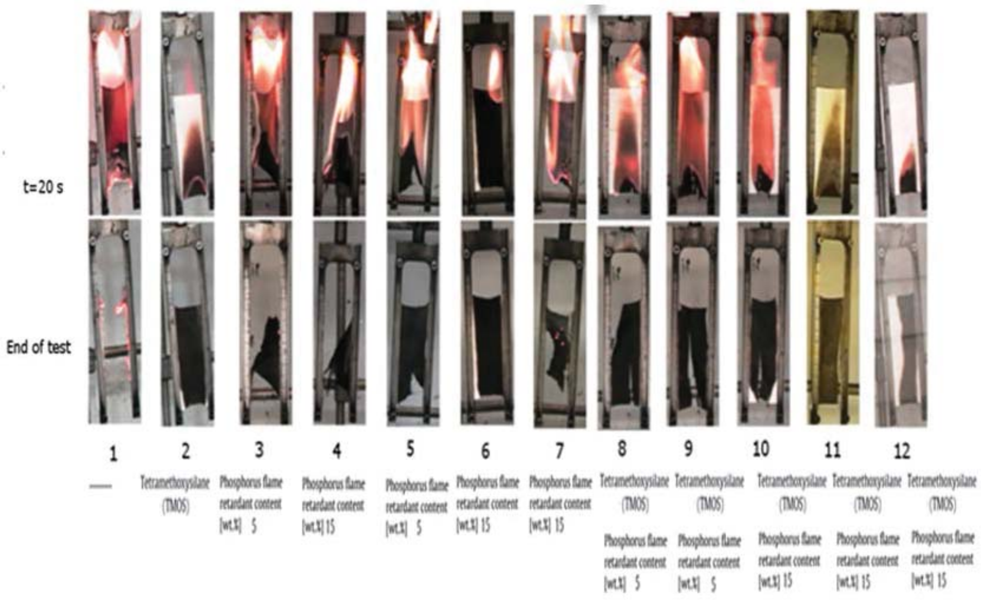

Figure 4. Cotton fabrics after vertical flammability tests 1, (Alongi et al., 2011).

Based on a synergistic effect, it was found that 5% and 15% of the most promising concentrations of phosphorus compounds were strongly improved flame retardancy of cotton fabrics (Lu & Ian, 2002; Alongi et al., 2011).

3.1. Non-Durable Flame Retardants For Cellulose

As is known for a long time, inorganic salts impart flame retardancy properties to the cellulosic fibers. However they are not resistant to water, sweat or rain. In 1820, scientists used borax and ammonium sulphate to give flame retardant properties to cotton. Nowadays, a mixture of borax and boric acid are used for cotton. This mixture provides safest carbon monoxide and smoke production (Tomasino, 1992; Kalın, 2008). However, ammonium sulfate and boric acid and borax mixtures found to be non-durable flame retardant finishes for cotton (Gürü et al., 2012; Wu, 2004). There are some studies on the using of boron and its compounds in the flame retardant finishes (Xie et al., 2013; Bilgiç & Dayık, 2013; Gemci & Gülşen, 2010; Kalın, 2008; Sricharussin et al., 2004; Mercimek, 2010; Wu, 2004).

In one study, borax, zinc borate and boric acid were applied to the cotton fabrics with Alfa-x flame-retardant chemical. Boron compounds and prepared solutions were applied to 100% cotton by pad batch method (Table 2). The flammability of the samples was investigated by combustion tests (TS EN ISO 6941: 2007 standard). Burning rate results of samples are given in Figure 5 (Kalın, 2008).

Table 2 Chemical content and mixing ratios of prepared solutions (Kalın, 2008).

Samples	Alfa-x (%)	Zinc Borate (%)	Borax (%)	Boric Acid (%)	pH
Reference	-	-	-	-	-
1	50	-	-	5	4.88
2	50	-	-	7.5	4.76
3	50	-	-	10	4.79
4	50	-	5	-	6.14
5	50	-	7.5	-	6.34
6	50	-	10	-	6.57
7	50	5	-	-	5.04
8	50	7.5	-	-	5.08
9	50	10	-	-	5.52
10	50	-	-	-	5.16
11	100	-	-	-	4.81

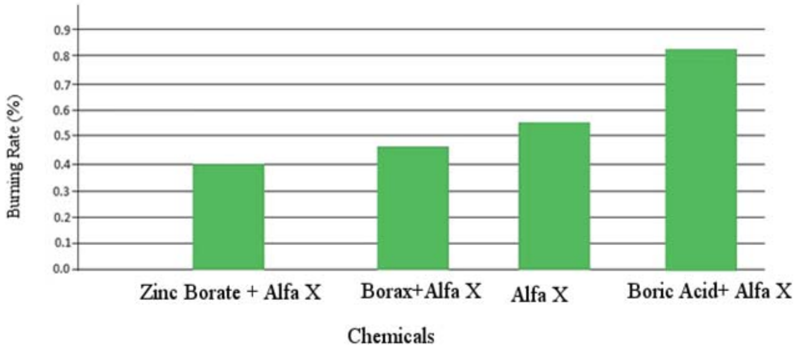

Figure 5. Burning rates of cotton fabrics(Kalın, 2008).

In consequence of burning tests, it was observed that the raw fabric not treated with finishing agents was burned compeletely. Besides the fabric samples treated with finishing agents provide high effective flame retardancy. Fire retardant chemicals used in this research were easily washed away from the fabric (Kalın, 2008).

In another study, flame retardancy properties of boric acid in the cotton fabric were investigated and 45° oblique burning test was applied to the samples. Changes in the strength of the samples were examined. As a result of this study it was determined that flame retardancy of the samples had no washing resistance and tensile strength values of samples were decreased (Akarslan, 2015).

Diammonium phosphate, ammonium sulfamate and ammonium bromide are commercially used for giving flame retardancy to cotton (Tomasino, 1992; Schindler & Hauser, 2004). Non-durable, semi-durable or durable flame retardant properties can be obtained with phosphorus compounds. Nitrogen is not effective when it used alone, however it acts synergistically with phosphorus (Tomasino, 1992).

3.2. Durable Flame Retardants For Cellulose

Altough inorganic salts have positive effects on flame-retardant properties of cellulose, they have no washing durability The most durable flame retardants for cellulosic fibers are phosphorous- and nitrogen based chemical systems. These systems form cross linked structures on the fiber or can react with the fiber. One of the most important ingredients of this finish is tetrakis (hydroxymethyl) phosphonium chloride (THPC) which reacts with urea to make an insoluble structure on cellulosic fibers (Tomasino, 1992; Gürü et al., 2010; Schindler & Hauser, 2004). Eventough the THPC-Urea system gives durable flame retardancy, treated cellulosic fabrics become stiffer and weaker. Their tensile strength values decrease as well as releasing formaldehyde during the finishing treatment. Then, THPC-urea system variations were developed for producing finishes that give fibers to less stiffness and damage (Proban process). Many other approches were tried. In one of these studies,using of *N*-methylol dimethylphosphonopropionamide (PYROVATEX CP) to obtain durable flame retardant finishing in cellulose fibers was investigated (Figure 6). This agent is applied to the fabric with melamine resin using a phosphoric acid as a catalyst (Tomasino, 1992; Dehabadi, 2012; Schindler & Hauser, 2004).

The other flame retardant named Fyrol 76 is an oligmeric phosponate and it is applied with N-methylol acrylamide and potassium persulphate. Many flame retardant finishing agents were applied with padding, drying, curing and oxidizing (Tomasino, 1992).

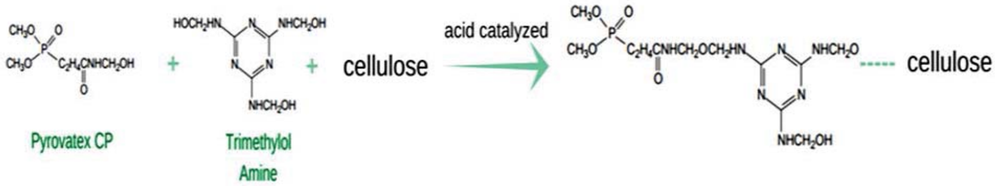

Figure 6 Reaction of Pyrovatex CP with cellulose with trimethylol amine (Dehabadi, 2012; int 3, int 4, 2017)

Textile fabrics blended with cotton could be treated with Tetraethoxysilane (TEOS) by sol-gel method with inorganic precursor of silica phases. These samples were evaluated with cone calorimeter. SEM images of fabric samples treated with TEOS are given in Figure 7 (Alongi et al., 1961).

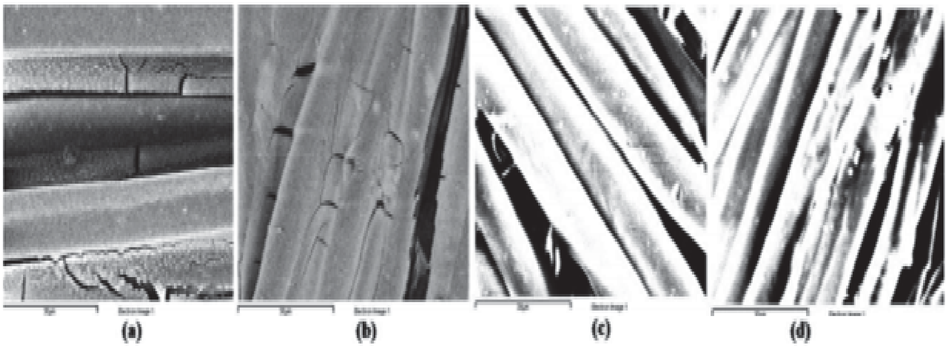

Figure 7 energy dispersive spectroscopy (EDS) mapping of (a) PET, (b) COT, (c) containing 15% COT (COT15), and (d) containing 35% COT (COT35) with TEOS3(Alongi et al., 1961)

LOI test results of the treated samples are given in Table 3.

Table 3 Combustion results from Cone Calorimetry and LOI Tests (Alongi et al., 1961).

Formulation	TTI(s)	δTTI(%)	LOI(%)
COT*35	14	-	21
COT35–TEOS1	26	+86	22
COT35–TEOS2	27	+93	22
COT35–TEOS3	24	+71	22
COT15	59	-	22
COT15–TEOS1	47	-20	23
COT15–TEOS2	46	-22	23
COT15–TEOS3	67	+14	23
COT	14	-	20
COT–TEOS1	16	+7	22
COT–TEOS2	9	-40	22
COT–TEOS3	18	+20	22
PET**	164	-	21
PET–TEOS1	78	-52	22
PET–TEOS2	72	-57	22
PET–TEOS3	62	-62	22
*Coton,**Polyester			

It was observed that silica films deposited on the fabric formed a protective layer against thermal degradation in the air (Alongi et al., 1961). Many flame-retardant finishing agents can be applied by filling, drying, curing and oxidizing (Tomasino, 1992). Because of inorganic structure of boron, it is not durable to wash. When sol-gel method implement boron layers on cotton fabric, samples gain wash strength. (Tomasino, 1992).

Tetraethoxysilane with a triple flame retardant could be applied to the silk fabric. The results were evaluated according to test results such as micro calorimeter combustion, smoke density, LOI (Zheng et al., 2017). Cross linking mechanism of the boron silica gel and silk fibers can be seen on Figure 8.

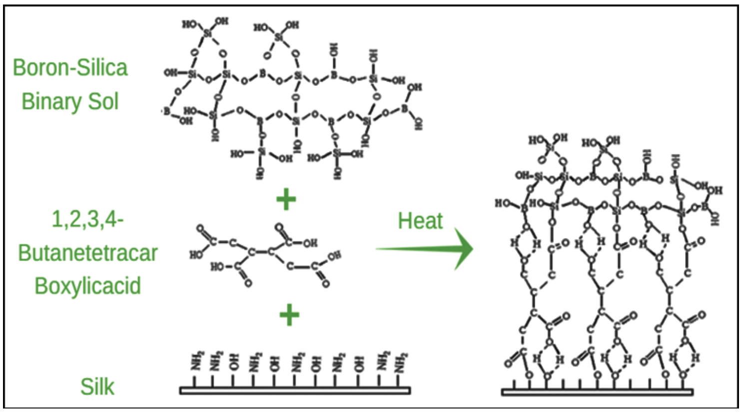

Figure 8 Cross linked silk fabric with boron-silica binary sol by BTCA (1,2,3,4-butanetetracarboxylicacid) (Zheng et al., 2017).

After sol-gel application the samples were washed 10 times and the durability of finish were evaluated. Applied method showed good flame retardancy with LOI value of over 34.5% on silk fabric. BTCA left on coating and increased the durability of washing on silk fabric but had a negative effect on LOI values (Zheng et al., 2017).

Polycarboxylic acid can be used to improve the wash fastness of the cellulosic fabrics. Formaldehyde-based N-methylol compounds including dimethylethylenedi-hydroxyethyl-urea (DMDHEU) have been used in the textile industry. However, studies have been initiated to develop formaldehyde-free crosslinking agents instead of formaldehyde releasing N-methylol compounds which are carcinogenic during production and storage. Polycarboxylic acids can strengthen the organic-inorganic bond by attaching a silica coating on the cellulosic fabric and also by forming an ester bridge with the ester bond between the silica layer of the cellulosic Sol precursor. (Succinic acid, glutaric acid adipic acid, maleic acid, dl-malic acid and tartaric acid have recently been used for providing durability in the cotton (Campbell & Francis, 19965; Gagliardi & Shippee, 1963; Kang et al., 1998; Mahlting et al., 2005; Huang, 2011).

4. NANOTECHNOLOGICAL APPROACHES FOR FLAME RETARDANTS (FR) TODAY

The history of cotton flame retardation is based on very prolonged life. New approaches are developed over the last five years have led more environmentally friendly systems. Therefore, the attention of the scientific world has turned to nanotechnology. There is a common consensus that nano objects created a very thin layer on the fabric surface may be the key to new FRs (Alongi et al, 2013; Selcen Kilinç, 2013; Liang et al., 2013). Among the nanotechnology approaches, nanoparticle adsorption, the derived Layer by Layer (LbL) assembly, sol–gel and dual-cure processes seem to deserve further investigations to achieve the best performances (Alongi & Malucelli, 2015).

4.1. Nano Particle Adsorption

Nanoparticle adsorption can be considered to place nanoparticles on the fabric surface. A nanoparticle suspension should be applied onto the fabric to create a nanometric distribution acting as a physical flame barrier. It is considered that, this approach is not stable in comparison to the systems in which the cross linker between cotton and nanoparticles is used, since the approach is based on ionic interactions between the substrate and the fabric. Table 4 summerises the collected data for treated cotton with different nanoparticles (Alongi et al., 2015).

Table 4.Nanoparticles investigated and collected results for treated-cotton by cone calorimetry (Alongi et al., 2015).

Nanoparticle	Formula	Results
Carbonate hydrotalcite	$Mg_6Al_2(CO_3)(OH_{16}).4(H_2O)$ carbonate salt	pkHRR reduction,TTI increase
Octapropylammonium POSS®	$R(SiO_x)$	pkHRR reduction,TTI increase
Silica	SiO_2	pkHRR reduction
Sodium cloisite	$M_x[Al_{4-x}Mg_x](Si)_8O_{20}(OH)_4$	pkHRR reduction,TTI increase
Sulphonate bohemite	AlO(OH) p-toluenesulphonate salt	pkHRR reduction,TTI** increase
Titania (anatase form)	TiO_2	pkHRR* reduction

*peak of heat release rate, ** time to ignition

4.2. Layer by Layer (LBL) assembly

LbL was discovered in 1966 by Iler. It is a simple process consisting of a gradual accumulation of films based on self-assembled coatings and electrostatic interactions (Iler, 1966). Through electrostatic interactions, the LbL apparatus must be immersed in a water-based solution with a counter-charged polyelectrolyte of the substrate. Thus, the positively and negatively charged layers formed on the surface are combined using the inversion of total surface charge in each immersion step (Figure 9) (Lawden & Hull, 2013).

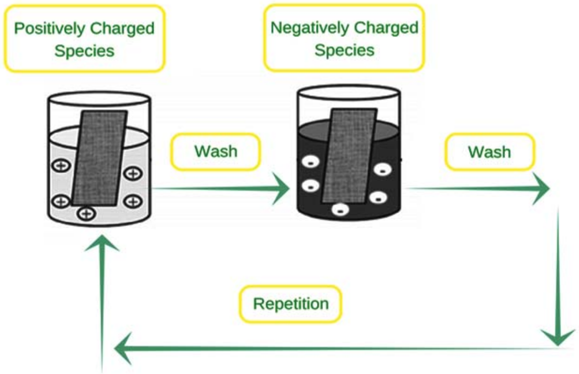

Figure 9 Scheme of LbL assembly (Alongi & Malucelli, 2015; Lawden & Hull, 2013).

LbL was thought to be an evolution of the nano particle adsorpion processing. By taking advantage of this approach, two types of structures can accumulate as solid or inorganic coatings on the surface (Alongi & Malucelli 2015; Lawden & Hull, 2013). Silica based materials were put on cotton fibers by Layer by Layer technique to improve their flame retardant properties. For this purpose, three different sedimentation procedures (dip, vertical and horizontal sprayers) were considered and compared (Alongi et al., 2013). SEM micrographs were presented in Figure 10 and cone calorimeter results are given in Table 5. As seen on Figure 10, different application methods exhibit different results.

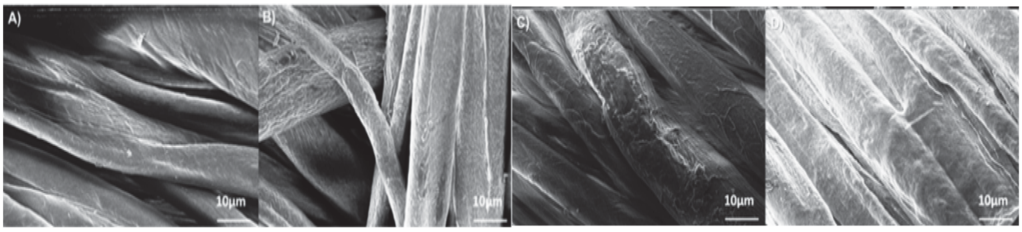

Figure 10. SEM micrographs of cotton fabrics: neat (A) and LbL-treated by dipping (B), vertical (C) and horizontal spray (D) (Alongi et al., 2013).

Table 5 Cone calorimetry data of neat and LbL-treated fabrics [41].

Sample	TTI(s)		RSR	Residue(g)
		Peak(1/s)	Time(s)	
COT	22	1.1	30	0.01
COT, silica, horizontal sprey	28	0.9	36	0.03
COT, silica, vertical sprey	20	0.8	34	0.04
COT, silica, dipping	20	0.8	28	0.04

As seen on Table 5 evaluating combustion tests have been proven that the horizontal spray provides the best flame resistance and a significant increase in the total burn time and amount of char. Cone calorimetry measurements have shown a significant increase in the duration of the ignition and a significant reduction in heat release rate and total heat release for fabrics treated with horizontal spray (Alongi et al., 2013).

The cotton fabric is treated with other flame retardant coatings consisting of branched polyethyleneimine (BPEI) and sodium montmorillonite (MMT) clays prepared by laminated (LbL) assembly (Figure 11) (Li et al., 2010).

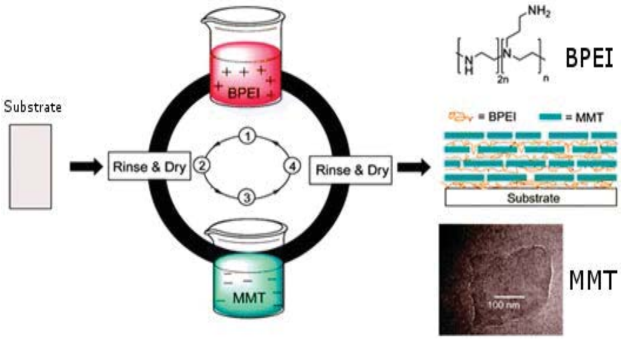

Figure 11. Schematic image of the LbL deposition process used to prepare clay-BPEI assemblies (Li et al., 2010).

All covered fabrics were exhibited a mesh structure and a fiber shape. Microcombustion calorimeter test results showed that all coated fabrics were exhibited reducing total heat release (Li et al., 2010).

4.3. Sol-gel and Dual-core Processes

Sol-gel technology enables the production of glassy materials added as porous dry gel or condensed materials. Starting with aqueous solutions of process precursors, they can be immobilized (even if they are as fragile as proteins in glass-like materials) (int 1, 2017). The sol-gel method has shown its potential in terms of synthesis of new materials with high homogeneity at the molecular level and exceptional physical and chemical synthesis. The sol–gel is a versatile synthetic route based on a two-step reaction (hydrolysis and condensation), starting from (semi) metal alkoxides (usually tetraethoxysilane, tetramethoxysilane, titanium tetraisopropoxide, aluminium isopropoxide). This leads the formation of completely inorganic or hybrid organic–inorganic coatings at or near room temperature (as seen on Figure 12) (Sakka, 2003).

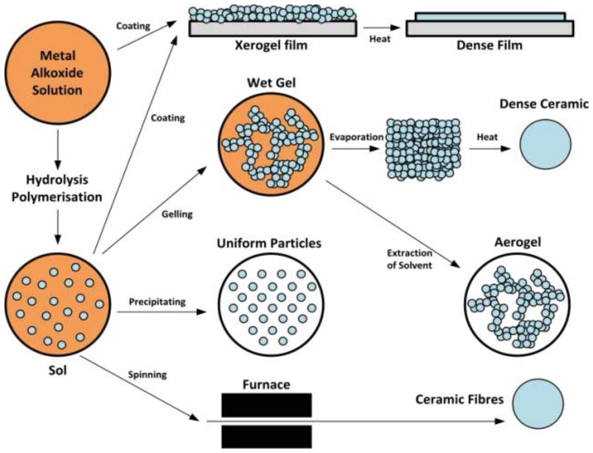

Figure 12. Sol-gel process overview (int 1, 2017; int 6, 2017)

Nature of (semi)metal atom and alkyl/alkoxide groups, structure of the (semi)metal alkoxide, water/alkoxide ratio, pH (acidic or basic conditions), temperature, reaction time and presence of co-solvents. All these parameters were used to determine the structure/morphology of the resulting oxidic networks (Sakka, 2003). In the sol-gel technique, both silane and phosphate-containing alkoxides such as TEOS (tetraethoxysilicate), TMOS (tetramethylortho silicate) alkoxides or DPTES (diethylphosphatoethyltriethoxysilane) are frequently used as the left precursor (Alongi & Malucelli, 2015; Sakka, 2003).

It is also important for textiles. Chloride, bromide, phosphorus, antimony, boron, based materials are used for providing flame retardant effects on textile surfaces. The combination of antimony-halogen or phosphorus nitrogen leads synergistic effects. The higher chemical concentration (about 300-500 g / L) used in conventional techniquescan be significantly reduced by using sol-gel method. Additionally, this method provides non-halogen, ecological and economic flame retardant activity (Camlibel & Arik, 2017).

In order to provide flame retardant properties on the cotton fabrics, it is necessary to prepare inorganic silica thin films and to investigate the effect of the films on thermal and burning behavior, as well.Modification of fabrics with the pure silica solgel precursor (3-

Aminopropyl)triethoxysilane (APTES) and three different sols were studied to examine the effect of APTES and hybrid sols consisting of phosphorus-conjugated diethylphosphite. Cotton fabrics were impregnated with soles by a filling process (Figure13). The thermal behaviors of the treated cotton samples were investigated by thermogravimetric / differential scanning calorimetry analysis (TGAeDTG / DSC) and compared with untreated cotton samples. Flame retardancy properties were tested according to the ASTM D 1230 standard method (Brancatelli et al., 2011).

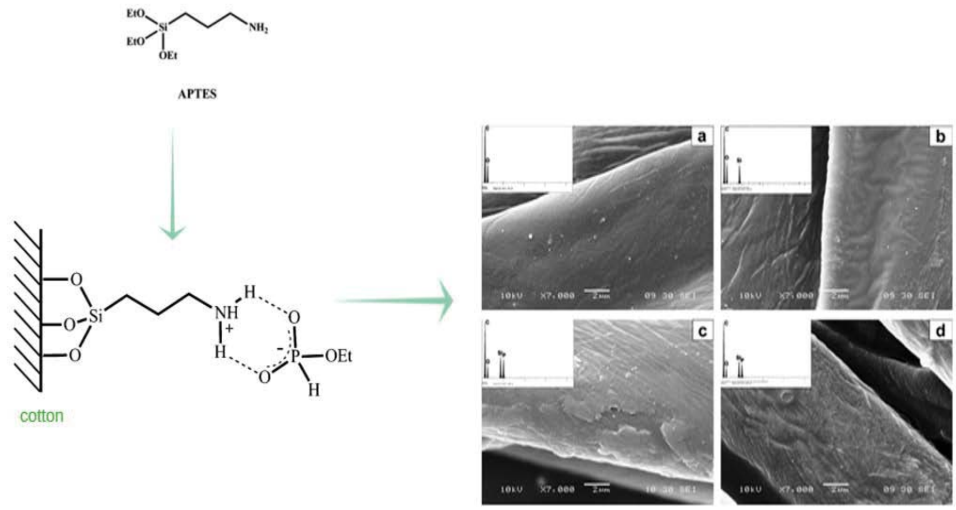

Figure 13 Chemical structures of the sol-gel precursor APTES, proposed interaction between the hydrolyzed APTES and DEP and SEM micrographs of cotton fabrics untreated (a), and treated with Silica (Si) (b), Silica-Phosphorus (Si-P) (c) and Silica-Phosphorous-Carbon (Si-S-P-C) (d) sols (Brancatelli, et al., 2011).

The results exhibited that coal residue properties and flame retardancy are a significantly improved by modifying fabrics with thin layers. Unfortunately, recommended coatings do not exhibit a high washing fastness. Thus, these fabrics are not proper for clothing (Brancatelli et al., 2011).

5. TEST METHODS FOR FLAME RETARDANTS.

There are a number of features that are taken into consideration in the evaluation of the flammability process. Burning behavior of the material is related to the surface structure of the materials. Many test methods developed depending on the variables that are included in the standards. Common standards are as follows according to the location of the material (Table 6);

Table 6 Selected tests for textiles (Alongi & Malucelli, 2015).

Test type	Nature of test	Standard	Textile type	Ignition source
Textile composite and product tests	Apparel not for protective clothing	BS EN 1103	Vertical clothing fabrics	Small flame
	UK small-scale composite test for furnishing fabric/fillings	BS 5852 Parts 1 and 2	Furnishing fabrics	Cigarette and simulated match flame
		BS 5852 or ISO 8191 Parts 1 and 2		Small flames and wooden cribs applied

				to small and full scale tests
		BS EN 1021 Parts 1 and 2		Cigarette and simulated match flame
		BS 6807	Bedding (mattresses)	Cigarette and match ignition tests
		BS EN 597 Parts 1 and 2		
		BS EN ISO 12952 Parts 1 and 2		International standard for cigarette and match ignition testing
		BS 6307 and ISO 6925	Carpets	Methenamine pill ignition source BS EN ISO 9239 Part 1 Reaction to fire test using a radiant source at 30° (~10 kW m^{2})
		BS EN ISO 9239 Part 1		

Test type	**Nature of test**	**Standard**	**Textile type**	**Ignition source**
		BS EN 13772	Curtains	Uses EN ISO 6941 fitted with an additional radiator source
		BS 5867 Part 2		Uses BS EN ISO 6941 for domestic and ISO 15025 for contract fabrics
		BS EN 1102		Uses EN ISO 6941 with 10 s ignition time
Simple fabric strip tests	Vertical strip method	BS 5867 Part 2	Curtains and drapes	Small flame
		BS 5722	Nightwear	Small flame
	Vertical strip method	BS EN ISO 6940 Part 1 ISO 15025	Vertical fabrics	Small flame
	US strip tests	ASTM D6413	Vertical fabrics	Small flame
		FMVSS 302	Horizontal fabrics	Small flame
Thermal protection (including protective clothing and manikin tests)	Protective clothing: general requirements	BS EN 340		Design, comfort, durability and labelling requirements.
	Resistance to radiant heat	BS EN ISO 6942		Exposure to radiant source
	Resistance to convective heat (flame)	BS EN 367		Determine heat transfer index
	Resistance to molten metal splash	BS EN ISO 9185		Molten metal
	Gloves against thermal risks	BS EN 407		Composite standard (including fire-fighters' and welders' gloves)

Test type	**Nature of test**	**Standard**	**Textile type**	**Ignition source**
	Fire-fighters clothing	BS EN 469		Composite standard
	Welders' and allied industrial clothing Protective clothing against heat and flame	ISO 11611		Composite standard
Tests undertaken with the addition of radiant heat including reaction to fire tests	Use of radiant flux plus specified ignition	EN ISO 9239 Part 1	Carpets: fabrics/composites o ofen for use in seatings	Irradiate with 30 gas heated panel (~10 kW m^{-2}) with small burner
		NF 92503, French 'M test'		
		ASTM E906 and FAR 25.853 Part 4	Aircraft seat assemblies, so-called 'Boeing' test	Irradiate under 35 kW m^{-2} with small flame ignite
	Protection against limited heat and flame	BS EN ISO 15025		Small flame
	Protective clothing – protection from limited flame spread	BS EN ISO 14116		Damage definition enables fabric classification
	Contact heat transmission	BS EN 702		Contact temperatures 100–500 ˚C
	Fire-fighters' hoods	EN 131911		
	Instrumented manikin testing of whole garments	BS ISO 13506		Prediction of burn injury in terms of 1st, 2nd and 3rd degree burn propensity
Durability tests	Cleansing and wetting procedures for use in flammability tests	BS 5651	All fabrics	Used on fabrics prior to submitting for standard ignition tests
	Commercial laundering	BS EN ISO 10528		
	Domestic laundering and dry cleaning	BS EN ISO 12138		
		BS EN ISO 6330		

6. CONCLUSION

The flame-retardant properties of cotton fabrics are rather weak and need to be improved. Boron compounds are used to improve these properties of cotton fabrics. In this review, boron compounds used to improve the flame retardant properties of cotton fabrics and their application methods have been investigated and summerized. This study is related to the R & D center's own equity project. This project investigated the use of boron and boron compounds to impart flame retardant properties to cotton fibers. Although the literature suggests that these compounds are not stable, low costs make boron compounds attractive. As is known, Turkey's boron reserves are huge and we want to use these resources as our flame retardant textile products. Further studies should be necessary on this issue.

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