

FLAME RETARDANT FINISHING OF COTTON FLEECE USING PHOSPHORUS
CONTAINING MALEIC ACID OLIGOMERS AND HYDROXYL-FUNCTIONAL
ORGANOPHOSPHORUS OLIGOMERS

by

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(Under the Direction of Charles Q. Yang)

ABSTRACT

The objective of this research was to reduce the flammability of cotton fleece using phosphorus containing maleic acid oligomers (PMAO) and hydroxyl-functional organophosphorus oligomer (HFPO). We found both PMAO and HFPO can be bound to the cotton fleece by esterification with cotton cellulose. The 45° flammability and limiting oxygen index data indicated that the treatment of cotton fleece using PMAO and HFPO reduced the flammability of cotton fleece effectively. The micro-scale combustion calorimetry data revealed that PMAO and HFPO reduced the peak heat release rate and heat release capacity of the treated cotton. The cotton fleece after treatment can pass the federal flammability test (16 CFR Part 1610) and achieve “Class 1” flammability. The use of TEA can modestly enhance the performance of PMAO and HFPO with no significant changes in fabric physical properties and was durable to multiple home laundering cycles.

INDEX WORDS: *cotton, fleece, flame retardant finishing, phosphorus-containing maleic acid oligomer, hydroxyl-functional organophosphorus oligomer.*

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DEDICATION

This thesis is dedicated to my parents, for their forever love and support.

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	v
CHAPTER	
1 INTRODUCTION	1
Significance of this Research	1
Objective of this Research.....	2
Reference.....	3
2 LITERATURE REVIEW	5
Flammability and Flame Retardant finishing of Cotton.....	5
Flame Retardant Finishing of Cotton Fleece.....	8
Federal Regulations of Clothing Textiles.....	12
Reference.....	14
3 FLAME RETARDANT FINISHING OF COTTON FLEECE FABRIC USING PHOSPHORUS-CONTAINING MALEIC ACID OLIGOMERS.....	18
Abstract	19
Introduction	20
Experimental	22
Results and Discussion.....	25
Conclusion.....	33
References	34

4	FLAME RETARDANT FINISHING OF COTTON FLEECE FABRIC USING HYDROXYL-FUNCTIONAL ORGANOPHOSPHORUS OLIGOMERS AND 1, 2, 3, 4-BUTANETETRACARBOXYLIC ACID	38
	Abstract	39
	Introduction	40
	Experimental	42
	Results and Discussion	45
	Conclusion	56
	References	57
5	CONCLUSIONS	60

CHAPTER 1

INTRODUCTION

Significance of This Research

The flame retardant properties of textile goods are very critical for the safety concerns of the US consumers. Cotton without a flame resistant treatment is highly flammable. Fabrics having Class III flammability that cannot pass the federal flammability test for general apparel ('16 CFR Part 1610: Standard for the Flammability of Clothing Textiles') are not allowed to be sold in the U.S. market [1].

Fleece is a fabric with a thick, soft nap or pile resembling sheep's wool. Fleece usually has higher flammability than most woven and knits due to its lower density and greater amount of air in its fuzzy surface. Cotton fleece without a flame retardant finish cannot meet the required federal flammability standard [2].

Recently, fleece fabric has become more and more popular in the U.S. and all over the world. As a conservative estimate, 36,000 tons of cotton fiber potentially needs chemical treatment if the new flame- retardant finishing technology to ensure that cotton fleece and other raised surface cotton fabrics meet the federal mandatory standard for the flammability of the general wearing apparel [3].

The most practical procedure to meet the federal safety requirement is to treat cotton fleece with a flame retardant. However, there are other ways to improve the flame resistance of cotton fleece, such as blending cotton fiber with a synthetic fiber, or changing the construction of

the fleece fabric [4-5]. However, blending is not effective enough for fleece to meet the federal standard and it sometimes changes the desired properties of 100 percent cotton fleece by altering the construction of the fleece fabric.

Conventional durable flame-retardant chemicals for cotton are based on organophosphorus compounds, such as tetrakis(hydroxymethyl) phosphonium chloride (THPC) and N-methylol dimethylphosphonopropionamide(MDPA) [6-8]. The latter has the trade name “Pyrovatex CP”. Both MDPA and THPC systems are not only expensive, but also can cause other problems, such as strong odor during a pad-dry-cure finishing process, the necessity for multiple alkaline washings after a curing process, and changes in the soft hand property of fleece. [10-12].

To overcome these disadvantages, polycarboxylic acids have been used to reduce the flammability of cotton blend fleeces [13-14]. The polycarboxylic acid-based flame retardant finishing system is a very promising non-formaldehyde-based finishing system. The treated cotton fleece achieves good flame resistant results with improved dimensional stability and a soft hand. However, the mechanism as to how polycarboxylic acids reduce the flammability of cotton fleece is not clear. The polycarboxylic acid-based system has not been fully studied yet and needs further investigation.

Objective of This Research

(1). To study a phosphorus-containing maleic acid oligomer (POMA) flame retardant finishing system. The effectiveness will be studied for 100 percent cotton fleece in the presence of NaH_2PO_2 . The reactivity, flammability, and durability will be studied.

(2). To study a hydroxyl-functional organophosphorus oligomer (HFPO) flame retardant finishing system. This will include the reaction, the introduction of phosphorus, effectiveness, and especially the phosphorus-nitrogen synergism.

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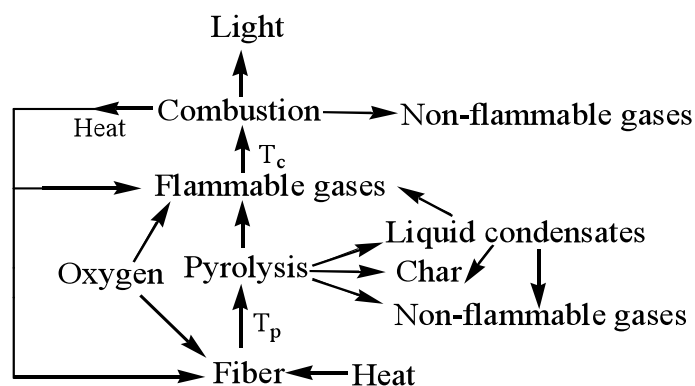
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CHAPTER 2

REVIEW OF LITERATURE

Flammability and Flame Retardant Finishing of Cotton

When cotton is subjected to heat and its temperature reaches the pyrolysis temperature T_p , it will pyrolyze producing carbonaceous char, volatiles and flammable gases (Scheme 1). As the temperature further rises and reaches the combustion temperature T_c , large quantities of heat and light are produced. The pyrolysis of cellulose occurs through two competing reactions: dehydration and formation of levoglucosan [1].



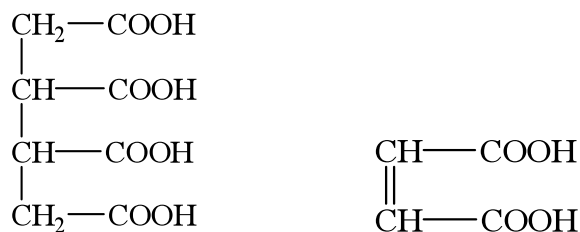
Scheme 1 The burning of cotton fiber [1]

Cotton has a high burning rate compared to other fabrics but this can be prevented by the application of flame-retardants. The conventional durable flame-retardant chemicals for cotton are based on organophosphorus compounds, such as tetrakis(hydroxymethyl) phosphonium chloride (THPC) and N-methylol dimethylphosphonopropionamide(MDPA) [2-4]. It is generally agreed that a phosphorus-containing flame retardant functions in the condensed-phase by enhancing char formation and producing more carbon dioxide and water instead of flammable

gas and tar [5]. However, the Proban process using THPC requires a special ammoniation chamber and the process has multiple steps. All these add a high cost to the final product. Pyrovatex CP finishing always involves the usage of a melamine resin; thus the treated cotton fleece has the potential to release formaldehyde and has a very stiff hand [6-7].

Recently, research has been done on the application of a hydroxyl-functional organophosphorus oligomer (HFPO) (trade name Fyrotex HP, produced by Akzo Nobel) to cotton fabric by using both dimethyloldihydroxyethyleneurea (DMDHEU) and trimethylolmelamine (TMM) as bonding agents to bond the HFPO to the cellulose [8-11]. Though good flame retardant performance and durability to multiple home launderings have been achieved, the flame retardant system with HFPO and bonding agent DMDHEU and TMM has the potential to release formaldehyde.

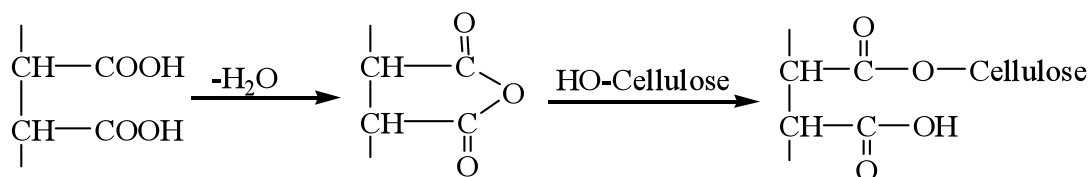
Since the late 1980's, extensive efforts have been made to use formaldehyde-free cross-linking agents for cotton to replace the traditional formaldehyde-based reagents as durable press (DP) finishing agents for cotton [12-13]. The 1,2,3,4-butanetetracarboxylic acid (BTCA), is the most effective DP agent of the polycarboxylic acids that have been studied so far. The structure of BTCA is shown in Scheme 2.



Scheme 2 The structure of BTCA **Scheme 3** The structure of maleic acid

Polycarboxylic acids, such as BTCA, have been studied as a non-formaldehyde durable press finishing agent for cotton. The two-step esterification process of cellulose by polycarboxylic acid is as follows in Scheme 4 [14]. First, a cyclic anhydride intermediate is

formed by the dehydration of two adjacent carboxyl groups. Second, an ester is formed by the reaction between the cyclic anhydride intermediate and the hydroxyl on cellulose.



Scheme 4 The esterification of cellulose by a polycarboxylic acid [14]

Yang et al. studied the HFPO, BTCA and triethanolamine (TEA) flame retardant finishing system on Nomex/cotton blend by using the TEA as co-reactant [15]. The addition of TEA in the flame retardant finishing system improved the hydrolysis resistance of the HFPO bound to the Nomex/cotton blend and enhanced the flame retardant performance of HFPO by means of phosphorus-nitrogen synergism. Moreover, TEA reduced the deposit of calcium salt on the treated fabric.

Maleic acid (MA) is an unsaturated carboxylic acid containing only two carboxyl groups in its molecular structure and is not able to form cross-links with cellulose. MA is extremely difficult to homopolymerize radically because of the strong electron-withdrawing effects and space hindrance caused by the two carboxyl groups. The structure of MA is shown in Scheme 3.

Yang et al. studied the in-situ polymerization of maleic acid and itaconic acid on cotton fabric [16]. They found that in-situ polymerization occurred only when both potassium persulfate and sodium hypophosphite were present on the cotton fabric. Both itaconic acid and maleic acid, polymerized in situ on cotton fabric in the presence of $\text{K}_2\text{S}_2\text{O}_8/\text{NaH}_2\text{PO}_2$ are able to crosslink cotton cellulose, thus imparting wrinkle resistance to the cotton woven fabric. Recent studies showed that the treatment of woven fabric with phosphorus-containing polymaleic acid

oligomers imparts wrinkle resistance to the treated woven fabric similar to that treated with DMDHEU, with improved tensile strength retention [17].

Flame Retardant Finishing of Cotton Fleece

All fabrics will burn to various degrees if exposed to flame or other intense heat sources long enough. The critical factor in determining flammability ratings for textiles is the amount of oxygen available. The more loose the fabric structure, the easier the air permeates and the more combustible is the fabric. Fleece with a raised fiber surface allows individual fibers or yarns to be readily exposed to possible ignition sources. The loose structure of a fleece allows air to penetrate and circulate easily, increasing the hazard level. The phenomenon when a flame travels rapidly over the fabric surface, singeing the fiber ends, is called "surface flash". This surface flash may not be dangerous unless sufficient flame is present to ignite the base fabric. [18]

Both the conventional durable flame-retardant chemicals: MDPA and THPC systems are not only expensive, but also can cause other problems, such as strong odor during a pad-dry-cure finishing process, the necessity for multiple alkaline washings after a curing process, and changes in the soft hand property of fleece. Therefore, the conventional phosphorus-based flame retardants are not suitable for the flame retardant finishing of cotton fleece [6-7].

The application of polycarboxylic acids to reduce the flammability of raised-surface fabric was introduced. The esterification of the carboxyl groups of polycarboxylic acids and hydroxyl groups on cotton enhances char formation in cellulose by creating a carbon-carbon network [19].

BTCA can also serve as bonding agent between cellulose and the hydroxy-functional organophosphorus oligomer (HFPO), which is a non-formaldehyde finishing system. However,

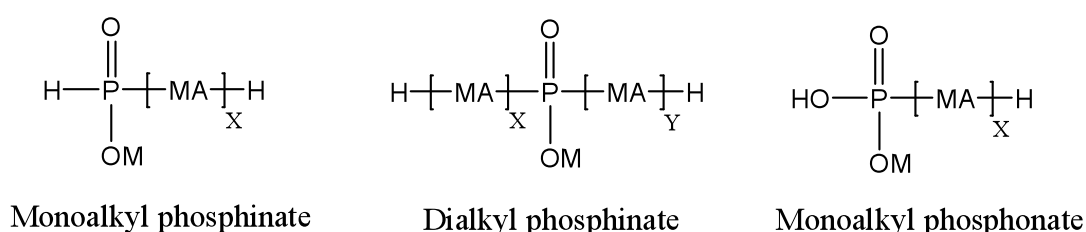
the flammability resistance of cotton fleece treated with HFPO and BTCA deteriorates quickly after several home laundering cycles due to the adsorption of calcium ion in the laundering process [11]. Yang and Qiu studied the application of HFPO/DMDHEU on cotton fleece [20]. They found that cotton fleece treated with HFPO/DMDHEU passes the federal flammability standard and shows high strength retention with little change in fabric whiteness, and is durable to multiple home launderings.

An unsaturated bi-functional carboxylic acid, such as maleic acid, is very difficult to polymerize since it does not polymerize under conditions commonly used for vinyl monomers. The maleic acid/ NaH_2PO_2 treatment was very effective in reducing the flammability of cotton fleece [21]. There were three reactions involved in the maleic acid/ NaH_2PO_2 system with cotton cellulose. The first reaction was the esterification reaction of maleic acid with cotton cellulose, which occurred at a lower curing temperature. The second reaction was the addition reaction of NaH_2PO_2 with the esterification product of maleic acid with cotton cellulose, which happened at a higher curing temperature than the esterification reaction and introduced phosphorus into the cotton cellulose. The third reaction was the cross-linking reaction of maleic acid/ NaH_2PO_2 with cotton cellulose.

Wu and Yang studied the application of maleic acid/ NaH_2PO_2 on cotton fleece and found that the treatment of maleic acid/ NaH_2PO_2 was very effective in reducing the flammability of cotton fleece [22]. The treated cotton fabric was very durable to multiple home launderings and showed increased dimensional stability.

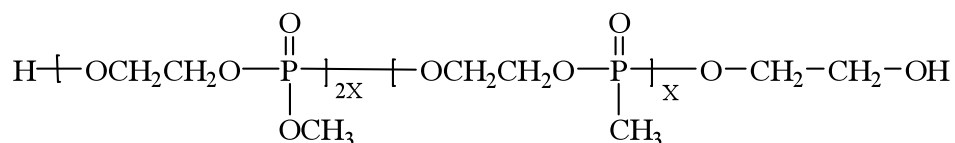
POMA has a molecular structure similar to that of BTCA: both have carboxylic acid groups bound to the adjacent $-\text{CH}_2-$ in their molecular backbones. POMA is usually synthesized by free radical polymerization of maleic anhydride in organic solvents, such as toluene, to form

poly (maleic anhydride)(POMAN), followed by hydrolysis of POMAN to form POMA [23-24]. The polymerization of maleic acid with sodium hypophosphite and initiator potassium persulfate was reported in a patent [25-27]. The product thus produced is a poly maleic acid oligomer containing a phosphinate composition. The structure is shown in Scheme 5. According to the reported applications of the polymaleic acid oligomer on cotton fabrics, durable press, wrinkle recovery, and other mechanical properties have shown improvement in the treated fabrics [28-30].



Scheme 5 The structure of polymaleic acid oligomer

Phosphorus-containing flame-retardants are the most effective agents for cotton. Maleic acid can be polymerized in the presence of sodium hypophosphite and potassium persulfate, and form a POMA with carboxylic acid groups bound to the adjacent $-\text{CH}_2-$ of its molecular backbone [19]. We can use this phosphorus-containing polymaleic acid oligomer to treat 100% cotton fleece to achieve a non-formaldehyde durable press flame retardant system.

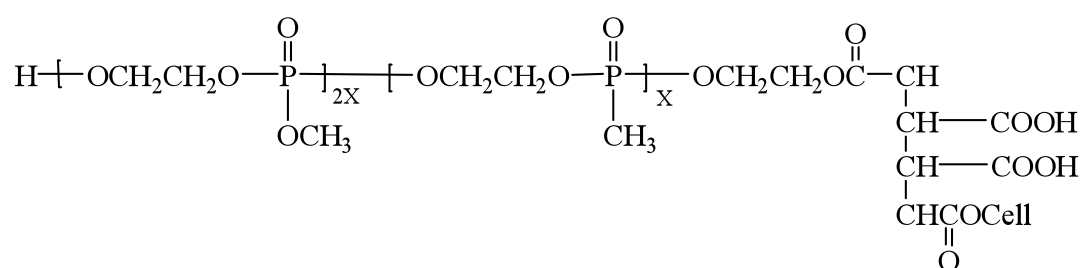


Scheme 6 The structure of HFPO

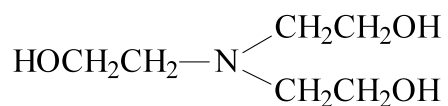
The HFPO is a water-soluble flame retardant with high phosphorus content. The structure of this compound is shown in Scheme 6 [15]. BTCA can esterify both the hydroxyl groups of

HFPO and cotton cellulose, and thus form a cross-linking network and achieve good flame resistance. (Scheme 7)

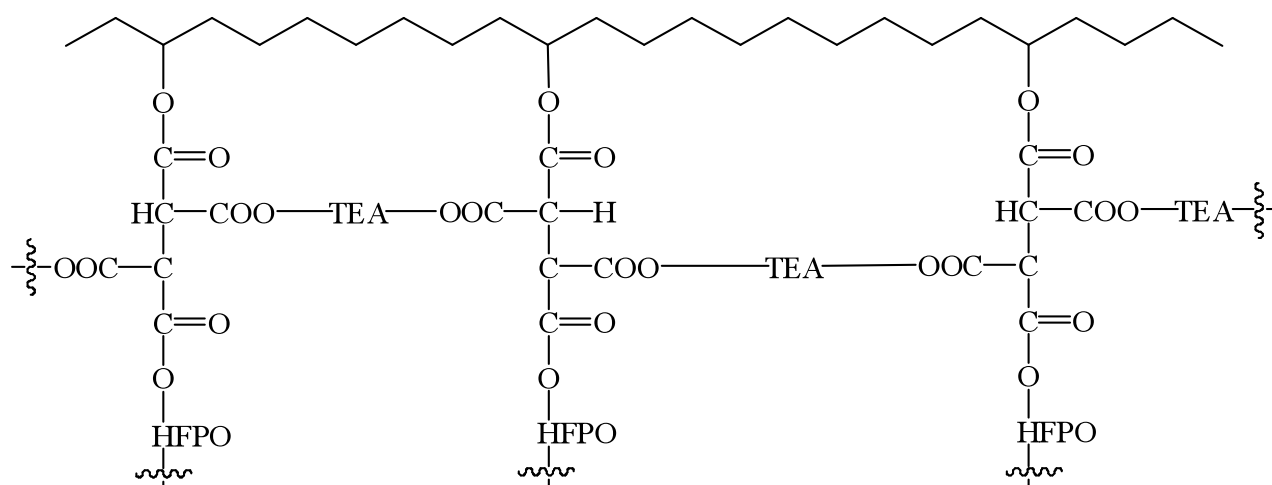
We also believe that the addition of TEA will enhance the flame retardant performance of HFPO/BTCA by bonding nitrogen to cellulose. The structure of TEA is shown in Scheme 8 and the crosslinking network formed by HFPO/BTCA/TEA on cotton is shown in Scheme 9. Since the hydroxyl groups on TEA can esterify the carboxyl groups on HFPO and form a cross-linking network with HFPO, BTCA and cellulose, a durable P-N synergism is theoretically achievable.



Scheme 7 The bonding of HFPO with cellulose by BTCA



Scheme 8 The structure of TEA



Scheme 9 Formation of BTCA/HFPO/TEA crosslinked network on cotton [15]

Federal Regulation of Clothing Textiles

16 CFR 1610-2007

The US consumer product safety commission proposed to amend its flammability standard of general wearing apparel '16 CFR 1610' in 2007. The Standard for the flammability of clothing textiles, '16 CFR 1610' provides a test apparatus and the procedures for testing clothing and textiles would be used as clothing [31].

The test apparatus, materials and test procedure are given in detail in the '16 CFR 1610': All the textiles shall be tested as received and after refurbishing procedures. The classification is based on the reported results before and after drycleaning and washing, whichever is lower. Further more, the dry cleaning should be done in a commercial dry-cleaning machine using perchloroethylene in a normal cycle.

Each specimen should be mounted in a specimen holder, brushed and later dried in an oven for 30 ± 2 min at 105 ± 3 °C, and then moved to a desiccator using silica gel as the desiccant. After the specimen was kept in the desiccators to cool down for no less than 15 min, it was later transferred to the flammability tester and hold in the apparatus at an angle of 45°. The specimen was exposed to a standard butane flame for 1 second to cause ignition, and the burning time and burning characteristics of 5 specimens were recorded and used as the basis to determine the flammability classifications for the cotton fleece.

According to the '16 CFR 1610', the flammability classifications for the fabrics with a raised surface are divided into the following three categories: (1) Class 1 standard was defined as normal flammability: fabric has burning time more than 7 s or has burning time between 0 and 7 s with no base burn (BB); (2) Class 2 standard was defined as intermediate flammability: fabric has burning time 4–7 s with BB; (3) Class 3 was defined as high flammability with rapid and

intense burning: fabric has burning time less than 4 s and BB. In addition, the raised surface textile fabric has Class 1 or Class 2 standard is considered acceptable. While clothing fabric has Class 3 flammability is defined to be failed to pass the federal government standard and not allowed to be sold in the US market.

ASTM Method D 1230

The ASTM Method D 1230-94 ('Standard Test Method for Flammability of Apparel Textiles', re-approved in 2001) is similar to '16 CFR 1610'. But it's not identical to the 16 CFR 1610 and it has been used as an alternative testing method for the textile industry [32].

The 45° flammability of the cotton fleece was measured in the following procedures according to ASTM Method D1230-94 ('Standard Test Method for Flammability of Apparel Textiles', re-approved in 2001). The specimen was mounted in a specimen holder, brushed and later dried in an oven for 30 min at 105°C, and then moved to a desiccator. After the specimen was kept in the desiccators to cool down for 90 min, it was later transferred to the flammability tester (Model TC-45 manufactured by Govmark, Bellmore, New York) and mounted at a 45° angle. The specimen was exposed to a standard butane flame for 1 second to cause ignition, and the burning time and burning characteristics of 5 specimens were recorded and used as the basis to determine the flammability classifications for the cotton fleece.

According to the ASTM D 1230, the flammability classifications for the fabrics with a raised surface are divided into the following three categories: (1) Class 1 standard was defined as normal flammability: fabric has burning time more than 7 s or has surface flash (SF) without BB regardless of burning time; (2) Class 2 standard was defined as intermediate flammability: fabric

has burning time 4–7 s with BB; (3) Class 3 was defined as high flammability with rapid and intense burning: fabric has burning time less than 4 s and BB.

Under the ASTM D 1230, the flammability of a textile fabric can be characterized as Class 1 only when both the fabric after one HL and that after a refurbishing procedure are tested and both achieved Class 1 standard. The refurbishing procedure includes first dry-clean followed by a home laundering cycle using AATCC standard detergent 1993.

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CHAPTER 3

FLAME RETARDANT FINISHING OF COTTON FLEECE FABRIC USING

PHOSPHORUS-CONTAINING MALEIC ACID OLIGOMERS

* Cheng, X. and Yang C.Q., submitted to Fire and Materials, 2/26/2009.

Abstract

The high flammability of cotton fleece makes it necessary to apply a flame retardant system on cotton fleece so that it can meet the federal regulation “Standard for the Flammability of Clothing Textiles” (16 CFR 1610). The objective of this research was to reduce the flammability of cotton fleece using the phosphorus-containing maleic acid oligomers (PMAO) synthesized by aqueous free radical polymerization of maleic acid. We found that PMAO can be bound to cotton fleece by etherification with cotton cellulose with sodium hypophosphite as the catalyst. Both the 45° flammability and limiting oxygen index data indicated that the treatment of cotton using PMAO reduced the flammability of cotton fleece. The micro-scale combustion calorimetric data revealed that PMAO reduced the peak heat release rate and heat release capacity of the treated cotton woven fabric. The cotton fleece treated with PMAO/ NaH_2PO_2 passed the federal flammability test (16 CFR Part 1610) and achieved “Class 1” flammability. The PMAO bound to cotton was durable to multiple home laundering cycles. The treated fleece also showed high strength retention with little change in fabric whiteness. The use of triethanolamine as an additive modestly enhanced the performance of PMAO with no significant changes in fabric physical properties.

Keywords: cotton, fleece, flame retardant finishing, micro-scale combustion calorimetry, phosphorus-containing maleic acid oligomer.

Introduction

The flammability of textile materials is a critical property regarding the safety of consumers. Cotton fleece has flammability higher than woven and knit fabrics due to its fuzzy surface, loose structure and low density. Without chemical treatment, 100% cotton fleece does not meet the U.S. federal flammability standard for apparel (“16 CFR Part 1610: Standard for the Flammability of Clothing Textiles”) and therefore can not be sold in the U.S. legally [1-4].

Chemical treatment using a flame retardant is probably the only practical procedure for treating cotton fleece so that it can meet the federal government flammability requirement, though other methods, such as blending cotton with polyester or changing the construction of the fleece fabric, can also be used to improve the flame resistance of cotton fleece. However, those approaches are not guarantees for the fleece to meet the government standard, and they may also change the desired property of cotton fleece.

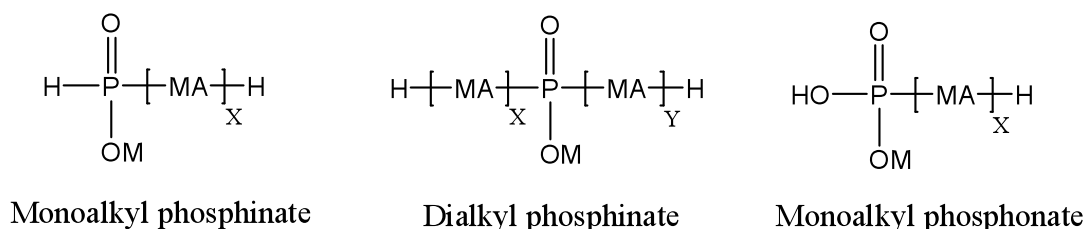
The conventional durable flame-retardant chemicals for cotton based on organophosphorus compounds, including tetrakis(hydroxymethyl) phosphonium chloride (THPC) and N-methylol dimethylphosphonopropionamide (MDPA) [5-7], have the potential to release formaldehyde, which must be considered as a major disadvantage for those chemicals since formaldehyde has recently been classified as a carcinogen by the World Health Organization [8]. THPC and MDPA are not only expensive, but also can cause other problems, such as strong odor during a pad-dry-cure finishing process, the necessity for multiple alkaline washings after a curing process, and changes in the soft hand property of fleece. Ammonium sulfate has been reported as a flame-retardant for cotton recently, but it cannot be bound to cotton and therefore is not suitable as a durable flame retardant for cotton [9]. In spite of high demand in the market place, cotton fleece is not commercially available in the U.S. because of

the lack of suitable flame retardants. Therefore, the flammability of cotton fleece remains as an unsolved problem for the industry.

Multifunctional carboxylic acids have been used as non-formaldehyde durable press finishing agents for cotton since the late 1980s [10]. In our previous research, we studied the esterification mechanism of polycarboxylic acids on cotton and developed new nonformaldehyde durable press finishing systems based on polycarboxylic acids [11-13]. Polycarboxylic acids have been used to reduce the flammability of fleeces of cotton and cotton blends, as reported in the literature [14-15]. We also investigated the use of inorganic phosphate-based compounds, a hydroxyl-functional organophosphorus oligomer in the presence of a bonding agent, and the combination of maleic acid (MA) and NaH_2PO_2 as flame retardant systems to treat cotton fleece [16-18].

Traditionally, poly(maleic acid) was synthesized by free radical polymerization of maleic anhydride in organic solvents to form poly(maleic anhydride), followed by hydrolysis to form poly(maleic acid) [19-20]. More recently, maleic acid (MA) was polymerized in an aqueous solution with a salt of persulfuric acid as the initiator [21-22]. In our previous research, we studied the aqueous polymerization of MA in the presence of a free radical initiator (such as sodium persulfate) and potassium hypophosphite, and the formation of phosphorus-containing maleic acid oligomers (PMAO) [23-24]. Matrix-assisted laser desorption/adsorption mass spectroscopy (MALDI-MS) and nuclear magnetic resonance spectroscopy (NMR) were used to characterize PMAO and to elucidate the polymerization mechanism [24]. The structures and the molecular weight distribution of PMAO, as shown in Scheme 1, were revealed by MALDI-MS and NMR [24]. The major products of aqueous polymerization of MA are PMAO with a degree of polymerization between 3 and 5 ($X+Y=3-5$ in Scheme 1). A salt of hypophosphite, such as

sodium hypophosphite, functions as a chain transfer agent in the polymerization system, and the amount of phosphonate is relatively very small [24]. The PMAO thus synthesized is used as durable press finishing agent for cotton [25].



Scheme 1. Structures of PMAO

The objective of this research was to investigate the effectiveness of PMAO as a flame retardant for cotton fleece in order to develop a commercially feasible, cost-effective, high performance, and non-formaldehyde flame retardant finishing system for cotton fleece.

Experimental

Materials

The cotton fleece with a density of 370 g/m² was supplied by Esquel Group (Gaoming, China). The cotton woven fabric was a desized and bleached plain-weave cotton cloth weighing 109 g/m² (Testfabrics style 400). PMAO was a commercial product (33% concentration) with the trade name “DM-3540” supplied by Dymatic Chemical Corp., Shunde, China. Sodium hypophosphite, succinic acid (SUA) and triethanolamine (TEA) were reagent grade chemicals supplied by Sigma-Aldrich, Milwaukee, Wisconsin.

Fabric Treatment and Home Laundering Procedures

The cotton woven fabric and cotton fleece were first immersed in a finishing solution, then passed through a laboratory padder with two dips and two nips. The cotton woven fabric was dried at 80°C for 2 min and cured in a Mathis oven at 170°C for 2 min. The cotton fleece was dried at 90°C for 4 min and finally cured at 175°C for 4 min. All concentrations presented here were based on weight of bath (w/w %). The wet pick-ups of the cotton woven fabric and cotton fleece were 98±2% and 105±2%, respectively. After treatment, the fabrics were subjected to different numbers of home laundering (HL) washing/drying cycles according to AATCC Method 124. The water temperature for laundering was approximately 46-47°C.

Fabric 45° Flammability Measurement

The 45° flammability of the cotton fleece was measured according to ASTM Method D1230-94. First, the specimen was mounted in a specimen holder, brushed and dried in an oven for 30 min at 105°C, and then moved to a desiccator. After the specimen was kept in the desiccators to cool down for 90 min, it was transferred to the flammability tester (Model TC-45 manufactured by Govmark, Bellmore, New York). The specimen was exposed to a standard butane flame for 1 second to cause ignition, and the burning time and burning characteristics of 5 specimens for each sample were recorded and used as the basis to determine the flammability classifications for the cotton fleece.

Fabric Limiting Oxygen Index (LOI) Measurement

The LOI of the cotton woven fabric was measured according to ASTM Standard Method D2863-08 after the fabric was subjected to one HL cycle.

Micro-scale Combustion Calorimetry (MCC) Measurement

The MCC measurement was performed using a MCC-2 micro-scale calorimeter produced by Govmark, Farmingdale, New York, according to ASTM D7309-2007 (using Method A). The

sample, approximately 5 mg, was heated to 550°C using a linear heating rate of 1°C/sec in a stream of nitrogen flowing at a 80 cm³/min flow rate. The thermal degradation products were mixed with a 20 cm³/min stream of oxygen prior to entering a 900°C combustion furnace. The fabric samples were first ground in a Wiley mill to form homogeneous powders. Each sample was run in three replicates and the data presented here are the averages of the three measurements. The microscale calorimeter provides peak heat release rate (PHRR) and heat release capacity (HRC) data of polymeric samples based on the oxygen consumption, heating rate, flow rate and the sample weight [26]. The units for PHRR and HRC data are w/g and J/(g·K), respectively.

Fabric Bursting Strength Measurement

The bursting strength of cotton fleece was measured according to ASTM D3786-08 using a “Truburst” bursting strength tester manufactured by James H. Heal & Company, Halifax, England. The testing area on a fabric specimen was 100 cm².

Fabric CIE Whiteness Index Measurement

The CIE whiteness index of cotton fleece was measured according to AATCC Method 110, using a “Macbeth Color-Eye” 7000A spectrometer made by Hunter Associates Laboratory.

Determination of Phosphorus Concentration on the Treated Fabrics

Approximately 2 g of a fabric sample taken from three different parts of a treated fabric was ground into a powder using a Wiley mill to improve sample uniformity. Concentrated H₂SO₄ was added to 0.1 g of fabric powder in a beaker, and then 10 ml of 30% H₂O₂ was added dropwise into the beaker, allowing the reaction to subside between drops. The reaction mixture was heated to 250°C to digest the powder and evaporate the water until a dense SO₃ vapor was generated. The completely digested sample as a translucent solution was transferred to a 50 ml

volumetric flask, diluted with de-ionized water. The solution thus prepared was analyzed using a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer to determine the percent concentration of phosphorus on the fabric.

FT-IR Spectroscopy Measurement

A Nicolet 760 Magna FT-IR spectrometer spectroscopy was used to determine the carbonyl band intensity of ester and carboxylate of the treated cotton fabric. The infrared spectra were presented at absorbance mode ($-\log R/R_0$). The resolution for all the infrared spectra was 4 cm^{-1} , and there were 120 scans for each spectrum. The diffuse reflectance spectrum of potassium bromide powder was used as the background. A small piece of a cotton fabric treated, cured and subjected to one HL was first immersed in a 0.1 M NaOH solution for 3 min to convert the free carboxyl groups to carboxylate anions to avoid the overlapping of an ester carbonyl band by a carbonyl band of free acid. The fabric sample thus treated was first dried using a paper towel to absorb excess solution, then further dried at $90\text{ }^\circ\text{C}$ for 10 min, and finally ground in a Wiley mill before it was analyzed by the FT-IR spectrometer to determine the intensities of the ester and carboxylate carbonyl bands. The carbonyl band absorbance in the infrared spectra was normalized against the 1317 cm^{-1} band associated with a C-H bending mode of cellulose. This analytical method was previously discussed in detail [27-28].

Results and Discussion

The Esterification of PMAO on Cotton

The cotton fleece was treated with PMAO and NaH_2PO_2 (mole ratio 2:1) at different concentrations. The pH of all the finishing solutions was adjusted to 2.5 using NaOH. The fabric thus treated was cured at 175°C for 4 min. In order to measure the ester carbonyl band intensity,

the cured fabric was laundered once to remove the unreacted acid and NaH_2PO_2 , dried and then treated with a 0.1 M NaOH solution at room temperature for 3 min to convert the free carboxyl groups on the fabric to carboxylate anions. The infrared spectra of the treated cotton fleece (Figure 1) showed two distinct carbonyl bands at around 1723 cm^{-1} and 1583 cm^{-1} due to the carbonyl stretching modes of ester and carboxylate anions, respectively. The ester carbonyl band intensity of the cotton fleece treated with PMAO is presented as a function of PMAO concentration in Figure 2. The ester carbonyl band increased from 0.13 to 0.49 as the PMAO concentration was increased from 1.0 to 10.0%, indicating an increasing amount of ester formed on the cotton fabric. The infrared spectroscopy data demonstrated that PMAO was able to bond to cotton by esterification with cotton cellulose.

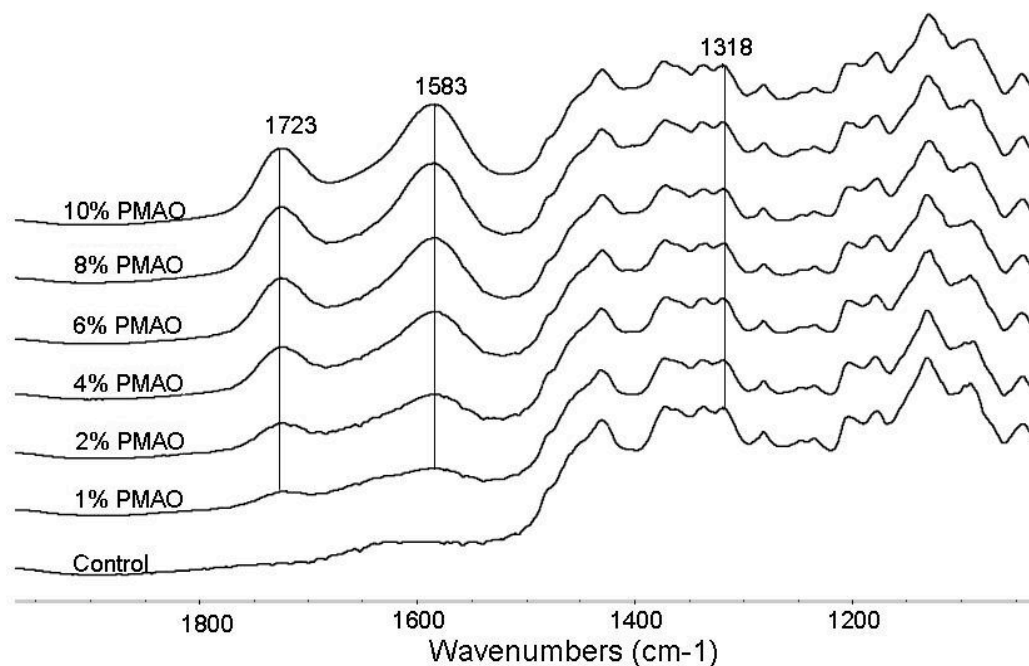


Figure 1. The infrared spectra of the cotton fleece treated with PMAO/ NaH_2PO_2 (mole ratio 2:1) at different concentrations after 1 HL cycle.

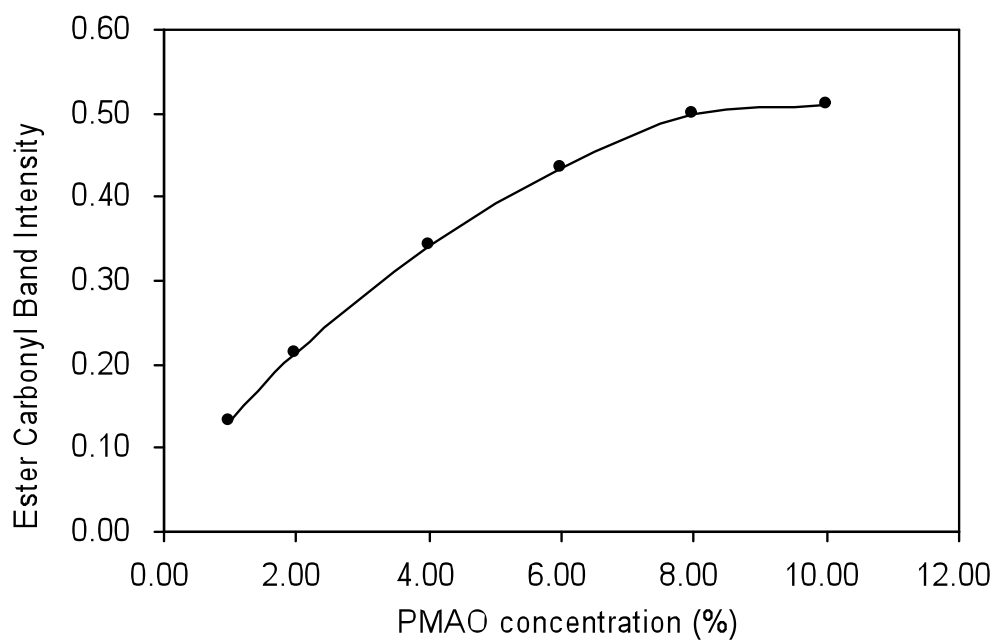


Figure 2. Ester carbonyl band intensity of the cotton fleece treated with PMAO/ NaH_2PO_2 (mole ratio 2:1) at different concentrations after 1 HL cycle.

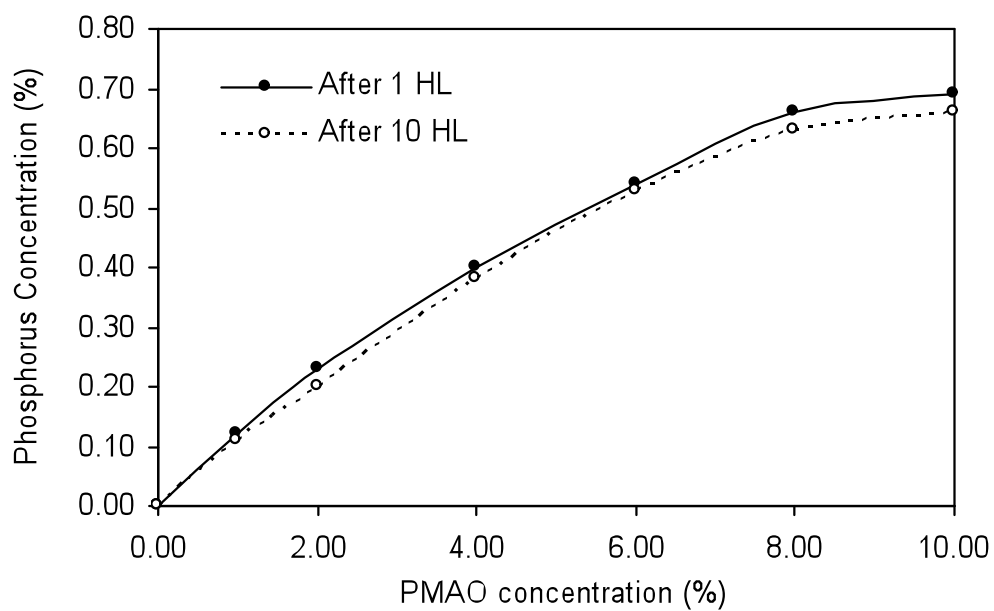


Figure 3. The phosphorus concentration of the cotton woven fabric treated with PMAO/ NaH_2PO_2 (mole ratio 2:1) at different concentrations after different HL cycles.

The phosphorus concentration of cotton woven fabric treated with PMAO and NaH_2PO_2 at different concentrations and subjected to 1 or 10 HL cycles is presented in Figure 3 and the phosphorus concentration ratio (1HL/10HL) is shown in Table 1. The phosphorus concentrations of the treated cotton fabric after 1 HL were very close to those after 10 HL (Figure 3) and the phosphorus concentration ratios (1HL/10HL) were in the range of 87-98% (Table 1). Therefore, the data presented here indicated that the PMAO bound to cotton had good hydrolysis-resistance and was durable to multiple home launderings.

Table 1. The phosphorus concentration ratio (1 HL/10 HL) of the cotton woven fabric treated with PMAO at different concentrations.

PMAO (%)	NaH_2PO_2 (%)	Phosphorus content ratio (1HL/10HL)
1.0	0.5	0.92
2.0	1.0	0.87
4.0	2.0	0.95
6.0	3.0	0.98
8.0	4.0	0.95
10.0	5.0	0.96

The Performance of PMAO as A Flame Retardant for Cotton Fleece

LOI is defined as the minimum percent oxygen in an environment that sustains burning under specific conditions, and is a commonly used quantitative analytical method to measure the flammability of textile materials [29-30]. The LOI (%) data of the cotton woven fabric treated with PMAO and NaH_2PO_2 (mole ratio 2:1) at different concentrations and subjected to 1 HL cycle is shown in Figure 4. The LOI of the untreated cotton woven fabric was 18.0%. It increased to 18.1% when the fabric was treated with 1.00% PMAO, and further increased to 20.5% as the PMAO concentration was increased to 6.00%. The LOI increased slightly to 20.7% as the PMAO concentration was increased to 10.00% (Figure 4). It is evident that the bonding of

PMAO to the cotton fabric reduces the fabric's flammability. Previously, we found that the esterification of polycarboxylic acids containing no phosphorus, such as succinic acid and 1,2,3,4-butanetetracarboxylic acid, with cotton fabric did not increase the LOI of the treated cotton fabric. The significantly increased LOI of the PMAO-treated cotton fabric here is evidently due to the presence of phosphorus on the cotton fabric (Table 1) by the esterification of PMAO.

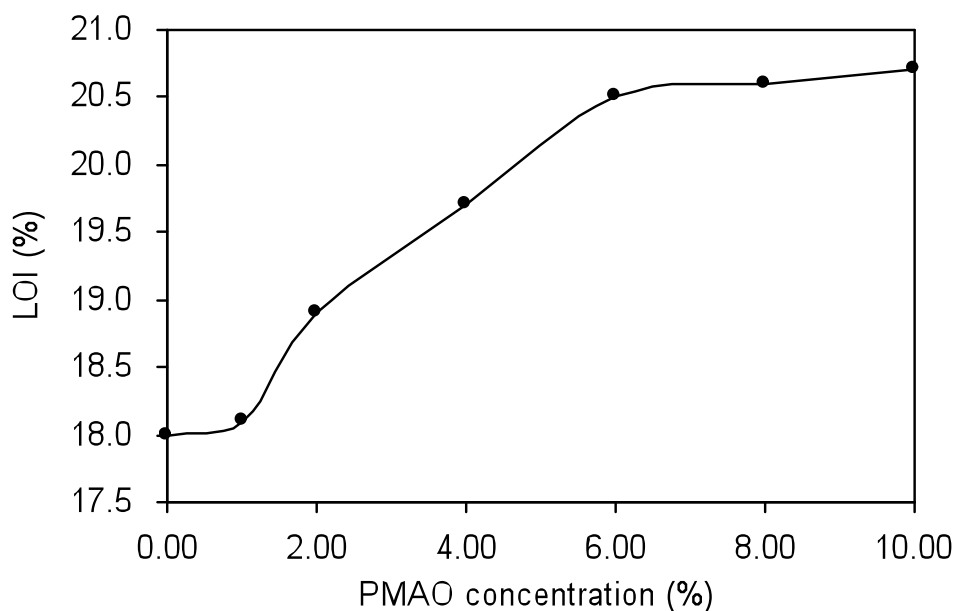


Figure 4. LOI (%) of the cotton woven fabric treated PMAO/ NaH_2PO_2 (mole ratio 2:1) at different concentrations after 1 HL cycle.

We further applied MCC to study the effect of PMAO for reducing the flammability of cotton. The HRC, PHRR, temperature at PHRR (T_{PHRR}), total heat release (THR) and char yield of the cotton woven fabric treated with PMAO were presented in Table 2. Treating the cotton using PMAO reduced the PHRR and HRC of cotton from 246 w/g and 277 J/(g·K) to 172 w/g and 193 J/(g·K), respectively. The T_{PHRR} was decreased from 384 to 354°C and THR was decreased from 10.4 to 7.4 KJ/g. The char yield increased from 5.8% for the untreated cotton to

14.8% for the PMAO-treated cotton (Table 2). Thus, the data presented here indisputably demonstrated that PMAO significantly reduced the flammability and increased the char yield of the treated cotton.

Table 2. The MMC data of the untreated cotton fabric, the cotton fabric treated with 6% PMAO and 3% NaH_2PO_2 , and that treated with 6% SUA and 3% NaH_2PO_2 . Both the treated fabrics were cured at 170°C for 2 min and subjected to 1HL cycle.

Sample description	Cotton untreated	Cotton treated with PMAO	Cotton treated with SUA
HRC [J/(g·K)]	277	193	209
PHRR (w/g)	246	172	184
T_{PHRR} ($^\circ\text{C}$)	384	354	367
THR(KJ/g)	10.4	7.4	9.2
Char yield (%)	5.8	14.8	10.8

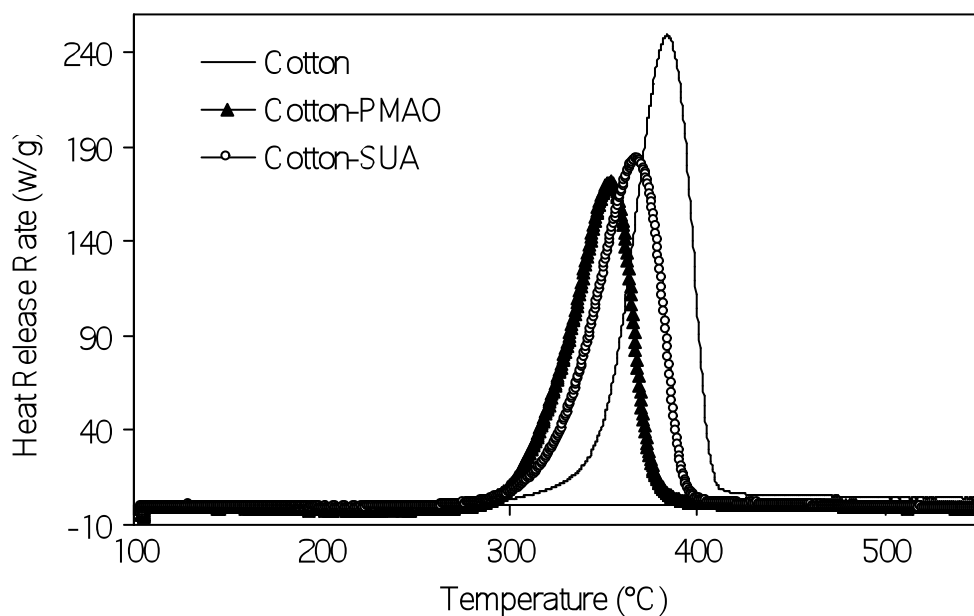


Figure 5. The heat release rate curves of the untreated cotton woven fabric, treated with 6% PMAO and 3% NaH_2PO_2 , treated with 6% SUA and 3% NaH_2PO_2 , and finally subjected to 1 HL cycle.

In our previous research, we discovered that SUA was effective in reducing the flammability of cotton fleece from “Class 3” to “Class 1” [18]. In this research, we used MCC to compare the effectiveness of PMAO and SUA on cotton. The heat release rate curves in Figure 5 indicated that the cotton fabric treated with SUA had a higher PHRR and HRC, higher T_{PHRR} , and lower char yield than that treated with PMAO. Therefore, we can conclude that PMAO is a more effective flame retardant on cotton than SUA. This was probably due to the presence of phosphorus in a PMAO molecule, which enhanced its flame retardancy for cotton.

The 45° flammability of the cotton fleece treated with PMAO at different concentrations and subjected to the combined dry-cleaning/home laundering (DC/HL) procedure is shown in Table 3. The untreated cotton fleece had both surface flash and base burn for all five specimens, and thus failed the 45° flammability test with “Class 3” flammability. At 0.50 and 1.0% PMAO concentrations, the flammability of the treated cotton fleeces remained “Class 3”. When the PMAO concentration was increased up to 2.0% and beyond, the treated cotton fleeces only had surface flash without base burn for all the five specimens for each sample, thus achieving “Class 1” flammability and passing the 16 CFR 1610 federal test.

Table 3. The 45° flammability of cotton fleece treated with PMAO/ NaH_2PO_2 (mole ratio 2:1) at different concentrations and subjected to a DC/HL procedure.

PMAO (%)	NaH_2PO_2 (%)	45° Flammability			
		No. of Spec. SF*	Ave. Burning Time (s)	No. of Spec. BB**	Class
0	0	5	1.2	5	3
0.50	0.25	5	1.3	5	3
1.0	0.50	5	1.3	2	3
2.0	1.0	5	1.3	0	1
4.0	2.0	5	1.2	0	1
6.0	3.0	5	1.3	0	1

Note: *Number of specimens with surface flash only; **number of specimens with both surface flash and base burn.

In our previous research on the use of HFPO and 1, 2, 3, 4-butanetetracarboxylic acid (BTCA) as a flame retarding system on cotton and cotton/nomex blend, we investigated the use of TEA as a reactive additive for the system to improve its performance. We found that by bonding cotton cellulose through its esterification with BTCA, TEA enhanced the flame retarding performance of HFPO by providing synergistic nitrogen [31-33]. In this research, we also evaluated the effect of TEA in the PMAO system. The cotton fleece was treated with PMAO/TEA/NaH₂PO₂ (mole ratio: 2:1:1) at different concentrations. Shown in Table 4 is the 45° flammability of the treated cotton fleece and subjected to the DC/HL procedure.

Table 4. The 45° flammability of cotton fleece treated with PMAO/TEA/NaH₂PO₂ (mole ratio 2:2:1) at different concentrations and subjected to a DC/HL procedure.

PMAO (%)	TEA (%)	NaH ₂ PO ₂ (%)	45° Flammability			
			No. of Spec. SF	Ave. Burning Time (s)	No. of Spec. BB	Class
0	0	0	5	1.2	5	3
0.50	0.50	0.25	5	1.4	3	3
1.0	1.0	0.50	5	1.2	0	1
2.0	2.0	1.0	5	1.1	0	1
4.0	4.0	2.0	5	1.1	0	1
6.0	6.0	3.0	5	1.1	0	1

The fleece treated with 0.50% PMAO and 0.25% TEA remained “Class 3”. The cotton fleece treated with 1.0% PMAO and 0.50% TEA passed the 45° flammability test and achieved “Class 1” flammability. Without TEA, the cotton fleece treated with 1.0% PMAO had only “Class 3” flammability (Table 3). The data presented here indicated that TEA as a reactive additive did improve the flame retarding performance of PMAO and further reduced the flammability of the treated cotton fleece, probably because the nitrogen of TEA enhanced the flame retardant performance of PMAO on cotton.

The Physical Properties of the Treated Cotton Fleece

The bursting strength and whiteness index of the cotton fleece treated with PMAO/TEA, which passed the 16 CFR 1610 tests, are presented in Table 5. The bursting strength and whiteness index of the cotton fleece without treatment were 238.6 kgf and 96, respectively. When the fleece was treated with 1.0% PMAO/TEA, the bursting strength and the whiteness index decreased slightly to 219.6 kgf (92% retention) and 95, respectively. As the PMAO concentration increased to 2.0%, the bursting strength was modestly reduced to 217.4 kgf (91% retention), while the white index remained the same (Table 5). The cotton fleece treated with 2.0% PMAO and TEA showed slightly decrease in the bursting strength and whiteness index (213.9 kgf and 93, respectively). Apparently, the cotton fleece treated with POMA/TEA achieved “Class 1” flammability with limited changes in its strength and whiteness.

Table 5. The bursting strength and whiteness index of the cotton fleece treated with PMAO/TEA/NaH₂PO₂ at different concentrations and subjected to a DC/HL procedure

PMAO (%)	TEA (%)	NaH ₂ PO ₂ (%)	Bursting Strength (kgf)	Whiteness Index (CIE)
0	0	0	238.6	96
1.0	1.0	0.5	219.6	95
2.0	0	1.0	217.4	95
2.0	2.0	1.0	213.9	93

Conclusions

(1) The esterification of cotton cellulose by PMAO successfully bonds phosphorus to cotton fabric and reduces the fabric’s flammability. The bonding of PMAO to cotton is hydrolysis-resistant.

(2) PMAO is an effective flame retardant agent for cotton fleece. The cotton fleece treated with PMAO is able to achieve the 16 CFR 1610 “Class 1” standard. The MCC data

proves that PMAO is more effective in reducing the flammability of cotton than SUA as indicated by more significant reduction in PHRR and HRC of the treated fleece. The use of TEA as an additive modestly enhances the performance of PMAO on cotton fleece.

(3) Both the applications of the PMAO and PMAO/TEA systems cause limited changes in strength and whiteness of the cotton fleece.

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CHAPTER 4**FLAME RETARDANT FINISHING OF COTTON FLEECE FABRIC: PART VI. THE
COMBINATION OF A HYDROXYL-FUNCTIONAL ORGANOPHOSPHORUS
OLIGOMER AND 1,2,3,4-BUTANETETRACARBOXYLIC ACID**

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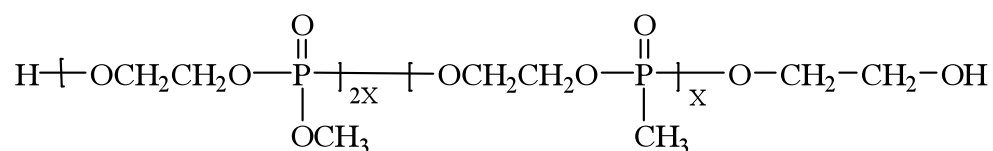
Abstract

The use of flame retardant finishing becomes necessary for cotton fleece to pass the U.S. government regulation “Standard for the Flammability of Clothing Textiles” (16 CFR 1610). The objective of this research was to reduce the flammability of cotton fleece using a flame retardant finishing system consisting of a hydroxyl-functional organophosphorus oligomer (HFPO) as a flame retardant and 1,2,3,4-butanetetracarboxylic acid (BTCA) as a bonding agent. We investigated the role triethanolamine (TEA) played as a reactive additive in the HFPO/BTCA finishing system on cotton fleece. We also applied micro-scale calorimeter (MCC) to study the effectiveness of HFPO and BTCA in reducing the flammability of cotton. BTCA alone was able to reduce the peak heat release rate (PHRR) of cotton as demonstrated by the MCC data. Combining BTCA with HFPO decreased PHRR further and also significantly reduced the decomposition temperature and the temperature at PHRR of cotton. The cotton fleece treated with HFPO/BTCA/TEA passed the federal regulation (16 CFR Part 1610) and achieved “Class 1” flammability. The treated cotton fleece was durable to multiple home laundering cycles. The use of TEA enhanced the performance of HFPO/BTCA and the treatment caused no significant changes in fabric physical properties.

Keywords: *cotton, fleece, hydroxyl-functional organophosphorus oligomer, 1, 2, 3, 4-butanetetracarboxylic acid, triethanolamine.*

Introduction

Cotton fleece is a popular fashion because of its appealing properties. However, it also has high flammability due to its fuzz surface and loose structure. The high flammability of cotton fleece is the major obstacle for wide uses of cotton fleece by the consumers. Without chemical treatment, cotton fleece is not able to meet the U.S. federal flammability standard (“16 CFR Part 1610: Standard for the Flammability of Clothing Textiles”), therefore it can not be sold in U.S. legally [1-4].



Scheme 1. HFPO

In our previous study, we developed a flame retardant finishing system based on a hydroxyl-functional organophosphorus oligomer (HFPO), shown in Scheme 1, in the presence of a bonding agent, such as dimethyloldihydroxyethyleneurea (DMDHEU), trimethylolmelamine (TMM) and 1,2,3,4-butanetetracarboxylic acid (BTCA), for cotton and cotton blends [5-8]. We also successfully applied the combination of HFPO and DMDHEU as a durable flame retardant finishing system for cotton fleece [9]. The treated cotton fleece achieved “Class 1’ flammability with high strength retention and little changes in fabric whiteness and hand. However, the DMDHEU used in the flame retardant system is a formaldehyde-based reagent, which must be considered as a major disadvantage because World Health Organization has classified formaldehyde as a carcinogen for human [10].

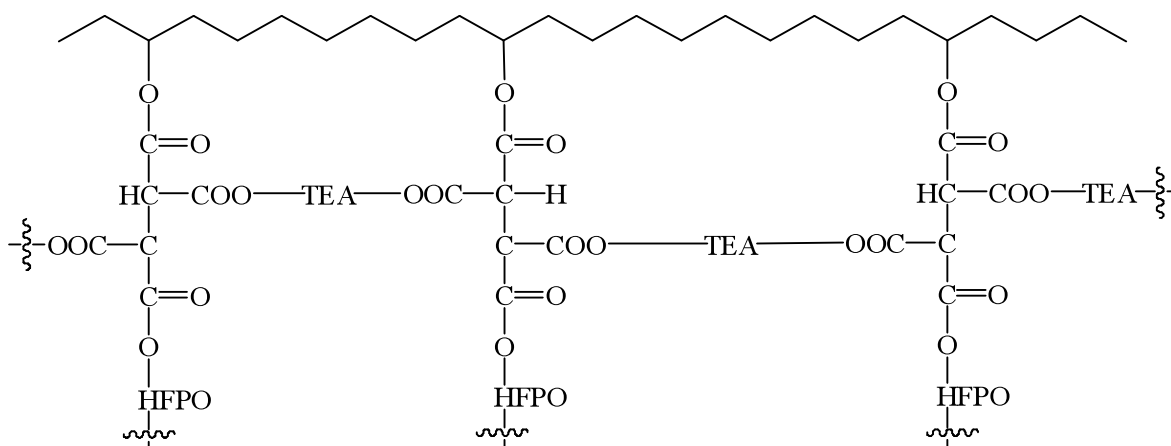
The applications of polycarboxylic acids as the flame retardants on cotton carpet and cotton/polyester blend fleece were reported previously [11-12]. BTCA has been known as the

most effective non-formaldehyde durable press agent for cotton [13-14]. BTCA, shown in Scheme 2, has four carboxylic acid groups and is able to form multiple ester-linkages with cotton cellulose when sodium hypophosphite is used as the catalyst [15-16]. In the presence of HFPO, BTCA is able to form a bridge between cotton and HFPO by esterifying both the hydroxyl group of cellulose and that of HFPO [9]. Thus, HFPO can be bound to cotton using a non-formaldehyde bonding agent.



Scheme 2. BTCA and TEA

The major disadvantage of using BTCA as the bonding agent for HFPO system is that BTCA does not have synergistic nitrogen to enhance the flame retardant performance of HFPO [8]. When the HFPO/BTCA system was applied to the Nomex/cotton military blend, we used triethanolamine (TEA), shown in Scheme 2, as a reactive co-reactant recently [17]. We discovered that TEA formed a crosslinked network on the Nomex/cotton blend by its esterification with the free carboxylic acid groups of the BTCA bound to cotton (Scheme 3), thus improved the hydrolysis resistance of the HFPO/BTCA on the fabric in addition of providing the synergistic nitrogen [17].



Scheme 3. Formation of HFPO/BTCA/TEA crosslinked network on cotton

The objective of this research was to investigate the use of HFPO/BTCA/TEA system to reduce the flammability of cotton fleece, and the roles TEA played as a reactive additive in the flame retardant system on cotton.

Experimental

Materials

The cotton fleece with a density of 370 g/m^2 was supplied by Esquel Group (Gaoming, China). The cotton woven fabric was a desized, scoured and bleached plain-weave cotton cloth weighing 109 g/m^2 (Testfabrics style 400). HFPO with the trade name of ‘Fyroltex HP’ (also known previously as ‘Fyrol 51’, CA Registry No. 70715-06-9) was supplied by Akzo Nobel Functional Chemicals, Dobbs Ferry, New York. BTCA, sodium hypophosphite and TEA were reagent grade chemicals supplied by Sigma-Aldrich, Milwaukee, Wisconsin.

Fabric treatment and home laundering procedures

The cotton woven fabric and cotton fleece were first immersed in a solution, then passed through a laboratory padder with two dips and two nips. The cotton woven fabric was dried at

80°C for 2 min and cured in a Mathis oven at 170°C for 2 min. The cotton fleece was dried at 90°C for 4 min and finally cured at 175°C for 4 min. All concentrations presented here were based on weight of bath (w/w %). In all the solutions, the BTCA/NaH₂PO₂ maintained a constant 2:1 (w/w) ratio. The wet pick-up of the cotton woven fabric and cotton fleece was 98±2% and 105±2%, respectively. After treatment, the fabrics were subjected to different numbers of home laundering (HL) washing/drying cycles according to AATCC Method 124. The water temperature for laundering was approximately 46-47°C.

Fabric 45° flammability measurement

The 45° flammability of the cotton fleece was measured according to ASTM Method D1230-94. A specimen was first mounted in a holder, brushed and then dried in an oven at 105°C for 30 min. Immediately after its drying, the specimen was moved to the desiccators and kept there to cool down for 90 min. It was then transferred to the 45° angle flammability tester (Model TC-45 manufactured by Govmark, Bellmore, New York). The specimen was exposed to a standard butane flame for 1 second to cause ignition. The burning time and burning characteristics (surface flash or base burn) of 5 specimens were recorded and used as the basis to determine the flammability classifications for the cotton fleece.

Fabric Limiting Oxygen Index (LOI) Measurement

The LOI of the cotton woven fabric was measured according to ASTM Standard Method D2863-97 after the fabric was subjected to one HL cycle.

Micro-scale Combustion Calorimetry (MCC) Measurement

The MCC measurement was performed with a Govmark MCC-2 micro-scale calorimeter produced by Govmark, Farmingdale, New York, according to according to the ASTM D7309-2007 (Method A). A sample (approximately 5 mg) was heated to 550°C using a linear heating

rate of 1°C/sec in a stream of nitrogen flowing at 80 cm³/min. The sample's thermal degradation products in the nitrogen gas stream were mixed with a 20 cm³/min stream of oxygen prior to entering a 900°C combustion furnace. The fabric samples were first ground in a Wiley mill to form homogeneous powders. Each sample was run in three replications and the data presented here are all the averages of the three measurements. The micro-scale calorimeter is able to provide peak heat release rate (PHRR) and heat release capacity (HRC) data of the polymeric sample based on the oxygen consumption, heating rate of the sample, flow rate and the sample weight [18].

Fabric Bursting Strength Measurement

The bursting strength of cotton fleece was measured according to ASTM D3786-08 using the tester manufactured by B. F. Perkins, Holyoke Mass, U.S.A. The testing area on a fabric specimen was 7.3 cm².

Fabric CIE Whiteness Index Measurement

The CIE whiteness index of cotton fleece was measured according to AATCC Method 110, using a "Macbeth Color-Eye" 7000A spectrometer made by Hunter Associates Laboratory.

Wrinkle Recovery Angle (WRA)

The WRA of cotton woven fabric was measured according to AATCC Standard Method 66-1990.

Determination of Phosphorus Concentration on the Treated Fabrics

Approximately 2 g of a fabric sample taken from three different parts of a treated fabric was ground into a powder using a Wiley mill to improve sample uniformity. Concentrated H₂SO₄ was added to 0.1 g of fabric powder in a beaker, and 10 ml of 30% H₂O₂ was added drop wise into the beaker, allowing the reactions to subside between drops. The reaction mixture was

then heated up to 250°C to digest the powder and to evaporate the water until a dense SO₃ vapor was generated. The completely digested sample as a translucent solution was transferred to a 50 ml volumetric flask, and then diluted with de-ionized water. The sample thus prepared sample was analyzed using a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the percent concentration of phosphorus on the fabric.

FT-IR Spectroscopy Measurement

A Nicolet 760 Magna FTIR spectrometer with a diffuse reflectance accessory was used to analyze the ester group of the treated cotton woven fabric. All the diffuse reflectance infrared spectrum were presented at absorbance mode ($-\log R/R_0$). The resolution for all the infrared spectra was 4 cm⁻¹, and there were 120 scans for each spectrum. The diffuse reflectance spectrum of potassium bromide powder was used as the background. A 2 cm by 2 cm piece taken from a larger treated and cured cotton fabric specimen subjected to one HL cycle was first immersed in a 0.1 M NaOH solution for 3 min to convert the free carboxyl groups to carboxylate anion to avoid the overlapping of an ester carbonyl band by a carbonyl band of free acid. The fabric sample thus treated was dried first using paper towel to absorb excess solution, then in a oven at 90 °C for 10 min, and the completely dried sample was ground in a Wiley mill before it was analyzed by the FT-IR spectrometer. The carbonyl band absorbance in the infrared spectra was normalized against the 1317 cm⁻¹ band associated with a C-H bending mode of cellulose. This analytical method was discussed in details previously [19-20].

Results and Discussion

Bonding of HFPO to Cotton and the Role of TEA

We first studied the chemical reaction on the cotton woven fabric treated with 12.0% HFPO, 4.0% BTCA and TEA at different concentrations. The pH of all the finishing solutions was adjusted to 2.5 using NaOH. The fabric thus treated was cured at 170°C for 2 min and subjected to HL cycle. The cotton fabric thus treated was rinsed using a 0.1 M NaOH solution at room temperature for 3 min to convert the free carboxyl groups on the fabric to carboxylate anions, and the ester carbonyl band intensity of the treated cotton fleece was presented as a function of TEA concentration in Figure 1. The data show that the ester carbonyl band intensity decreased from 0.56 to 0.48 as the TEA concentration was increased from 0 to 6.0% (Figure 1), indicating the total amount of the ester formed on the cotton fabric decreases when the concentration of TEA was increased.

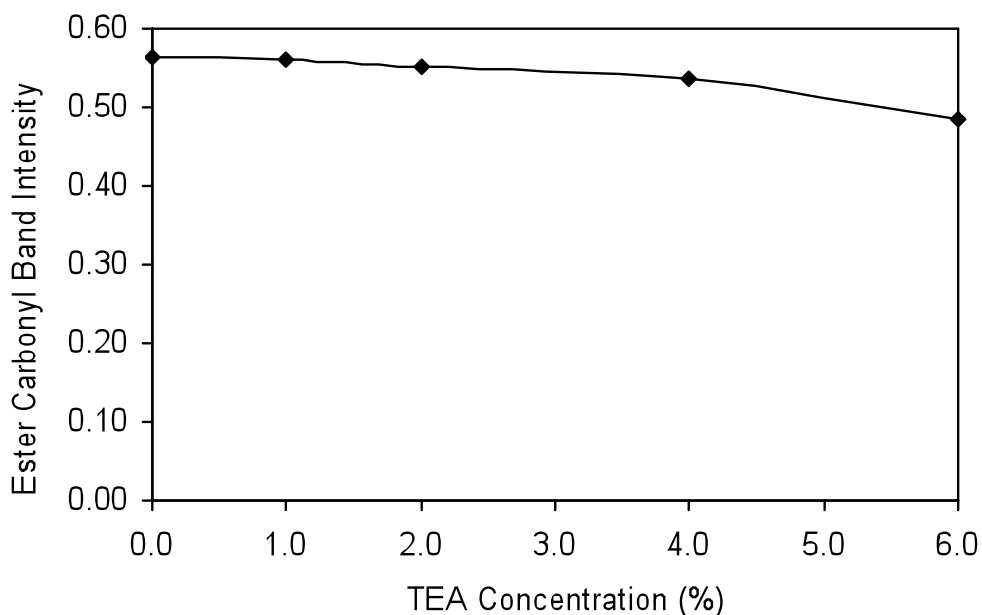


Figure 1. The ester carbonyl band intensity of the cotton woven fabric treated with 12.0% HFPO, 4.0% BTCA and TEA at different concentrations and subjected to one HL cycle.

HFPO, TEA and cotton cellulose have hydroxyl groups and all are able to esterify the BTCA applied to cotton under the curing condition, therefore an increase in the TEA concentration resulted in an increase in the esterification of TEA and a decrease in the esterification of cotton. Because the amount of the ester retained on the cotton fabric after laundering depends on the esterification of cotton by BTCA, the amount of ester on the cotton fabric decreased consequently at higher TEA concentrations as shown in Figure 1.

Table 1. WRA of the cotton woven fabric treated with 12.0% HFPO, 4.0% BTCA and TEA at different concentrations, cured and subjected to one HL cycle.

HFPO (%)	BTCA (%)	TEA (%)	WRA (W+F, °)
12.0	4.0	1.0	255
12.0	4.0	2.0	254
12.0	4.0	4.0	228
12.0	4.0	6.0	221

The WRA of the cotton fabric treated with HFPO, BTCA and TEA at different concentrations and subjected to one HL cycle is presented in Table 1. The WRA of the treated cotton decreased from 255 to 221° as the TEA concentration increased from 1.0 to 6.0% (Table 1). BTCA had four carboxylic acid groups bound to the adjacent carbons in its molecular backbone. Therefore it was able to form a 5-membered cyclic anhydride intermediate that can be esterified by cotton cellulose [15]. The ester crosslinking of cotton by BTCA imparted wrinkle-resistance to cotton fabrics [21]. The decrease in WRA shown in Table 1 was due to the increasing esterification of BTCA by TEA at higher TEA concentrations and consequently the decrease in the esterification and the crosslinking of cellulose by BTCA. This observation was consistent with the decrease in the total ester at higher TEA concentration discussed above.

The phosphorus concentration of the cotton fabric treated with HFPO, BTCA and TEA at different concentrations and subjected to one HL cycle was presented in Figure 2. The phosphorous content decreased from 1.1 to 0.50% as the TEA concentration increased from 0 to 6.0%. An increasing amount of TEA on the cotton fabric resulted in the decrease in the amount of phosphorus bound to the cotton fabric because both TEA and HFPO were hydroxyl-functional compounds, and they competed to esterify BTCA.

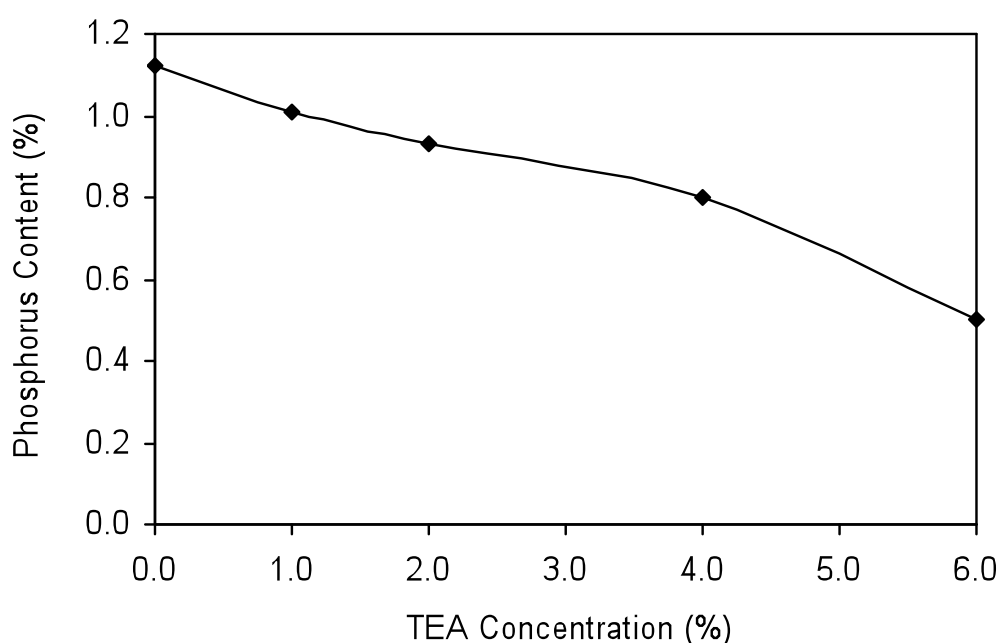


Figure 2. The phosphorus concentration of the cotton woven fabric treated with 12.0% HFPO, 4.0% BTCA and TEA at different concentrations and subjected to one HL cycle.

The LOI data of the cotton fabric treated with 12% HFPO, 4.0% BTCA, 2.0% NaH_2PO_2 and TEA at different concentrations before and after one HL cycle was shown in Figure 3. Before laundering, the LOI of the treated fabric increased from 25.5 to 27.2% as the TEA increased from 0 to 6.0%. Since the treated cotton fabric was not washed and the only difference among those samples with different LOI were the TEA concentration, the increase in LOI value

was evidently due to the increase in the nitrogen content on those fabric samples as a result of higher TEA concentrations used in the HFPO/BTCA/TEA formulas. Thus, the data presented in Figure 3 proved that TEA provided synergistic nitrogen to enhance the flame retarding performance of HFPO.

The LOI data of the cotton fabric treated and subjected to one HL cycle shown in Figure 3 demonstrated a different trend. The decrease in LOI was due to the removal of HFPO, BTCA and TEA not bound to cotton as well as the removal of the catalyst (NaH_2PO_2). The LOI first increased from 21.4 to 22.0% as the TEA concentration increased from 0 to 2.0%, then decreased to 20.2% as the TEA concentration further increased to 6.0% (Figure 3). The change in LOI of the treated cotton fabric after laundering reflects the two conflicting influences of TEA on the flammability of the treated cotton.

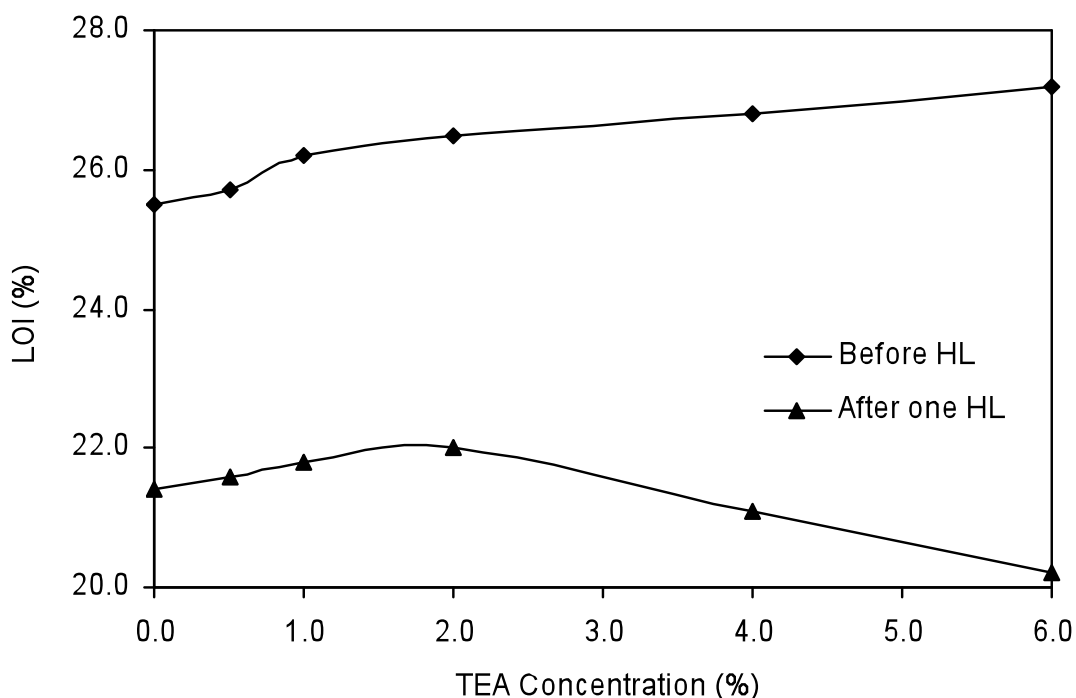


Figure 3. LOI (%) of the cotton woven fabric treated with 12.0% HFPO, 4.0% BTCA and TEA at different concentrations with and without one HL cycle.

The first increase in LOI from 21.4 to 22.0% indicates that when the TEA concentration is low, its positive effect of providing synergistic to the HFPO system predominated. The decreases in LOI at higher TEA concentrations revealed that as the TEA concentration became higher than 2.0%, TEA's negative effect of reducing the HFPO bound to cotton by competing with HFPO to esterify cotton cellulose outweighed its positive effective and consequently the LOI of the treated fabric decreased as shown in Figure 3. Therefore, the data prove that the optimization of TEA concentration in the finishing system is necessary, and the use of TEA can improve the effectiveness of HFPO as a flame retardant system for cotton after the optimization.

The Flammability of the Cotton Fleece Treated with HFPO/BTCA/TEA

The 45° flammability of the cotton fleece treated with HFPO/BTCA/TEA at different concentrations and subjected to different refurbishing procedures was shown in Table 2. The cotton fleece without treatment had both surface flash and base burn for all the five specimens, thus failed the 45° flammability test with “Class 3” flammability. The fleece treated at 3.0% HFPO and 1.0% BTCA remained “Class 3” flammability after subjected to either one HL cycle or the combined dry-clean/home laundering (DC/HL) procedure. By adding 0.5% TEA, the cotton fleece treated at 3.0% HFPO and 1.0% BTCA passed the 45° flammability test and achieved “Class 1” flammability (Table 2). When the HFPO concentration was increased to 6.0 and 9.0%, all the treated cotton fleece passed the 16 CFR 1610 test and achieved “Class 1” flammability (Table 2). The data demonstrated that the HFPO/BTCA system was effective in reducing the flammability of cotton fleece and the use of TEA improved the flame retardant performance of the HFPO/BTCA system.

Table 2. The 45° flammability of cotton fleece treated with different concentrations of HFPO/BTCA/NaH₂PO₂ (mole ratio 6:2:1) with or without TEA after DC/HL procedure.

HFPO (%)	BTCA (%)	TEA (%)	Refurbishing	45° Flammability			
				No. of Spec. SF*	Ave. Burning Time (s)	No. of Spec. BB**	Class
0	0	0	1 HL [§]	5	1.2	5	3
			1 DC/HL [§]	5	1.1	5	3
3.0	1.0	0	1 HL	5	1.3	2	3
			1 DC/HL	5	1.1	2	3
3.0	1.0	0.5	1 HL	5	1.1	0	1
			1 DC/HL	5	1.4	0	1
6.0	2.0	1.0	1 HL	5	1.1	0	1
			1 DC/HL	5	1.1	0	1
9.0	3.0	1.5	1 HL	5	1.1	0	1
			1 DC/HL	5	1.1	0	1

*Number of specimen with surface flash only; **Number of specimen with both surface flash and base burn; [§] HL: home laundering, DC/HL: the combination of dry-clean and home laundering.

We applied MCC to study quantitatively the effect of HFPO and BTCA on the flammability of cotton. The cotton woven fabric was treated with BTCA and the combination of BTCA and HFPO at two different concentration levels. The HRC and PHRR of the cotton fabric thus treated were presented in Table 3 and the PHRR versus temperature curves were shown in Figures 4 and 5.

The HRC and PHRR of the untreated cotton were 277 J/(g·K) and 246 (w/g), respectively. When the cotton fabric was treated with 2.0% BTCA, the HRC and PHRR of the treated cotton decreased to 233 J/(g·K) and 210 (w/g), respectively. When the cotton fabric was treated with 3.0% BTCA, the HRC and PHRR decreased further to 206 J/(g·K) and 185 (w/g), respectively (Table 3). The MCC data clearly revealed that treating cotton with BTCA alone reduced the flammability of cotton. The temperature at PHRR for untreated cotton was also

reduced from 384 °C modestly to 378 and 376°C after the cotton fabric was treated with 2.0 and 3.0% BTCA, respectively.

Table 3. The HRC and PHRR of the untreated cotton fabric and the cotton fabric treated with different concentrations of HFPO/BTCA/NaH₂PO₂ after 1 HL cycle.

HFPO (%)	BTCA (%)	HRC [J/(g·K)]	PHRR (w/g)
0	0	277	246
0	2.0	233	210
6.0	2.0	197	176
0	3.0	206	185
9.0	3.0	163	146

We also observed that when the fabric treated with 2.0% BTCA and additional 6.0% HFPO, the HRC and HRR of the fabric thus treated were decreased from 233 J/(g·K) and 210 (w/g) to 197 J/(g·K) and 176 (w/g) respectively (Table 3). A similar trend was also observed when 9.0% HFPO was added to 3.0% BTCA for the treatment of the cotton fabric. Thus, the data presented here demonstrated that the flammability of the cotton was further reduced when the HFPO is used together with BTCA to the treatment. We also observed that the adding of HFPO to BTCA had an even more drastic impact on reducing the decomposition temperature of cotton in Figures 4 and 5. Adding 6.0% HFPO to 2.0% BTCA reduced the temperature at PHRR by 54°C (from 378 to 324°C), and the adding 9.0% HFPO to 3.0% BTCA reduced the temperature at PHRR by 65°C (from 376 to 311°C).

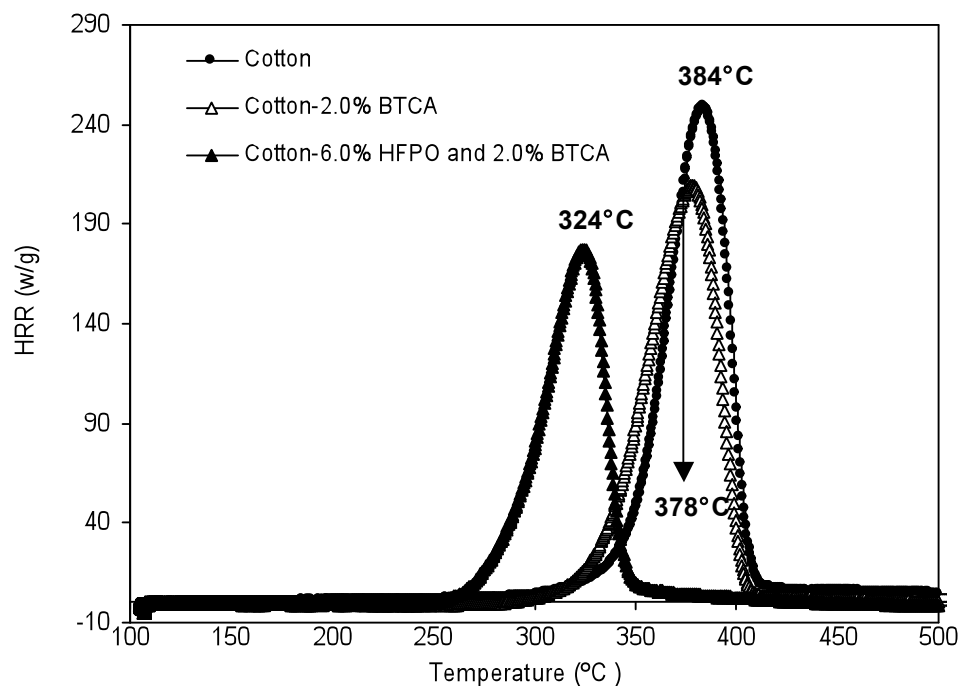


Figure 4. The HRR curves of the untreated cotton woven fabric, and the cotton woven fabric treated with 2.0% BTCA, and that treated with 6.0% HFPO and 2.0% BTCA (after one HL cycle).

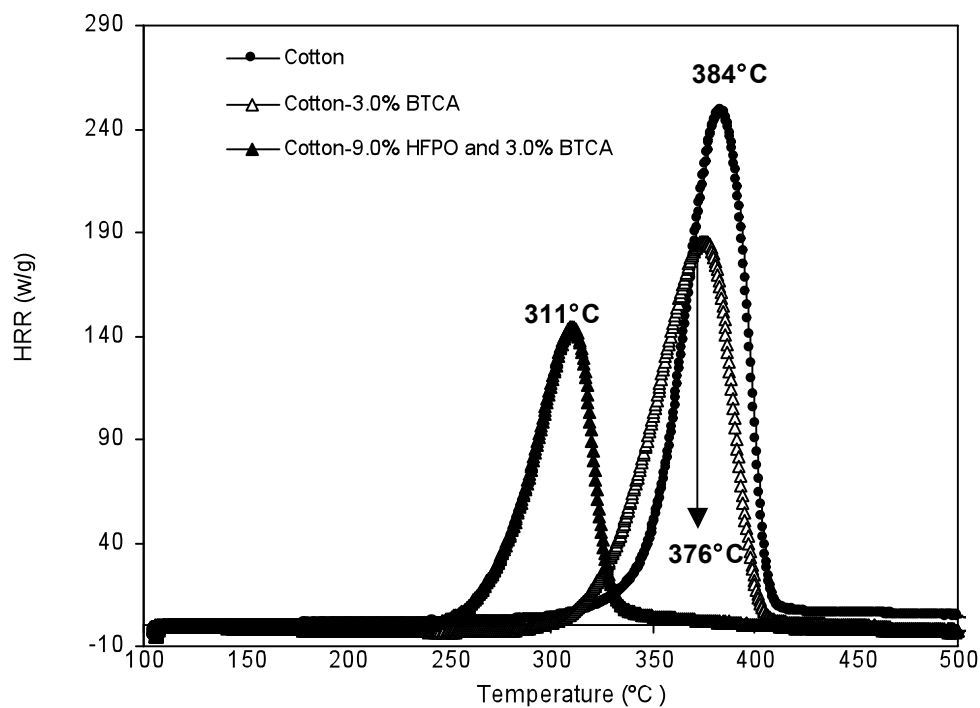


Figure 5. The HRR curves of untreated cotton woven fabric, the cotton woven fabric treated with 3.0% BTCA, and that treated with 9.0% HFPO and 3.0% BTCA (after one HL cycle).

We investigated the durability of the treated cotton fleece to multiple HL cycles (Table 4). The 45° flammability of the cotton fleece treated with HFPO/BTCA/TEA at different concentration levels after multiple HL cycles was presented in Table 4. The cotton fleece treated with 3.0% HFPO, 1.5% BTCA and 0.5% TEA maintained “Class 1” flammability, but failed the test after 10 HL cycles with all the five specimens having both surface flash and base burn, whereas the cotton fleece treated with 6.0% HFPO, 3.0% BTCA and 1.0% TEA remained to have “Class 1” flammability after 10 HL cycles (Table 4). Therefore, higher concentration was necessary to ensure the treated cotton fleece retaining the “Class 1” flammability after higher number of laundering cycles.

Table 4. The 45° flammability of cotton fleece treated with HFPO/BTCA/TEA at different concentrations and subjected to multiple HL cycles.

HFPO (%)	TEA (%)	HL cycles	45° Flammability			
			No. of Spec. SF*	Ave. Burning Time (s)	No. of Spec. BB**	Class
3.0	0.5	1 HL [§]	5	1.1	0	1
		1 DC/HL [§]	5	1.4	0	1
		5 HL	5	1.2	0	1
		10 HL	5	1.3	5	3
6.0	1.0	1 HL	5	1.1	0	1
		1 DC/HL	5	1.1	0	1
		5 HL	5	1.2	0	1
		10 HL	5	1.3	0	1

We studied the phosphorus concentration of cotton woven fabric treated with HFPO/BTCA/TEA (weight ratio 6/2/1) at two concentration levels after the treated fabric was subjected to 1, 5 and 10 HL cycles (Table 5). The phosphorus concentration ratio (10HL/1HL) of the fabric treated with 3.0% and 6.0% HFPO was 67% and 78%, respectively. One also observed that phosphorus concentration ratio (10HL/5HL) of the fabric thus treated in the range

of 90-92%. Therefore, the data indicated that the HFPO bound to cotton had good hydrolysis-resistance on the cotton fabric.

Table 5. Phosphorus concentration of the cotton woven fabric treated with HFPO/BTCA/TEA and subjected to different HL cycles.

HFPO (%)	TEA (%)	No. of HL cycles	Phosphorus Concentration (%)
3.0	0.5	1	0.18
		5	0.13
		10	0.12
6.0	1.0	1	0.46
		5	0.40
		10	0.36

The Physical Properties of the Treated Cotton Fleece

The stiffness, CIE whiteness index and bursting strength of the cotton fleece treated with HFPO/BTCA/TEA were shown in Table 6. Previously, the data presented already indicated that the cotton fleece treated with 3.0 and 6.0% HFPO passed the 16 CFR 1610 flammability test (Table 4). The stiffness of the untreated cotton fleece was 472 mg·cm, whereas it became 475 mg·cm when the fleece was treated with 3.0% HFPO. The stiffness became 453 and 458 mg·cm after the fleece was treated with 6.0 and 9.0% HFPO, respectively. Apparently, the treatment caused very little decrease in the softness of the cotton fleece.

The CIE whiteness index was 96 and 95 for the untreated cotton fleece before and after one HL cycle, respectively (Table 6). After the treatment, it was still in the range of 95-96, indicating no change in the whiteness of the treated fleece.

The bursting strength of the untreated fabric was the highest: 9.1 kgf/cm², and it became 6.3 kgf/cm² after the fleece was treated with 3.0% HFPO, representing 69% retention of the original strength (Table 6). One observed that the strength retention of the treated fleece increased as the HFPO concentration was increased. It was increased to 80% when HFPO

concentration was increased to 9.0%. The improved fabric strength at higher HFPO concentration was probably due to the reduced crosslinking of cotton when both the HFPO and TEA concentration were increased. The reduction in the fabric bursting strength by 20-30% caused by the treatment represented the acceptable strength loss for the flame retardant finishing procedure.

Table 6. The stiffness, CIE whiteness index and bursting strength of the cotton fleece treated with HFPO/BTCA/TEA.

HFPO (%)	TEA (%)	Stiffness (mg·cm)		CIE whiteness Index		Bursting strength (kgf/cm ²)	Bursting strength retention (%)
		Measured	Standard derivation	Before HL	After 1 HL		
0	0	472	3.6	96	95	9.1	-
3.0	0.5	475	4.2	95	95	6.3	69
6.0	1.0	453	0.7	95	96	6.5	71
9.0	1.5	458	1.3	95	96	7.3	80

Conclusions

(1) The MCC data proved that BTCA by itself was able to reduce the flammability of cotton, and the treating cotton fabric with the combination of HFPO and BTCA further decreased cotton's flammability and it also caused a significant reduction in the temperature at PHRR and the decomposition temperature.

(2) The combination of HFPO and BTCA was effective in reducing the flammability of cotton fleece to achieve the "Class 1" flammability. The addition of TEA as a reactive additive was able to enhance the performance of HFPO/BTCA upon the optimization of TEA concentration. TEA provided synergistic nitrogen, but it also competes with HFPO and cellulose

to esterify BTCA, thus reduces the bonding of HFPO onto cotton. The treatment using HFPO/BTCA/TEA is durable to multiple home launderings.

(3) The application of HFPO/BTCA/TEA causes limited fabric strength loss whereas it caused no change in fabric stiffness and whiteness of the treated cotton fleece.

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CHAPTER 5

CONCLUSIONS

Phosphorus-containing maleic acid oligomers flame retardant finishing system

(1) The esterification of cotton cellulose by PMAO successfully bonds phosphorus to cotton fabric and reduces the fabric's flammability. The bonding of PMAO to cotton is hydrolysis-resistant.

(2) PMAO is an effective flame retardant agent for cotton fleece. The cotton fleece treated with PMAO is able to achieve the 16 CFR 1610 "Class 1" standard. The MCC data proves that PMAO is more effective in reducing the flammability of cotton than SUA as indicated by a more significant reduction in PHRR and HRC of the treated fleece. The use of TEA as an additive modestly enhances the performance of PMAO on cotton fleece.

(3) Both the applications of the PMAO and PMAO/TEA systems cause limited changes in strength and whiteness of the cotton fleece.

Hydroxyl-functional organophosphorus oligomers flame retardant finishing system

(1) The MCC data proved that BTCA by itself was able to reduce the flammability of cotton, and the treating cotton fabric with the combination of HFPO and BTCA further decreased cotton's flammability and it also caused a significant reduction in the temperature at PHRR and the decomposition temperature.

(2) The combination of HFPO and BTCA was effective in reducing the flammability of cotton fleece to achieve the “Class 1” flammability. The addition of TEA as a reactive additive was able to enhance the performance of HFPO/BTCA upon the optimization of TEA concentration. TEA provided synergistic nitrogen, but it also competes with HFPO and cellulose to esterify BTCA, thus reduces the bonding of HFPO onto cotton. The treatment using HFPO/BTCA/TEA is durable to multiple home launderings.

(3) The application of HFPO/BTCA/TEA causes limited fabric strength loss whereas it caused no change in fabric stiffness and whiteness of the treated cotton fleece.