FLAME RETARDANT FINISHING FOR COTTON USING A HYDROXY-FUNCTIONAL ORGANOPHOSPHORUS OLIGOMER

by

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(Under the Direction of Charles Q. Yang)

ABSTRACT

New durable flame retardant finishing systems based on a hydroxy-functional organophosphorus oligomer (HFPO) and a bonding agent have been developed for cotton. In this research, both dimethyloldihydroxyethyleneurea (DMDHEU) and trimethylolmelamine (TMM) have been used as the bonding agents between HFPO and cotton. DMDHEU is more effective for crosslinking cotton cellulose and for crosslinking between HFPO and cotton than TMM, but the bonding formed by DMDHEU between cotton and HFPO is more durable to multiple laundry cycles than that formed by TMM. The mixture of DMDHEU and TMM were also used as a crosslinking agent for HFPO and cotton, the ratio of DMDHEU and TMM has a significant influence on the flame resistance, durability, and mechanical performance of treated cotton. An increase in the DMDHEU/(DMDHEU+TMM) ratio in the mixture increases the amount of HFPO bound to cotton, increases the laundry durability, and reduces the fabric tensile strength retention.

Both DMDHEU and TMM are nitrogen providers for HFPO-based flame retardant finish system to enhance the flame resistance of cotton by means of phosphorus-nitrogen synergism. TMM was a more effective nitrogen provider than DMDHEU to improve the flame resistance of treated cotton. The mechanism of phosphorus-nitrogen synergism has been investigated by studying the thermal decomposition of treated cotton cellulose. The interaction of phosphorus-nitrogen retards the thermal decomposition of cellulose by depolymerization, and promotes the dehydration process, thus increasing the amount of solid char, and substantially improving the flame resistance of treated cotton. The extent of dehydration, not the dehydration temperature has a profound effect on the flame resistance of treated cotton.

The comparison of two reactive organophosphorus flame retardant finishing systems: N-methylol dimethylphosphonopropionamide (MDPA) and HFPO has also been studied. The amount of the flame retardant agent bound to cotton is significantly higher for the HFPO system than that for the MDPA system when equal moles of the phosphorus and N-methylol group are applied to cotton. The MDPA/TMM treated fabric has a higher initial limiting oxygen index (LOI) than that of the HFPO/TMM treated fabric due to the nitrogen content in the MDPA molecule. The flame resistance of cotton is identical for both the HFPO and MDPA system when there are equal amount of phosphorus and nitrogen on the fabric. The stiffness of both HFPO/TMM and MDPA/TMM treated fabric significantly increased when a high TMM concentration was used. And MDPA/TMM treated fabric showed higher dimensional change during the laundering cycles and higher formaldehyde release level.

There is a non-linear correlation between char length and LOI of flame retardant cotton. The fabric weight per unit has a significant influence on the non-linear correlation between char length and LOI.

INDEX WORDS: Cotton, Crosslinking, Flame retardant finishes, DMDHEU, Methylolmelamine, Phosphorus-nitrogen synergism, Reactive organophosphorus chemicals, Regression model, Statistical analysis, Thermal decomposition.

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DEDICATION

This dissertation is dedicated to my wife, Yan Xu, my children, Wen and Alexander, my parents, Axing Wu and Yazheng Fei, and my parents-in-law, Kang Xu and Hongzheng Tong, for their support and patience.

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CHAPTER 1

INTRODUCTION

The flammability of cotton products is one of the major problems posed to scientists and technologists at the present time. Resistance to burning is a useful property that can be imparted to cotton fibers and fabrics. There is the potential for 2-3 million bales of cotton to be affected by flammability regulations and issues. The apparel portion of this is more than 1 million bales, with the remainder including categories such as home furnishing, bedding, tent cloth, carpets, aircraft and automobile interior fabrics and industrial fabrics [1].

Government regulations, insurance company requirements, building codes, and voluntary standards dictate where and when flame-resistant textiles must be used [2]. Also in today's litigious environment, textile producers are becoming increasingly concerned with the liability to which they may be exposed if someone accuses their products of causing an injury or fatality.

Cotton and cellulosic textiles in general, while being among the most flammable of materials. Hazards from flammable fabrics were recognized for many centuries and repeated attempts have been made to cope with them [3]. Cotton is the most commonly used of textile fibers. It is not surprising that most efforts in the field of flame retardancy were made on modifying the flaming properties of cotton fibers.

There are currently several different types of chemical finishes that can be applied to cellulosic materials to impart flame retardant properties. Of these systems, only a few create finished fabrics that can be laundered and dry-cleaned without losing their flame retardant qualities. These treatments are generally referred to as “durable flame retardant finishes” and, for the most part, can be summed up by referencing two types of commercial finishing chemistries: precondensate ammonia cure; and N-methylol functional phosphorus esters [4-6]. It is surprising that more than thirty years have been passed since these chemistries were first developed, and they still remain the dominant means for creating durable flame retardant cotton. Nevertheless, several limitations, in many cases, undesirable facets are associated with these finishing techniques.

There have been several versions of the tetrakis (hydroxymethyl) - phosphonium chloride (“THPC”) cross-linking chemistry used over the years, with the precondensate ammonia process being the most recent of these versions [7-9]. Although the precondensate ammonia process may easily be the most durable treatment on the market, the technology is far from simple. The application process involves the use of an ammoniation chamber and strict control of application conditions to obtain consistent results. In additional to demanding application conditions, the costs for implementing this technology and the regulatory issues associated with the use of ammonia gas make this technology far from ideal, especially to new arrivals to the market.

N-methylol functional phosphorus chemistry, although not as durable as the precondensate ammonia chemistry, has also found a wide customer base in the flame retardant cotton industry due to its ease of application and its use of traditional pad/dry/cure textile finishing equipment. Most N-methylol functional phosphorus chemistry is based on the use of N-methylol dimethylphosphonopropionamide (MDPA) with the commercial version of “Pyrovatex CP” in conjunction with a melamine formaldehyde resin to enhance its flame resistance, both of which contribute to the emission of significant levels of formaldehyde during both fabric application and the lifetime of the treated garments [10-12].

My research here arose from the limitations list above, and the desire for alternative flame retardant finishing chemistries and potential new markets. The main goal of the research is to develop new durable flame retardant finishing systems for fabrics and garments of cotton, which involve the use of a hydroxy-functional organophosphorus oligomer (HFPO) and a bonding agent. Therefore, the federal mandatory textile flammability standards can be met by the textile and garment manufactures and the market share of cotton fiber can be maintained and increased in the future.

The objectives of this research are as follows:

(1) To develop new durable phosphorus-based flame retardant finishing systems for cotton. The flame retardant systems should have excellent flame resistance, environmentally-friend, low add-on levels and cost effectiveness.

(2) To compare DMDHEU and melamine-formaldehyde resin as the bonding agent for the flame retardant finishing system. Comparison includes the covalent bonding between flame retardant and cotton, and the flame resistance, durability, and the mechanical properties of treated cotton.

(3) To study the phosphorus-nitrogen synergism of the new flame retardant finishing systems. The mechanism of phosphorus-nitrogen synergism will be investigated by studying the thermal decomposition on treated cotton cellulose.

(4) To compare two reactive organophosphorus flame retardant agents: MDPA and HFPO. These comparisons are the reaction of flame retardant agents on cotton, the flame resistance, durability, formaldehyde level, and the mechanical properties of treated cotton.

(5) To establish a correlation between vertical test and limiting oxygen index on cotton.

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CHAPTER 2

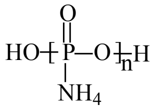
REVIEW OF LITERATURE

Flame Retardants Mechanism

The desire for textiles having a reduced tendency to ignite and burn has been recognized for considerable time during man's record history. Whilst the use of asbestos as a flame resistant material has been recorded in Roman times, perhaps one of the earliest significant contributions in recent history was Wyld's patent of 1735 [1]. This describes a finishing treatment for cellulosic textiles based on aluminum, ferrous sulphate and borax. Almost a century later, in 1821, Gay-Lussac [2] published perhaps the first systematic study of the use of flame retardants (FR). These ideas laid the foundation for the early theories of flame retardancy of textiles.

Cotton and cellulosic textiles in general, while being among the most flammable of materials, may be rendered flame-retardant by well-established means [3]. Cotton is the most commonly used of textile fibers. It is not surprising that most efforts in the field of flame retardancy were made on modifying the flaming properties of cotton fibers. Table 2.1 lists a simplified selection of suitable flame retardants for cellulosic textiles, which indicates that a major criterion used for selecting a finish is its durability to aftercare or end-use exposure condition. The development of practical flame retardant systems and meaningful test method has been understandably accompanied by intensive speculation and research into the mechanisms of flame retardancy. The complexity and probable multiplicity of these mechanisms was recognized, and by 1947 [4] several early possibilities had been advanced. These included action of the flame retardant directing thermal degradation to fuel-poor pyrolytic paths, flame retardant external coating of the substrate to exclude oxygen, internal barrier formation to prevent evolution of combustible gases, inert gas evolution to dilute fuel formed by pyrolysis, and thermal activity to dissipate heat away from the flame front. The condensed-phase and free radical vapor-phase proposals are now generally recognized as the primary, though not the only, effective flame retardant mechanisms [5].

Table 2.1. Summary of flame retardant treatments for cotton [6]

Type	Durability	Structure/formula
Salts:		
(1) Ammonium polyphosphate	Non- or semi-durable	 $HO{-}[P(=O)(NH_4){-}O]_n{-}H$
(2) Diammonium Phosphate	Non-durable	$(NH_4)_2HPO_4$
Organophosphorus:		
(1) Cellulose reactive methylolated phosphonamides	Durable	N-methylol dimethylphosphonopropionamide
(2) Polymeric tetrakis (hydroxymethylol) phosphonium salt condensates	Durable	THPC-urea-NH_3 condensate
Back-coating:		
(1) Chlorinated paraffin waxes	Semi-durable	$C_nH_{(2n-m+2)}Cl_m$
(2) Antimony-halogen	Semi- to fully durable	Sb_2O_3 (or Sb_2O_5) Decabromodiphenyl oxide

1. Condensed-Phase Mechanism

The overall process leading to burning of a polymeric substrate can be schematically visualized as in Fig 2.1 [7]. The substrate, under the influence of externally applied heat, undergoes thermal decomposition (pyrolysis) with the generation of combustible fuel.

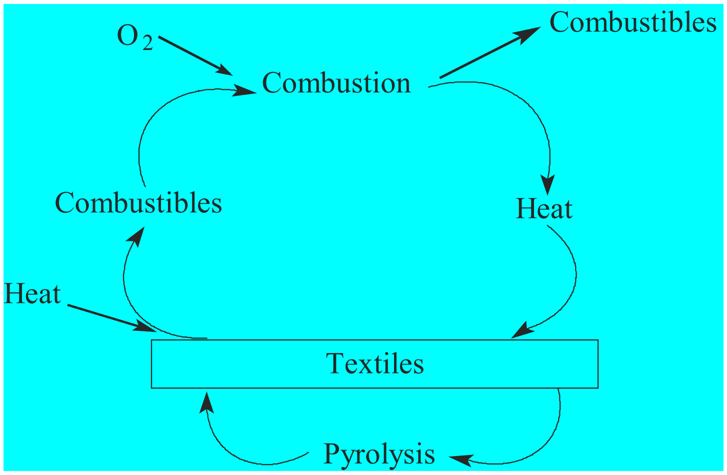


Figure 2.1. Diagram of polymer fire (From Ref.7)

Only a part of this fuel is combusted in the flame by combining with atmospheric oxygen. The other part remains and can be combusted with the use of a catalyst by an excess of oxygen. The flame provides a part of its heat for the continued pyrolysis of substrate, perpetuating the cycle. Another part of the heat is dissipated and lost to the environment. The ease of pyrolysis, i.e., the minimum temperature at which pyrolysis occurs, and the character and amount of gaseous product determine the flammability of substrate. Cellulose decomposes by a noncatalyzed route to tarry depolymerization products, notably levoglucosan, which then decomposes to volatile combustible fragments such as alcohols, aldehydes, ketones, and hydrocarbons [8-10]. A flame retardant that acts via a condensed-phase mechanism catalyzes the decomposition of cellulose more effectively, through the formation of water vapor and char, and reduces the formation of volatile flammable gas. The reduction of volatile flammables and the increased residual carbonaceous char caused by a condensed-phase-active FR can be affected by two principal modes of action: dehydration and cross-linking. These processes have been established [15-18] for cellulosics, and probably operate to some extent in other polymers as well [19-20].

Cross-linking was initially recognized as promoting char formation in cellulosics [21-22] by creating a carbon-carbon network whereby chain cleavage, which produces volatile components is retarded. Cross-linking generally, but not always, reduces the flammability of a polymer. A recent detailed study [23] of the effects of cross-linking on the pyrolytic behavior of cellulosics indicated that cross-linking can promote stabilization of the polymeric structure by providing additional bonds that are stronger than hydrogen bonds and that have to be broken before stepwise degradation of the cellulose chains can occur. However, low degrees of cross-linking can decrease thermal stability by breaking or weakening hydrogen bonds. These processes are reflected in thermal, energetic, and flammability characteristics of cross-linked cotton [24]. Thus, the LOI of cotton increased marginally with increased formaldehyde cross-linking, because in highly crystalline cotton, cross-linking occurs to a much smaller extent.

2. Vapor-Phase Mechanism

In the condensed-phase mechanism, the effect of the flame retardant is concentrated on decreasing the amount of fuel produced in the pyrolysis. In the vapor-phase mechanism, the pyrolytic processes remain essentially the same with or without FR; however, the mode of combustion in the flame is changed.

The amount of fuel consumed in the flame and consequently the amount of heat generated are decreased with an increase in the amount of flame retardant. The amount of heat returned to the polymer surface is therefore also diminished and the pyrolysis is slowed down or halted as the temperature of the surface decreases. Since the flame-retarding effect is being exerted in the gas phase only, it follows that the flame retardant moiety has to reach the gas phase, i.e., it has to be volatile and reach the flame. Alternatively, it has to decompose and furnish the active flame retardant fraction of its molecule to the vapor phase. The remaining char after the combustion will retain a much smaller percentage of the FR chemicals as compared with the condensed-phase flame retardant. Chemical analysis of the char is therefore one of the ways in which the mode of activity of the FR chemical can be determined [25-26]. Furthermore, the flammability in the vapor-phase mechanism should be basically independent of the structure of the polymeric substrate. It should also not introduce any changes in the pyrolytic process, which ideally should proceed as if there would have been no FR chemical incorporated in it. The composition of the volatiles in the flame should therefore also not be influenced by the presence of the vapor-phase-active FR agent [27].

The vapor-phase activity of the flame retardant is attributed to its interference in the combustion reactions in the flame. Polymers like other fuels produce, upon pyrolysis, species capable of reacting with air oxygen and producing the H_2-O_2 reaction scheme, which propagates the fuel combustion by the branching reaction [28-29].

$$\bullet H + O_2 \rightleftharpoons \bullet OH + O\bullet \qquad (1)$$

$$\bullet O + H_2 \rightleftharpoons \bullet OH + H\bullet \qquad (2)$$

The main exothermic reaction in the flame is

$$\bullet OH + CO \rightleftharpoons CO_2 + H\bullet \qquad (3)$$

which provides most of the energy maintaining the combustion. To slow down or stop the combustion, it is imperative to hinder the chain branching reactions (1) and (2).

The inhibiting effect of halogen derivatives, usually chlorine and bromine, which are considered to operate via the vapor-phase mechanism, occurs by first releasing a halogen free radical,

$$RX \rightleftharpoons R\bullet + X\bullet \qquad (4)$$

where free radical of R is the residue of the flame retardant molecule after having lost X free radical.

The halogen free radical reacts with the fuel producing hydrogen halide

$$RCH_3 + X\bullet \rightleftharpoons RCH_2\bullet + HX \quad (5)$$

The halogen halide is believed to be the actual flame inhibitor by affecting the chain branching.

$$\bullet H + HX \rightleftharpoons H_2 + X\bullet \qquad (6)$$

$$\bullet OH + HX \rightleftharpoons H_2O + X\bullet \qquad (7)$$

According to experimental results [30], reaction (6) is twice as fast as (7) and the high value of the ratio H_2/ OH free radical in the flame front indicates that (6) is the main inhibiting reaction. In this case, it is the competition between reaction (6) and (1), in which the active hydrogen atoms are consumed, which determines the inhibiting effect. Reaction (1) produces two free radicals for each H atom consumed, whereas reaction (6) produces one relatively unreactive halogen atom (not active in the H_2-O_2 scheme).

Antimony-halogen flame retardants mainly act via a vapor-phase mechanism, and some phosphorus flame retardants can also exert vapor-phase flame retardant action.

3. Physical Effects

Flame retardancy by physical effects can be brought about by a number of different activities that may occur in the condensed phase as well as in the gaseous phase. On the other hand, conventional FR agents, whether based on phosphorus or halogen, owe a certain part of their activity to these effects, especially when considering the sizable amounts of FR chemicals applied. The FR chemicals that are applied for the physical effects are, however, mainly inorganic [31-32].

One of the main effects of these materials is dilution of the organic part of the structure and dividing it into insulated domains by filling the pores and the amorphous regions of the polymer. Pyrolyzing the structure becomes more difficult because larger amounts of heat are needed to reach the pyrolysis temperature. The amount of combustible gases will be lower and less heat will be generated in the flame. Consequently, less heat will be available for sustained pyrolysis of the polymer. The rate of heating and of pyrolysis will also decrease by virtue of the insulating effect of the filler being finely dispersed in the polymer or coating it.

This "heat sink" effect is enhanced by a higher specific heat and a lower thermal conductivity of the fillers, which may include alumina, mica, feldspar, clay, talc, pumice, zinc oxide, and other materials. Another heat sink effect is due to the possible endothermic decomposition of the filler, aluminum trihydrate, which releases 3 moles of water into the gaseous phase and consumes 1170 J/g [33] as heat of dehydration. A similar effect occurs for $CaCO_3$:

$$Al_2O_3.\ 3H_2O \rightarrow Al_2O_3\ (s) + 3H_2O\ (g) \qquad (8)$$

$$CaCO_3\ (s) \rightarrow CaO\ (S) + CO_2\ (g) \qquad (9)$$

These decompositions tend to decrease further the temperature of the pyrolyzing polymer, and thus additionally contribute to the flame retardant effect. Alumina trihydrate in amounts of 40-60% has been found to be much more effective than the anhydrous alumina[34], showing the thermal effect of the decomposition to be more significant than that of the heat sink, whereas the effect is limited to the condensed-phase. The gases given off in these decompositions will dilute the combustion gases and the oxygen in the flame and serve as an additional heat sink in the gaseous phase, especially if they react endothermically with flame species.

Another physical effect is coating and insulation. Here the flame retardant forms a protective layer of glass or char that hinders the passage of the combustible gases from the pyrolyzing polymer to the flame front and at the same time acts as an insulating barrier that hinders the transfer of heat to the surface of the polymer. The flame-retarding effect of boron derivatives on cotton was already in 1821 ascribed to the formation of an impenetrable glassy layer [35]. Boric acid and its hydrated salts have low melting points and dehydrate in stages:

$$2H_3BO_3 \xrightarrow[-2H_2O]{130\text{-}200^{o}C} 2HBO_2 \xrightarrow[-H_2O]{260\text{-}270^{o}C} B_2O_3 \qquad (10)$$

The metaboric acid has three melting points at 176°C, 200.9 °C, and 236°C, whereas the boron oxide softens at 325°C, but only above 500°C does it become fluid enough to flow.

The solubility of the borate salts changes with the ratio Na_2O:B_2O_3 and temperature, and highly soluble mixtures can be produced due to polyions being formed. Borax dissolves upon heating in its own water of hydration, produces a frothy mass, and finally changes to a clear melt. A mixture of 7:3 borax: boric acid is an effective flame retardant for cellulose. This mixture does not crystallize and upon heating produces a clear glassy layer that adheres uniformly to cellulose fibers. The water vapor from the hydration of the borax-boric acid mixture swells the surface of the fibers between 80-200°C and then a uniform intumescent coating on that surface solidifies as decomposition of the polymer continues. The solidified foam should be stable at 500°C.

Flame Retardants for Cellulosics

Flame retardant finishes present on specific textiles, based on the durability of flame resistance, are defined as non-durable, semi-durable, and durable with respect to a given condition.

1. Non-durable flame retardants for cellulosics

Non-durable flame retardants for cellulosics are generally water-soluble inorganic salts that are easily removed by water, rain, or perspiration. They provide only temporary protection and therefore periodic reprocessing becomes necessary to maintain the flame retardant effect. There are several groups of these materials. One group is based on boron derivatives, boric acid, and borax, sometimes in conjunction with ammonium salts of sulfuric and phosphoric acid, urea, and ammonium bromide [36].

Another group consists of inorganic acids, acidic salts, and salts capable of releasing an acid upon its ammonium salt. One example is sulfamic acid (H_2NSO_2OH) and its ammonium salt. The acid hydrolyzes upon boiling with water to sulfuric acid and the salts to bisulfates. Phosphoric acid and its diammonium salt belong to the same group. They are highly effective flame retardants and smoldering inhibitors. Sometimes $(NH_4)_2HPO_4$ (DAP) is used in mixtures with ammonium sulfate and hexamethylene tetramine as a buffer [37]. Additions of dicyandiamide, urea, and borates have also been suggested [36]. An important feature of DAP is its effectiveness in suppressing glowing, for which only 0.5% of P is needed.

Metallic salts can also be considered as non-durable FR agents. Their action is based on acidity released at the ignition temperature of the cellulose. $ZnCl_2$ is effective in flame and glow suppression. Another group of inorganic, non-durable FR compounds decompose or sublime on heating, releasing large amounts of nonflammable gases that dilute the flame. Carbonates, halides, ammonium salts, and highly hydrated salts belong to this category.

2.Semi-durable flame retardants for cellulosic

Cotton treated with semi-durable flame retardants should withstand a limited number of washes. These materials are ammonium polyphosphate, and usually insoluble salts of amphoteric cations and anions-stannates, tungstates, aluminates, borates, and phosphates of Zn, Sn, Al and easily reducible metallic oxides-Sn, Fe, Pb, Ti, Cr, Zr, Ce, Bi, W, and As [38]. Direct application of insoluble salts has its limitations and best results occur by internal precipitation following application of a reagent solution. For instance, metastannic acid, H_2SnO_3 may be formed following hydrolysis of an applied stannic salt, such as $SnCl_4$, or by acidification of a soluble stannate. In a similar manner, chromium hydroxide and tungstic acid may be precipitated by similar respective methods [39-40].

3. Durable flame retardants for cellulosic

(1) Tetrakis (hydroxymethyl) phosphonium deratives

The phosphonium derivatives comprise the most commercially important durable flame retardant group currently used for cellulosic fibers and, in particular, cotton. The available finishing agents are based on phosphonium salts having the general formula:

$$[(CH_2OH)_4P^+]_n X^{n-} \qquad (11)$$

where X^{n-} is commonly Cl^-, OH^-, or SO_4^{2-} [41]. The most important is tetrakis (hydroxymethyl) phosphonium chloride (THPC) initially described in 1921 by Hoffman and recognized as having commercial potential by Reeves and Guthrie [42]. It is prepared as a crystalline solid from phosphine, formaldehyde and hydrochloric acid at room temperature [43]:

$$PH_3 + 4CH_2O + HCl \rightarrow (HOCH_2)_4P^+Cl^- \qquad (12)$$

THPC is a reducing agent and reacts with many other chemicals containing active hydrogens, e.g., N-methylol compounds, phenols, polybasic acids, and amines, to form insoluble polymers on cellulose substrates. The essential chemical and processing stages for THPC-urea are shown in Figure 2.2, which requires an ammonia cure and a final oxidative stage. The THPC and urea are probably in a 2:1 molar ratio with a molar P:N ratio of 1:1. The chloride is generally preferred

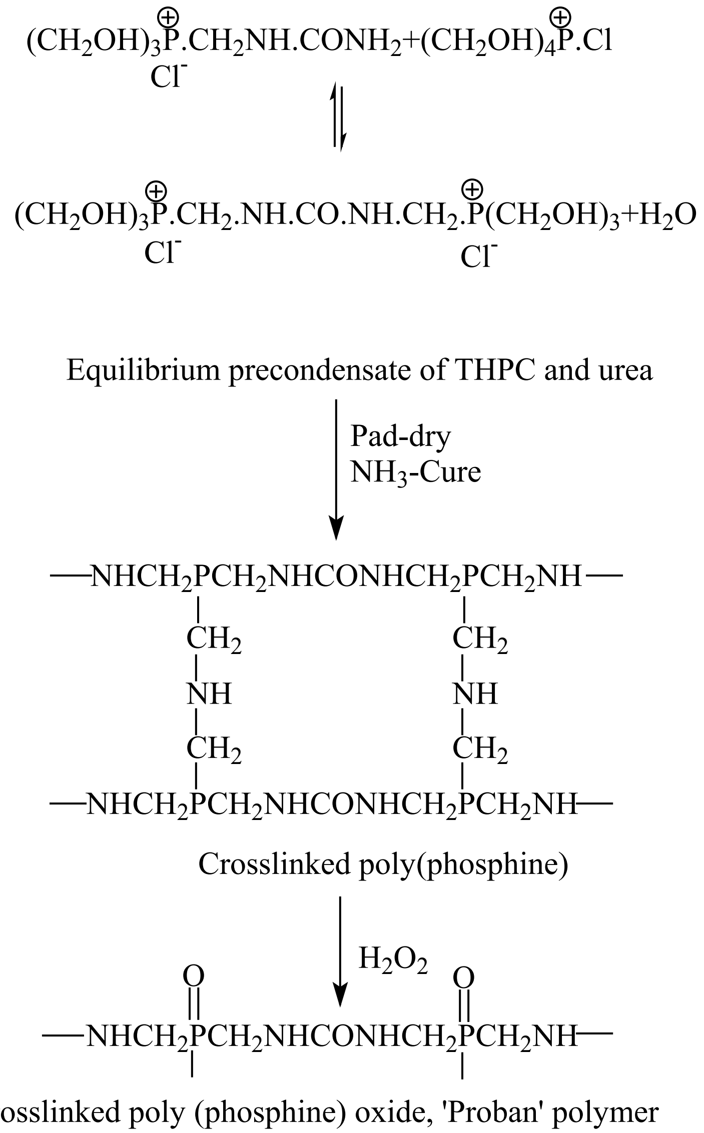
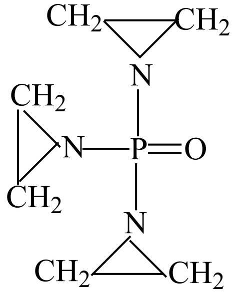


Figure 2.2. Outline chemistry of the THPC-urea-NH_3 (Proban) process

relative to other salts, such as the sulphate (THPS), because as a univalent anion, the salt-urea complex achieves a higher degree of penetration into the fiber microstructure. Experience has shown that the divalent sulphate complex, which is considerably larger, leads to lower levels of penetration with consequent reduction in durability. Although the THPC-amide process is highly effective, it has a number of limitations: the fabrics are stiff; mechanical properties, such as tensile and tear strengths are severely reduced; there is uneven treatment due to migration of the ingredients during the drying and curing stages [44]; there is susceptibility to acid and basic hydrolysis [46]; and there is release of free formaldehyde during the process [46].



APO

A considerable number of modifications were suggested to this process [47-51]. THPC-APO treatment, the THPC reacts rapidly with alkylenimines such as tris (1-aziridinyl) phosphine oxide (APO) or sulfide (APS) to yield a polymeric product by interaction with cellulose and cross-linking inside the fibers and with each other. This is a highly effective and durable flame-retardant at relatively low add-ons. A high wrinkle recovery is also obtained as well as glow resistance and rot resistance. However, this highly promising process has been discontinued because of toxicity and suspected carcinogenicity of APO and its precursor, ethylene amine [52]. Continuing efforts to eliminate chlorides from the THPC-amide treatments and the need for a treatment for lighter-weight fabrics led to the development of THPOH treatment. THPC or THPS (sulfate) reacts with NaOH as follows [53-54]:

$$(HOCH_2)_4P^+Cl^- + NaOH \rightarrow (HOCH_2)_4P^+OH^- \qquad (13)$$

$$(HOCH_2)_4P^+OH^- \rightarrow (HOCH_2)_3P + CH_2O + H_2O \qquad (14)$$

$$(HOCH_2)_3P + CH_2O \rightarrow (HOCH_2)_2PCH_2OCH_2OH \qquad (15)$$

The product of these reactions appears to be an equilibrium mixture of THPOH and THP. The reaction has to be carried out within the pH range of 7.5-7.8. At a higher pH, the unreactive tris (hydroxymthyl) phosphine oxide (THPO) is formed. A durable flame retardant finish based on THPOH, TMM, and urea was developed and applied to cotton fabrics with a conventional procedure [55]. The fabrics were only moderately stiff and had a lower tendency to yellow when exposed to hypochlorite bleach than the THPC-amide fabrics did.

In another development, fabrics impregnated with THPOH without amides were cured by ammonia in a specially designed gas chamber, after partial drying to 10-20% moisture. The reaction of THPOH with ammonia produces water, which combines with NH_3 to form NH_4OH. Since NH_4OH reacts with THPOH to produce soluble polymers instead of insoluble products, the water and NH_4OH must be removed from the gas chamber and a stringent humidity control has to be maintained. The THPOH-ammonia process gives a good flame resistant effect without strength loss and stiffening. The durability of the flame resistance is lower than that with the THPC-amide finish. In addition, the P:N ratio is high, e.g., 3.5:1, and therefore the process is also more expensive.

(2) Phosphonate treatments

From the reaction of dialkylphosphite with acrylamide, a dialkylphosphonopropionamide is obtained, which interacts with formaldehyde to yield the methylol derivative [56]. This material is marketed by Ciba-Geigy under the commercial name “Pyrovatex CP” and is applied together with TMM from a single bath by a pad-dry-cure acid-catalyzed procedure. The TMM is added to increase the nitrogen content for the synergistic effect with the phosphorus. To afford high levels of phosphorus (2-3%) and accompanying flame retardancy, some fabric stiffening may occur. Furthermore, to prevent unacceptably high loss in strength from the phosphoric acid catalyst used to cure the finish, efficient neutralization by alkaline after treatment is essential [57].

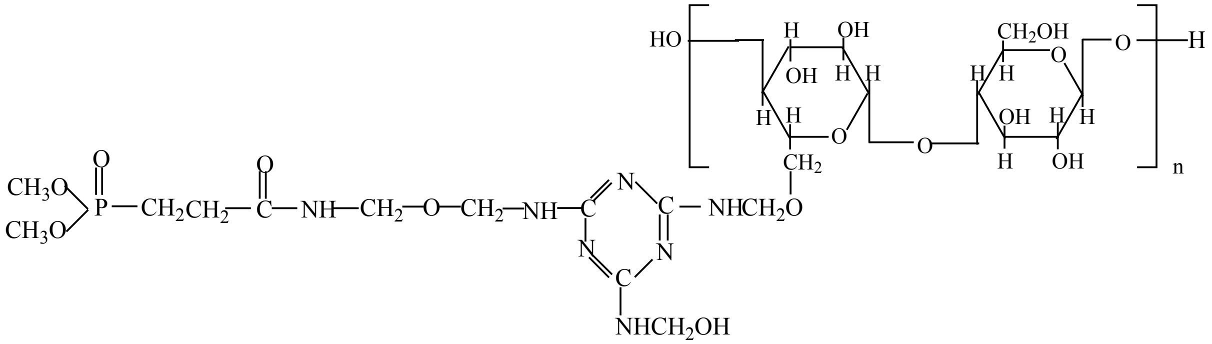
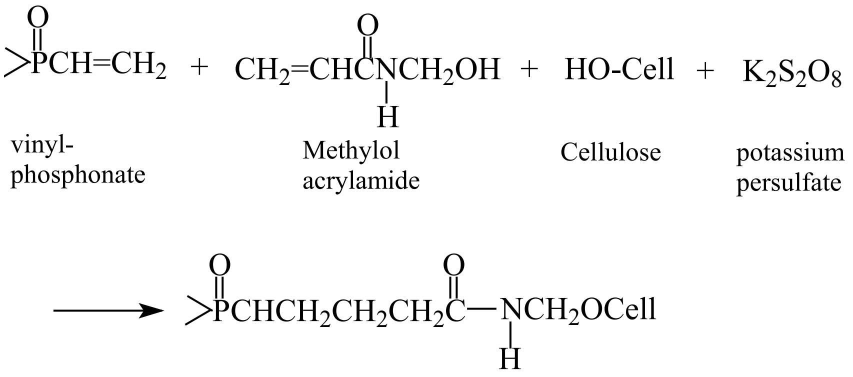


Figure 2.3. Chemistry of Pyrovatex CP

An oligomeric vinyl phosphonate finish, Fyrol 76, was developed by Eisenberg and Weil [58]. Its major difference from the other finishes is that it is cured (made insoluble) by a free radical mechanism. The formula of Fyrol 76 is given as [59]:



$$>\overset{O}{\overset{\|}{P}}CH=CH_2 + CH_2=CH\overset{O}{\overset{\|}{C}}\underset{H}{\underset{|}{N}}CH_2OH + HO\text{-}Cell + K_2S_2O_8$$

$$\longrightarrow >\overset{O}{\overset{\|}{P}}CHCH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}CH_2OCell$$

Figure 2.4. Chemistry of Fyrol 76

Fyrol 76 is water-soluble, contains 22.5% P, and is used with methylol-acrylamide and a free-radical catalyst, e.g. persulfate, with a conventional pad-dry-cure-wash procedure with little odor in the plant. Cure temperatures are in the range of 150-175°C. It is claimed that the hand of the fabrics is soft; tearing-strength retentions on knits are 60-80%. The fabrics exhibit wrinkle recovery and durable press properties [60]. The process has been demonstrated on cotton flannel, knits, printed cloth, sheeting, terry cloth, corduroy, and heavy-weight fabrics for tenting, cotton-rayon blend, and a number of cotton-polyester blends [61]. Fyrol 76 has been applied to cotton-polyester blends with the acrylamide or TMM coreactant. Bromine derivatives have also been added [62-63].

(3) Durable flame retardnacy by cellulose esterification

It is not surprising, therefore, that considerable efforts have been made to develop fully durable FR treatments with low add-ons of chemicals that would overcome the environmental and toxicity problems, and the processing cost. The first endeavors in this direction were made on phosphorylation of cellulose by phosphoric acid and diammonium phosphate [64-68]. Phosphorylation can be carried out with many agents: ortho, meta-, pyro-, poly-hexameta-phosphoric acid, ortho-, pyro-, poly-, meta-phosphorous acid, $POCl_3$, diammonium phosphate, and urea-phosphoric acid. The phosphorylation is carried out by a pad-dry-cure procedure,

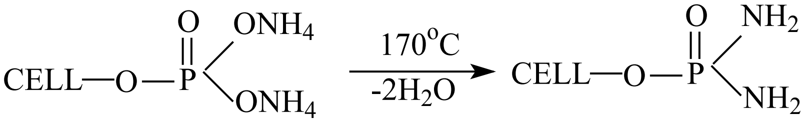


Figure 2.5 Chemistry of cellulose esterification

usually with high yield. The cellulose is severely degraded by the drying and curing at the higher temperatures and the low pH values involved. The flame resistance of the cellulose esterified with ethyl-, phenyl-, or boron-substituted phosphoric acid is inferior [66]. Urea assists the phosphorylation and it is believed that it serves as a limited swelling agent for the cellulose and a solvent for the phosphorylating agent, since it is in the molten state in the range of curing temperatures.

(4) Sulfation-phosphorylation

Sulfation of cellulose with ammonium sulfamate (AS) in the presence of urea or urea-based cross-linking agents imparts to cellulose an excellent flame resistance that is durable to over 50 alkaline soft- and hard-water launderings [69-71]. A weight gain of ~10% corresponding to 3% bound sulfur was found necessary to obtain this effect. The sulfated fabrics exhibited a high degree of afterglow. It was shown that this severe after-glowing could be overcome by the addition of phosphorus either by after-treatment with DAP, which is not durable, or by a combined and simultaneous sulfation and phosphorylation treatment with ammonium sulfamate and phosphorus triamide.

(5) Esterification with phosphoramides

Cellulose can be esterified with methyl and chloromethyl phosphoramides

$ClCH_2P(O)(NH_2)_2$ (CMPDA), $CH_3P(O)(NH_2)_2$ (MPDA) and $CH_3P(O)(NHNH_2)_2$

with high yields of P [72-75]. The highest yields were obtained on the dihydrazide, whereas the diamide $CH_3P(O)(NH_2)_2$ gave P yields in a high extent. The least reactive are the amidate and the hydrazidate in which $-OCH_3$ and $-OC_2H_5$ groups replace one of the $-NH_2$ or $NHNH_2$ groups. It appears that the phosphorylation of the cellulose occurred with one of the amide groups so that one other amide group remained attached to the fiber. Upon hydrolysis, this amide group would hydrolyze and the acid cellulose phosphonate would have only half the cation exchange capacity of the monoester phosphates; their affinity to calcium ions is therefore lower. The physical properties are similar to those obtained upon sulfation-phosphorylation. Urea, formaldehyde, or TMM added in small amounts assist in preventing the yellow discoloration of the cellulose phosphonates. A small degree of wrinkle recovery is also observed, similar to the case of phosphorylation with phosphorus triamide [76].

Phosphorus-Nitrogen Synergism

Phosphorus-nitrogen synergism is defined as an effect greater than that predicted on the basis of additivity of the activities of individual FR components. The enhancing effect of a non-FR additive on a FR system is also usually termed synergism [77]. There are several ways to evaluate synergism: (1) a calculation definition is that if the slope of the response curve versus concentration of A is greater at a given concentration of A with B present than without B present, then B is synergizing A at that concentration of A and B; (2) a statistical definition is that if the fit of experimental flammability data to the concentrations of the effective ingredients in a regression equation is improved by the inclusion of a positive “interaction term”, then “synergism” can be declared [78].

Some work on the quantitative basis of the interaction of nitrogen and phosphorus in cellulose flame retardancy has been done. The interaction of phosphorus and nitrogen in cotton treated with “Pyrovatex CP” and various nitrogen-based chemicals was studied in detail [79], a nearly perfect linear relationships between LOI and % P or % N was observed. These results are the best evidence for interpreting the phosphorus-nitrogen synergism. Willard and Wondra [79] also found that flammability depended on the concentration of phosphorus and structure of the nitrogen based compounds, and that the limiting oxygen index (LOI) can be increased, left unchanged, or even decreased by increasing the nitrogen content. It appears worthy of note that the best synergistic result was observed with a melamine having relatively nonbasic NH-groups, while poorer results came with a fully substituted urea lacking NH-groups, and the poorest (actually antagonistic) results occurred with a fully substituted urea having a tertiary amine group. A further study at USDA [80] revealed that in a finish based on THPC and 0.8% nitrogen from different sources, the best and next best flame resistance was observed with nitrogen in the form of aminoethyl group, and carbamoylethyl group respectively; on the other hand, poor flame resistance, even inferior to the nitrogen-free control, was observed where the nitrogen was present as cyanoethyl groups. A study was also made [80] to explain the deleterious effect of the nitrile structure on flame retardancy. It was found that during pyrolysis of the fabrics containing nitrile structures much of the phosphorus was lost by volatilization, whereas the other fabrics without nitrogen or with the amine or amide groups retained nearly all of the phosphorus in the ash when pyrolyzed. It was clear that the melamine-formaldehyde resin was an effective synergist for urea-phosphate. However, there were controversial results on the synergism of DMDHEU [78, 80].

The mechanism of the nitrogen compound interaction with phosphorus on cellulose has not been studied in detail [80-84]. It is reasonable to expect that the mechanism of phosphorus-nitrogen synergism is related to the phosphorylation of cellulose. Nitrogen compound have been shown to promote the thermal polycondensation of phosphoric acid to polyphosphoric acid [85-86]. The nitrogen compounds used as synergists, for example, methylolmelamine, have some flame retardant activity in their own right, incorporation of amino structures in carbohydrates is reported to favor decomposition at lower temperatures to water plus char [87]. Combinations of nitrogen compounds such as urea, methylolmelamine with acids such as phosphoric acid produce, upon exposure to flame, intumescent chars which because of their good thermal insulating character tend to protect the underlying combustible substrate [88]. For some of the structures employed in practical cellulose flame retardancy, such as N-methylol dimethyl phosphonopropionamide, a nucleophilic attack by the nitrogen groups on the alkyl-O-P linkage may take place first which would cause the phosphorus to be retained as a nonvolatile amine salt or acid. Elemental analyses of char residues [89] show that effective N-P combinations leave a substance analyzing as P-N-O in the residue. PNO is described in the chemical literature as a thermally stable amorphous substance [90]. The research at Clemson [91] studied the effect of incorporating a P-N bond into phosphorus flame retardant on cotton. The interaction of the phosphorus and nitrogen compounds catalyzed the degradation of cellulose more effectively, probably through the formation of some intermediate products. The appropriate nitrogen compounds can assist the phosphorylation of cellulose by phosphorus-containing flame retardants. Another phosphorus-nitrogen synergism theory was also proposed by Lyons. It was said that nitrogen acids may form an acid char formation, and that nitrogen oxides may act as free-radical traps in the vapor phase. However, it is difficult to find any experimental support for the these suggestions.

In our past research [92], we found that both melamine and DMDHEU function as nitrogen providers for a reactive organophosphorus phosphate/phosphonate (HFPO) system, thus enhancing its flame retardancy. We also found that TMM is a more efficient nitrogen provider than DMDHEU for the system. The cotton fabric treated with HFPO/TMM has significantly higher initial LOI than that treated with HFPO/DMDHEU. However, the mechanistic aspects and the phosphorus-nitrogen difference of TMM and DMDHEU are not known.

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CHAPTER 3

COMPARISON OF DMDHEU AND MELAMINE-FORMALDEHYDE AS THE BONDING AGENTS FOR A HYDROXY-FUNCTIONAL ORGANOPHOSPHORUS FLAME RETARDANT AGENT ON COTTON[1]

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[1] Wu, W and Yang CQ, 2004. Journal of Fire Sciences, 22:125-141.Reprint here by permission.

ABSTRACT

It is necessary to use a crosslinking agent to bond a flame retarding hydroxy-functional organophosphorus oligomer (HFPO) to cotton so that the flame resistance of the treated cotton fabric can be durable to multiple home laundering. Both dimethyloldihydroxyethyleneurea (DMDHEU) and trimethylolmelamine (TMM) have been used as the bonding agents between HFPO and cotton. The vertical flammability, limiting oxygen index (LOI) and phosphorus content after different numbers of laundering cycles as well as the wrinkle resistance and tensile strength of the cotton fabric treated with HFPO/DMDHEU and HFPO/TMM was investigated and compared in this research. We found that DMDHEU is more effective for crosslinking cotton cellulose and for crosslinking between HFPO and cotton than TMM. We also found that the bonding formed by DMDHEU between cotton and HFPO is more durable to multiple laundering than that formed by TMM. TMM is a more effective nitrogen provider than DMDHEU to enhance the flame resistance of the treated cotton fabric through phosphorus-nitrogen synergism; therefore the presence of TMM in the flame retardant finishing system significantly increases the flame resistance of the treated fabric. DMDHEU, as an effective crosslinking agent for cotton, cause more fabric strength loss than TMM.

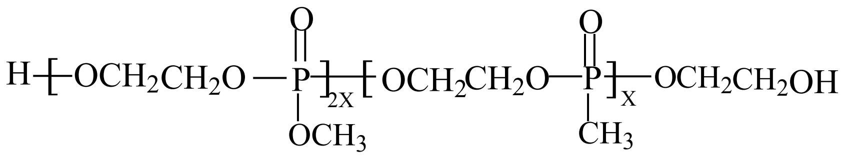
INDEX WORDS: Cotton, Crosslinking, DMDHEU, Durable flame retardant finishes, Trimethylolmelamine, Organophosphorus chemicals.

INTRODUCTION

Reducing the flammability of fibrous materials, such as textile fibers and fabrics, has been one of the major challenges facing the scientific and industrial communities. Flame resistance is a desirable property that can be imparted to cotton fabrics by means of chemical finishing. Currently, the commercially available durable flame retardants for cellulosic fibers include the pre-condensate/ammonia process (known as "Proban") and reactive organophosphorus flame retardant compounds, such as N-methylol dimethy-phosphonopropionamide and its commercial versions with the trade name of "Pyrovatex CP" [1-2]. To achieve durable flame retarding performance, those reagents were designed to react with cellulosic substrate or to self-condense under conventional finishing conditions. However, the reactive organophosphorus flame retarding system contains significant levels of formaldehyde, a known carcinogen. The "Proban" technology requires the use of an ammoniation chamber, which is not compatible to most of the finishing operations in the industry. Those finishing treatment may also cause significant fabric strength loss and adverse effect on fabric handle properties [3].

In our previous research, we developed a nonformaldehyde flame retarding system for cotton based on a hydroxy-functional organophosphorus oligomer (HFPO), such as the one shown in Scheme 3.1 as the flame retardant agent and a polycarboxylic acid as the bonding agent [4]. We also studied the chemical reactions on the cotton fabric treated with HFPO and 1,2,3,4-butanetetracarboxylic acid (BTCA) [5-6].

N-methylol reagents, such as DMDHEU, have long been used in the textile industry as the crosslinking agents for cotton to produce wrinkle-resistant cotton fabrics and garment [7]. TMM resins are used as crosslinking agents for wood pulp cellulose to impart high wet strength



$$H{+}OCH_2CH_2O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OCH_3}{|}}{P}}{+}_{2X}{+}OCH_2CH_2O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{P}}{+}_{X}-OCH_2CH_2OH$$

Scheme 3.1

retention to paper [8]. TMM is also used as a nitrogen-provider for N-methylol dimethyphosphonopropionamide flame retardant agent [9].

In our previous research, we investigated the correlation between LOI and the phosphorus content of the cotton treated with the HFPO/DMDHEU and HFPO/TMM systems [10, 11]. In this research, we studied and compared the reactivity of DMDHEU and TMM in the flame retarding systems based on HFPO, examined the phosphorus-nitrogen synergism, and evaluated the flame retarding performance as well as strength retention of the cotton fabric treated with two different flame retarding systems.

EXPERIMENTAL

Materials

The fabric used was a desized, scoured, and bleached 40x40 cotton printcloth weighing 108 g/m^2 (Testfabrics Style 400). The hydroxy-functional organophosphorus oligomer with the commercial name of “Fyroltex HP” was supplied by Akzo Nobel Chemical Inc., Dobbs Ferry, New York. DMDHEU with the commercial name of “Freerez 900” was supplied by Noveon, Cleveland, Ohio. The trimethylolmelamine (TMM) with the trade name of “ECCO REZ M-300” was supplied by Eastern Color & Chemical Company, Greenville, South Carolina. The catalysts (ammonium chloride and phosphorous acid) were all reagent-grade chemicals supplied by J.T. Baker, New Jersey, and Aldrich, Wisconsin, respectively.

Fabric Treatment and Home Laundering Procedures

The fabric was first immersed in a finish solution containing HFPO, DMDHEU or TMM, and a catalyst, then passed through a laboratory padder with two dips and two nips, dried at 90°C for 3 min, and finally cured in a Mathis curing oven at 165°C for 2.5 min. NH_4Cl and H_3PO_3 were used as the catalysts for DMDHEU and TMM, respectively. The weight ratios of NH_4Cl/DMDHEU and H_3PO_3/TMM were 0.04 and 0.03 in all the formulas, respectively. All the concentrations presented here are based on weight of bath (w/w, %). Both the concentrations (w/w) of DMDHEU and TMM are based on 100% solid. The wet pick-up of the cotton fabric was approximately 105±3%. After curing, the treated cotton fabric was subjected to different number of home laundering (HLTD) cycles with the use of "AATCC Standard Detergent 1993". The home laundering procedure was done according to AATCC Test Method 124-1996 ("Appearance of Fabrics After Repeated Home Laundering"). The water temperature for laundering was approximately 46°C.

Fabric Performance Evaluation

The vertical flammability of the cotton fabric was measured according to ASTM Standard Method D6413-99. The limiting oxygen index (LOI) of the cotton fabric was measured according to ASTM Standard Method D2863-00. The tensile strength of the fabric was measured according to ASTM Standard Method D5035-95. The conditioned wrinkle recovery angle (WRA) was measured according to AATCC Standard Method 66-1998. The fabric tensile strength and WRA were evaluated after one laundering cycle.

Determination of Phosphorus Concentration on the Treated Cotton Fabric

Approximately 2g of treated cotton fabric taken from different parts of a larger fabric specimen were ground in a Wiley mill into a powder to improve sample uniformity. 2 ml of concentrated H_2SO_4 were added to 0.1 g of cotton powder. 10 ml of 30% H_2O_2 was added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250ºC to digest the powder and to evaporate the water until dense SO_3 vapor is produced. The completely digested cotton sample as a clear solution was transferred to a 50-ml volumetric flask, and then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the phosphorus concentration.

RESULTS AND DISCUSSION

The cotton fabric was treated with DMDHEU/NH_4Cl and TMM/H_3PO_3 at different concentration levels individually, and then cured at 165ºC for 2.5 min. The conditioned WRA of the cotton fabric treated with DMDHEU and that treated with TMM is plotted against the concentration of the crosslinker in Figure 3.1. For both the fabric treated with DMDHEU and that treated with TMM, the WRA increased as the concentration of crosslinkers was increased (Figure 3.1). The WRA of the cotton fabric treated with DMDHEU is evidently much higher than that of treated with TMM, and the difference in WRA between the two crosslinkers increased as their concentration was increased (Figure 3.1). The WRA of the fabric treated with 5% DMDHEU is 33º higher than that treated with 5% TMM. The significantly higher WRA for the fabric treated with DMDHEU demonstrates that DMDHEU is more reactive for crosslinking cotton than TMM.

DMDHEU (Scheme 3.2) has four hemiacetal groups to react with the hydroxyl groups of cellulose to form crosslinking among cellulose molecules. The two groups derived from

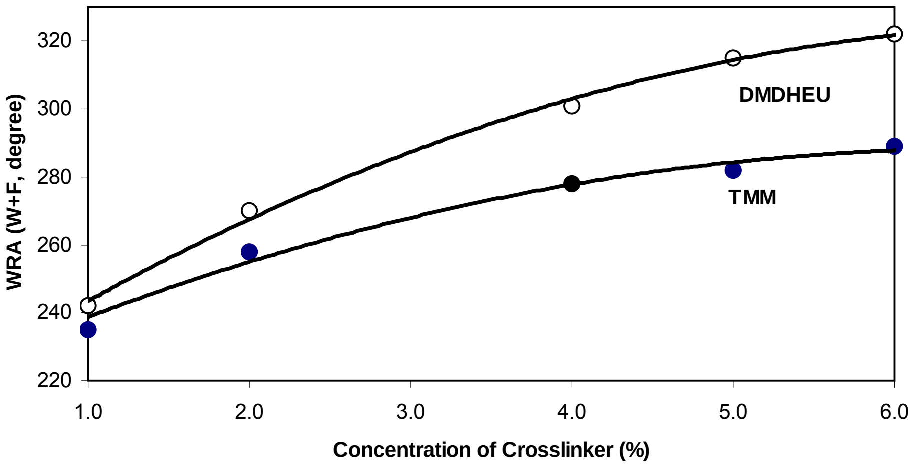


Figure 3.1. The WRA of cotton fabric treated with DMDHEU or TMM at different concentrations and cured at 165ºC for 2.5 min.

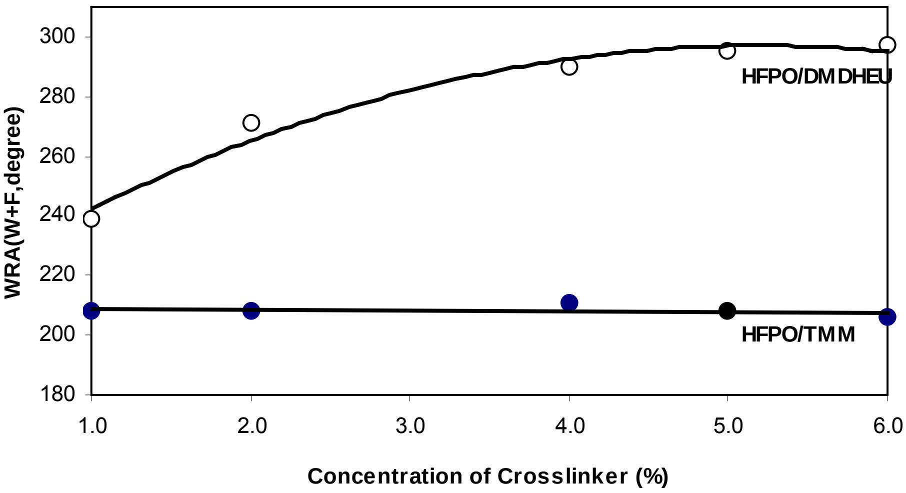
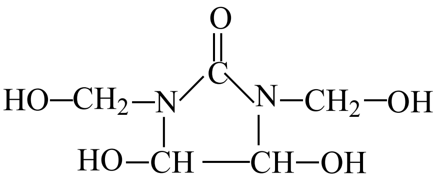


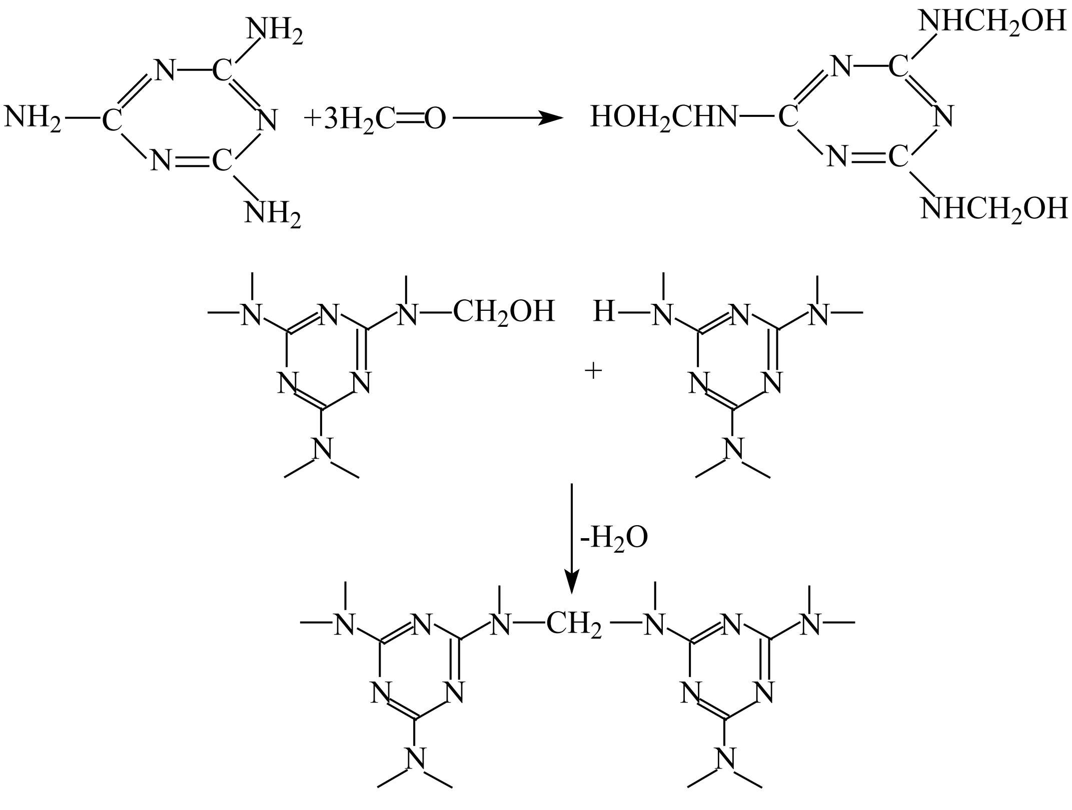
Figure 3.2. The WRA of cotton fabric treated with 32% HFPO and a crosslinker at different concentrations and cured at 165°C for 2.5 min.

formaldehyde in a DMDHEU molecule is significantly more reactive than those derived from glyoxal.



Scheme 3.2

Methylolated melamine, a class of formaldehyde-based melamine resin, is the reaction product of melamine and formaldehyde at slightly alkaline conditions (Scheme 3.3). It is able to self-condense between methylol and amine groups to form polymers with methylene



Scheme 3.3

bridges [12], shown in Scheme 3.3, in addition to forming crosslinkages between cellulosic hydroxyl groups on cotton. Consequently, TMM is a less efficient crosslinking agent for cotton than DMDHEU as indicated by the lower WRA of the treated cotton fabric shown in Figure 3.1.

The cotton fabric was also treated with 32% HFPO in combination with DMDHEU or TMM at different concentration levels, and then cured at 165ºC for 2.5 min. The conditioned WRA of the fabric thus treated is shown as a function of the concentration of the crosslinker in Figure3.2. For both DMDHEU and TMM, the WRA of the treated fabric significantly decreased as the HFPO was present in the treatment solutions. The WRA of the fabric treated with 5% DMDHEU was 315º, and it decreased to 295º when the fabric was treated with 5% DMDHEU and 32% HFPO (Figure 3.2). This was an indication that the hydroxyl of the HFPO competed with cellulosic hydroxyl to react with DMDHEU, thus reducing the amount of crosslinkages among cellulose molecules.

The WRA of the cotton fabric treated with TMM increased from 231 to 289º as the TMM concentration increased from 1.0 to 6.0% (Figure 3.1). The WRA of the cotton fabric treated with HFPO/TMM was drastically reduced when 32% HFPO was present together with TMM. Figure 3.2 shows that the WRA of the fabric treated with HFPO/TMM remained practically unchanged as the concentration of TMM was increased from 1.0 to 6.0% (Figure 3.2). The WRA of the fabric treated with HFPO/TMM in the 206-211º range is very close to that of the control fabric (around 200º), thus indicating that in the presence of 32% HFPO, the overwhelming majority of TMM reacted with HFPO, self condensed or singly bound to cellulose, and the amount of TMM crosslinking cotton was insignificant.

The tensile strength in the filling direction of the cotton fabric treated with TMM at different concentrations and that treated with 32% HFPO and TMM at different concentration levels, and cured at 165º for 2.5 min is shown in Figure 3.3. As the concentrations of TMM increased from 1.0 to 6.0%, the fabric strength decreased from 16.2 to 13.5 kg (Figure 3.3). The reduction of the fabric tensile is a result of crosslinking of cellulose molecules by TMM, since crosslinking cellulose reduced the tensile strength of cotton fabrics [13]. When 32% HFPO was present in combination with TMM, the tensile strength of cotton fabric thus treated remained unchanged in the same TMM concentration range (1.0-6.0%) (Figure 3.3). The nearly 100% fabric strength retention confirms that in the presence of 32% HFPO, the amount of TMM crosslinking on the cotton was insignificant.

Presented in Figure 3.4 is the tensile strength in the filling direction of cotton fabric treated with DMDHEU at different concentrations and that treated with 32% HFPO and DMDHEU at different concentrations and cured at 165º for 2.5 min. The data show that the presence of HFPO together with DMDHEU significantly reduced the fabric strength loss due to the reaction between DMDHEU and HFPO, which reduces the amount of crosslinking of cellulose formed by DMDHEU.

The percent phosphorus content of the cotton fabric treated with 32% HFPO in combination with DMDHEU or TMM at different concentration levels, cured at 165ºC for 2.5 min, and subjected to 1 and 12 home laundering cycles is presented in Figures 3.5 and 3.6, respectively. The cotton fabric treated with 32% HFPO contained 5.26% phosphorus before laundering. The cotton fabric treated with 32% HFPO and 1.0% DMEHEU had 1.64% phosphorus (31% retention) after one laundering cycle, and the phosphorus content increased to 4.38% (83% retention) when the DMDHEU concentration increased to 10% (Figure 3.5). For the cotton fabric treated with HFPO/TMM, its phosphorus concentration increased from 1.10% (21% retention) to 2.80% (53% retention) when the TMM concentration was raised from 1.0 to

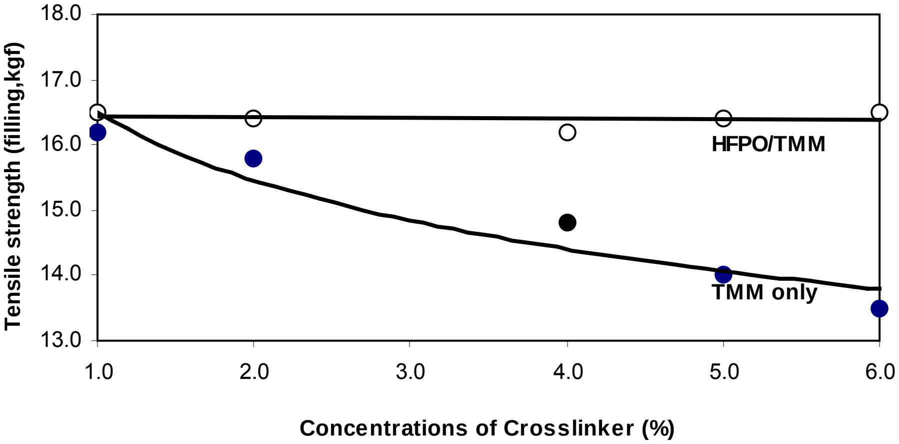


Figure 3.3. The tensile strength in the filling direction of the cotton fabric treated with 32% HFPO in combination with TMM of different concentrations, and that treated with TMM of different concentrations, and cured at 165ºC for 2.5 min.

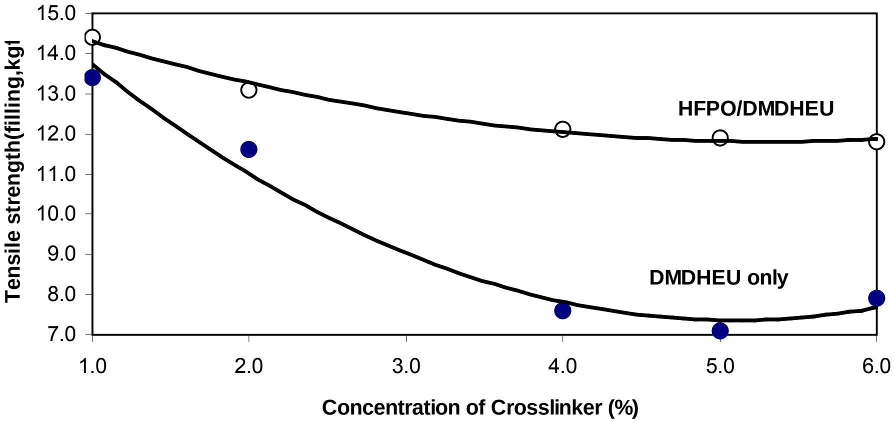


Figure 3.4. The tensile strength in the filling direction of the cotton fabric treated with 32% HFPO in combination with DMDHEU of different concentrations, and that treated with DMDHEU of different concentrations, and cured at 165ºC for 2.5 min.

6.0% (Figure 3.5). The amount of HFPO bound to the cotton fabric by DMDHEU is notably higher than that bound by TMM. Thus, the data presented here clearly indicate that DMDHEU is more efficient for binding HFPO to cotton.

After the treated cotton fabric was subjected to 12 home laundering cycles, the phosphorus content on the fabric treated with HFPO/DMDHEU ranged from 1.07 to 4.10% on the fabric, representing 20 to 78% retention, when the DMDHEU concentration increased from 1.0 to 10.0%, respectively (Figure 3.6). When TMM was used as the crosslinker, the phosphorus content increased from 0.40 to 1.84%, representing 8 to 35% retention, in the same crosslinker concentration range. The data show that the difference in phosphorus content between the cotton fabric treated with HFPO/DMDHEU and that treated with HFPO/TMM became more pronounced as the number of home laundering cycles was increased to 12. Thus, the data clearly demonstrate that the bonding between HFPO and cotton formed by DMDHEU is more durable to multiple home launderings than that formed by TMM.

The LOI of the cotton fabric treated with 32% HFPO in combination with a crosslinker (DMDHEU or TMM) at different concentrations and cured at 165ºC for 2.5 min before laundering is plotted against the concentration of the crosslinker in Figure 3.7. All the flame retarding finish solutions used to treat the cotton fabric contained the same concentration (32%) of HFPO, and the phosphorus of the treated cotton fabric was around 5.3% before laundering. The LOI of the fabric treated with HFPO/DMDHEU and that treated with HFPO/TMM increased as the concentration of the crosslinkers increased, thus indicating both crosslinkers, i.e., DMDHEU and TMM, enhance the flame retarding performance of the treated cotton fabric. The enhancing effects of a nonflame retarding additive to a flame retarding agent are one of the two definitions of synergism [9]. The data show that TMM is a more efficient nitrogen provider,

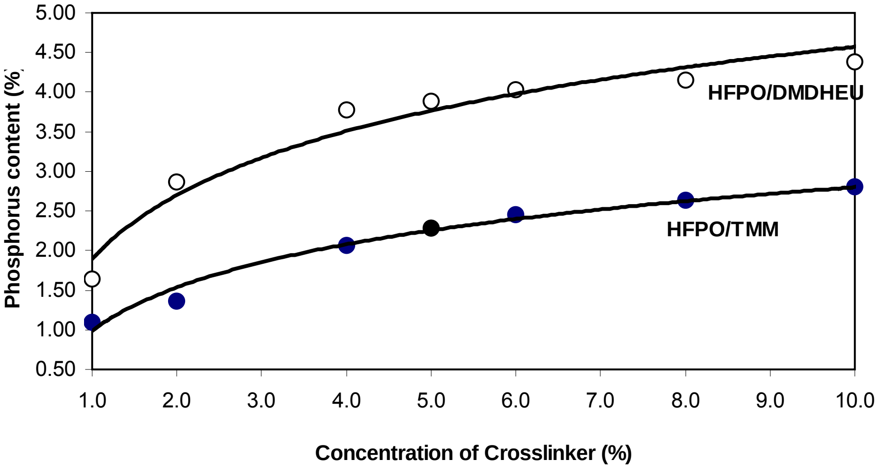


Figure 3.5. The phosphorus content of the cotton fabric treated with treated with 32% HFPO in combination with a crosslinker (DMDHEU or TMM) at different concentrations, cured at 165ºC for 2.5 min and subjected to 1 home laundering cycle.

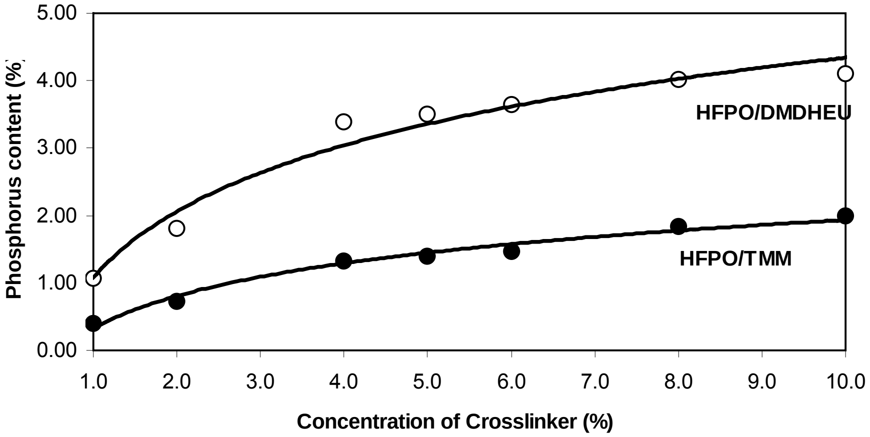


Figure 3.6. The phosphorus content of the cotton fabric treated with treated with 32% HFPO in combination with a crosslinker (DMDHEU or TMM) at different concentrations, cured at 165ºC for 2.5 min and subjected to 12 home laundering cycles.

because the cotton fabric treated with HFPO/TMM has significantly higher LOI than that treated with HFPO/DMDHEU at the same HFPO and crosslinker concentrations (Figure 3.7).

The LOI of the treated cotton fabric subjected to 1 and 12 home laundering cycles is presented as a function of the concentration of the crosslinker in Figures 3.8 and 3.9, respectively. One observes that the LOI of the fabric treated with HFPO/TMM was lower than that treated with HFPO/DMDHEU when the crosslinker concentration was below 4.0% (Figures 3.8). The relatively lower LOI for the fabric treated with HFPO/TMM is due to the relatively lower phosphorus content of the fabric as shown in Figures 3.5. When the TMM concentration increased to 6.0% and beyond, the LOI of the treated fabric was similar or higher than that treated with HFPO/DMDHEU (Figures 3.8 and 3.9). The enhancement in flame retarding performance provided by TMM due to phosphorus-nitrogen synergism became more significant at higher TMM concentrations since TMM is a more efficient nitrogen provider. The fact that the difference between the fabric treated with HFPO/DMDHEU and that treated with HFPO/TMM became smaller after 12 washes, as shown in Figure 3.9, is evidently due to the low durability of the HFPO/TMM system. The vertical flammability of the treated cotton fabric presented in Table 3.1 is consistent with LOI data shown in Figure 3.8 and 3.9.

The cotton fabric was treated HFPO at different concentrations and 6% crosslinker, and cured at 165ºC for 2.5 min. The LOI of the fabric thus treated before laundering is plotted against the HFPO concentration in Figure 3.10. The LOI of the cotton fabric treated with HFPO/TMM increased from 32.8 to 34.1 as the HFPO concentration increased from 25 to 45%, whereas it increased from 29.7 to 31.9 for the fabric treated with HFPO/DMDHEU at the same

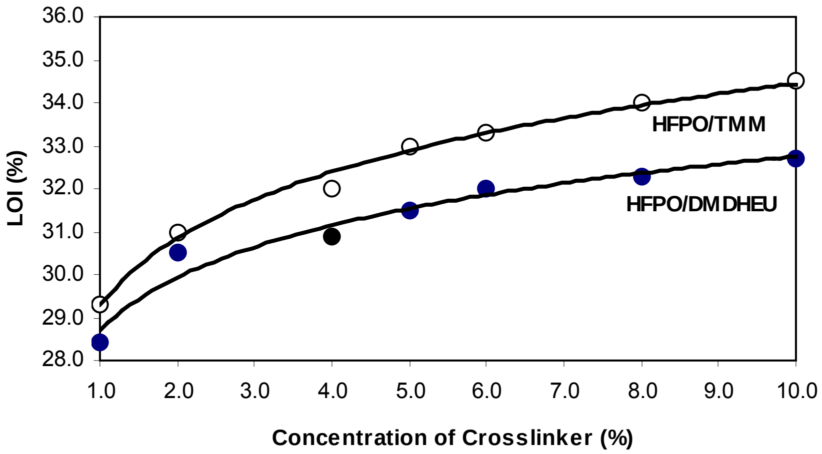


Figure 3.7. The LOI of the cotton fabric treated with 32% HFPO and a crosslinker (DMDHEU or TMM) at different concentrations and cured at 165ºC for 2.5 min (before wash).

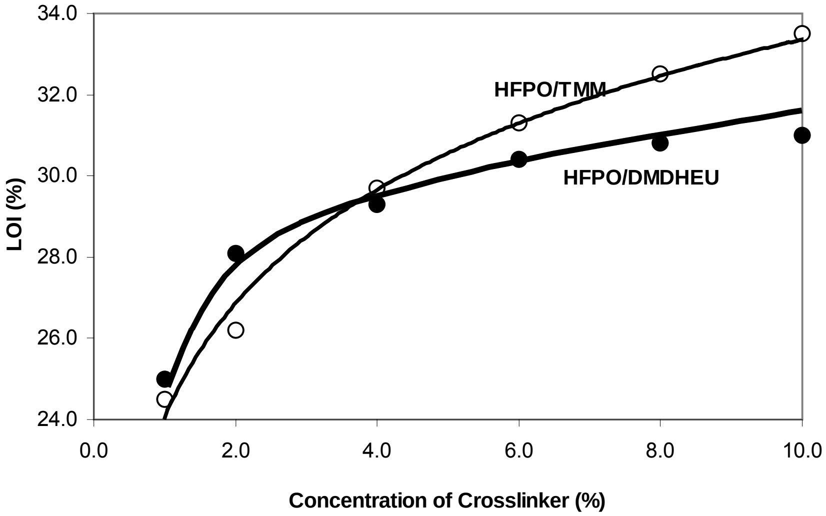


Figure 3.8. The LOI of the cotton fabric treated with 32% HFPO and a crosslinker (DMDHEU or TMM) at different concentrations and cured at 165ºC for 2.5 min (after 1 home laundering cycle).

concentration range (Figure 3.10). Thus, the data presented in Figure 3.10 provides additional evidence that TMM is a more effective nitrogen provider for the HFPO-based flame retarding system.

The phosphorus content of the cotton fabric treated with 6% DMDHEU and HFPO at the concentration range 25-45% after one home laundering ranged from 3.12 to 4.53%, whereas it was 2.43 to 3.02% for the fabric treated with HFPO/TMM at the same concentration (Figure 3.11). After 12 home laundering cycles, the phosphorus content of the cotton fabric treated with HFPO/DMDHEU ranged 2.59-3.69%, which is significantly higher than that treated with HFPO/TMM (1.93-2.31%)(Figure 3.12). The difference in phosphorus content between the fabric treated with HFPO/DMDHEU and that treated with HFPO/TMM increased as the number of laundering cycle increased. The cotton fabric treated with 35% HFPO and 6.0% DMDHEU

Table 3.1. The vertical flammability of the cotton fabric treated with 32% HFPO, in combination with DMDHEU and TMM of different concentrations, and cured at 165^{o}C for 2.5 min.

Crosslinker (%)	Char length (mm)	
	After 1 HLTD	After 12HLTD
DMDHEU 1%	128	>300
DMDHEU 2%	106	127
DMDHEU 4%	98	111
DMDHEU 5%	100	105
DMDHEU 6%	99	127
DMDHEU 8%	94	110
DMDHEU 10%	83	93
TMM 1%	>300	>300
TMM 2%	>300	>300
TMM 4%	124	255
TMM 5%	130	150
TMM 6%	139	114
TMM 8%	53	106
TMM 10%	77	86

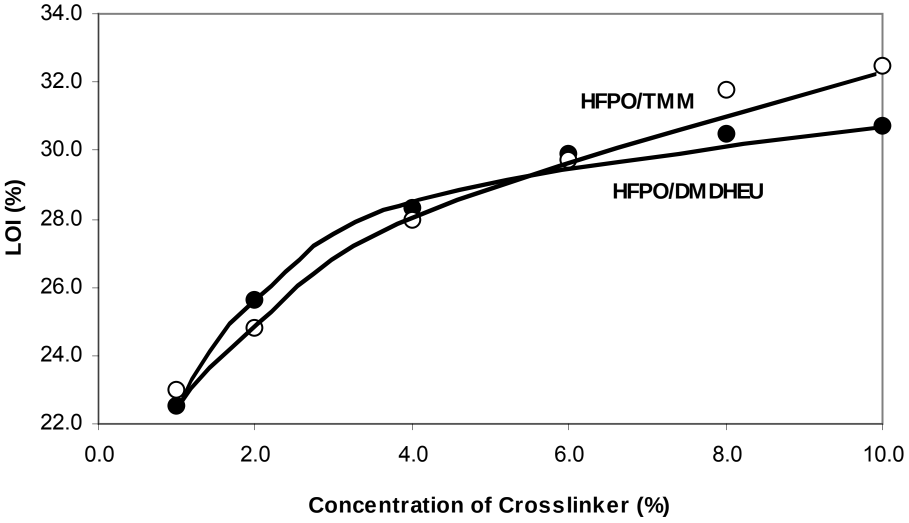


Figure 3.9. The LOI of the cotton fabric treated with 32% HFPO and a crosslinker (DMDHEU or TMM) at different concentrations and cured at 165ºC for 2.5 min (after 12 home laundering cycles).

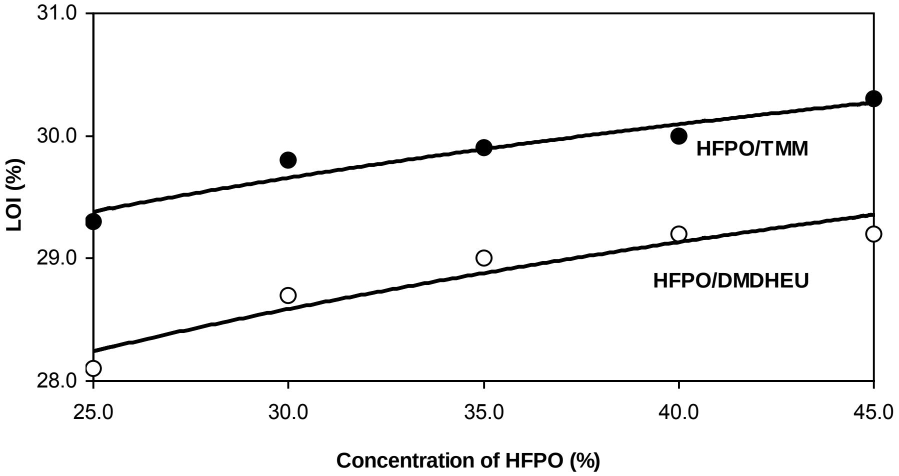


Figure 3.10. The LOI of the cotton fabric treated with 6% crosslinker in combination with HFPO at different concentrations (before wash).

Table 3.2. The LOI of the cotton fabric treated with 6% cross-linking agents and HFPO at different concentrations, cured at 165°C for 2.5 min, and subjected to 1 and 12 home laundering cycles.

HFPO (%)	Crosslinker (%)	LOI (%)	
		1 HLTD	12 HLTD
25	DMDHEU 6	28.4	28.1
30	DMDHEU 6	29.5	29.2
35	DMDHEU 6	29.2	29.0
40	DMDHEU 6	29.4	29.2
45	DMDHEU 6	29.5	29.2
25	TMM 6	30.9	29.3
30	TMM 6	31.3	29.8
35	TMM 6	31.4	29.9
40	TMM 6	31.6	30.0
45	TMM 6	31.8	30.3

Table 3.3. The vertical flammability of the cotton fabric treated with 6% cross-linking agents and HFPO at different concentrations, cured at 165°C for 2.5 min, and subjected to 1 and 12 home laundering cycles

HFPO (%)	Crosslinker (%)	Char length (mm)	
		1 HLTD	12 HLTD
25	DMDHEU 6	96	148
30	DMDHEU 6	97	109
35	DMDHEU 6	91	113
40	DMDHEU 6	94	109
45	DMDHEU 6	111	119
25	TMM 6	90	110
30	TMM 6	85	109
35	TMM 6	105	111
40	TMM 6	79	99
45	TMM 6	104	114

retained 3.77% phosphorus after one laundering cycle, which was 36% higher than that treated with HFPO and TMM at the same concentration (2.78%). After 12 laundering cycles, the phosphorus content on the fabric treated with HFPO/DMDHEU was 69% higher than that treated with HFPO/TMM. The data demonstrate that DMDHEU is not only much more effective for binding HFPO to cotton than TMM, and the crosslinking between HFPO and cotton formed by DMDHEU is also more durable to multiple home laundering than that formed by TMM.

The LOI and vertical flammability of the cotton fabric treated with 6% DMDHEU and HFPO at different concentrations and cured at 165ºC for 2.5 min is presented in Table 3.2 and 3.3 respectively. After one laundering cycle, the LOI of the fabric treated with HFPO/TMM is significantly higher than that treated with HFPO/DMDHEU. After 12 laundering cycles, the LOI of the fabric treated with HFPO/TMM was still higher than that treated with HFPO/DMDHEU in spite of the fact that the phosphorus concentration on the cotton fabric treated HFPO/DMDHEU was approximately 70% higher than that treated with HFPO/TMM at the HFPO concentration range of 30-45% (Table 3.2).

The cotton fabric was treated with HFPO and a crosslinker (DMDHEU or TMM) at a 3:1 (w/w) ratio, and the HFPO concentration ranged from 4 to 40%. The treated fabric was cured at 165ºC for 2.5 min. The LOI and vertical flammability of the cotton thus treated before and after 1 and 12 laundering cycles are presented in Table 3.4. The fabric treated with HFPO/TMM demonstrated better flame retarding performance at almost all cases in Table 3.4.

In summary, both DMDHEU and TMM function as bonding agent for HFPO and also as nitrogen provider to enhance the flame retarding performance of the treated cotton fabric. DMDHEU is a more effective crosslinker between HFPO and cotton, and the bonding formed by DMDHEU is also more durable to home laundering. When the concentrations of HFPO and the

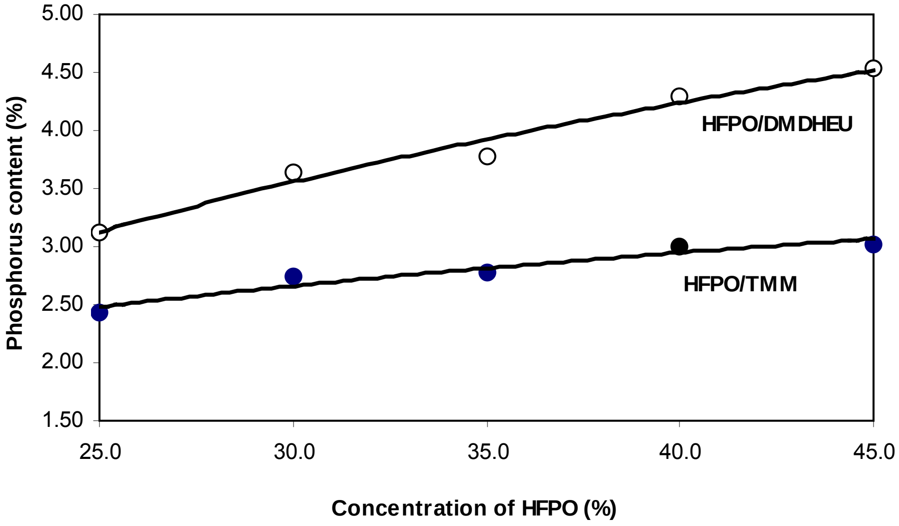


Figure 3.11. The phosphorus content of the cotton fabric treated with 6% crosslinker in combination with HFPO at different concentrations (after 1 home laundering cycle).

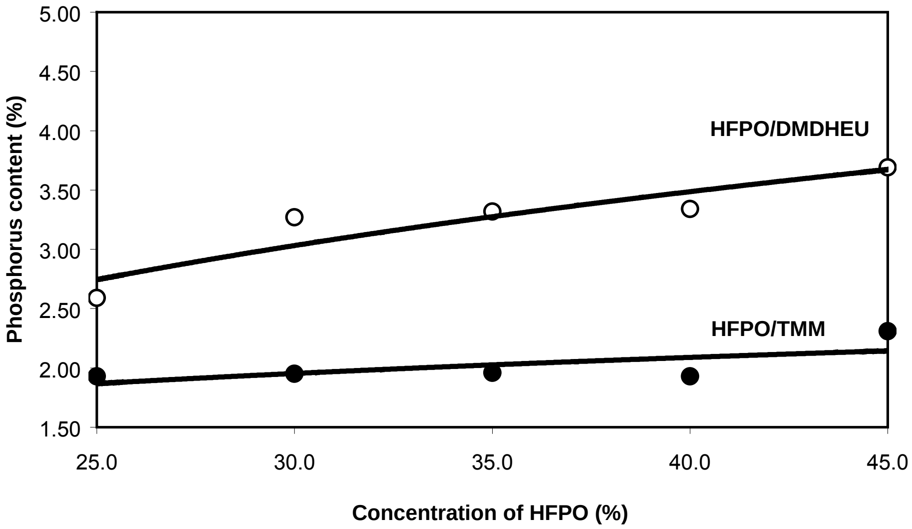


Figure 3.12. The phosphorus content of the cotton fabric treated with 6% crosslinker in combination with HFPO at different concentrations (after 12 home laundering cycles).

Table 3.4. The flammability of the cotton fabric treated with different concentrations of HFPO/cross-linking agents (3:1), cured at 165°C for 2.5 min.

HFPO (%)	Crosslinker (%)	LOI (%)			Char length (mm)		
		Before wash	1 HLTD	12 HLTD	Before wash	1 HLTD	12 HLTD
4	DMDHEU 1.3	22.5	20.0	19.7	>300	>300	>300
8	DMDHEU 2.7	23.6	21.5	21.4	>300	>300	>300
16	DMDHEU 5.3	28.3	27.1	25.0	98	107	>300
32	DMDHEU 10.7	32.5	30.6	30.5	92	95	104
40	DMDHEU 13.3	34.5	32.9	31.7	77	81	98
4	TMM 1.3	23.0	20.3	19.1	>300	>300	>300
8	TMM 2.7	26.2	23.5	22.3	>300	>300	>300
16	TMM 5.3	29.6	28.3	26.9	93	98	124
32	TMM 10.7	34.5	33.6	33.4	79	86	89
40	TMM 13.3	35.8	34.3	34.6	78	87	89

crosslinker reaches certain levels, however, the effect of phosphorus-nitrogen synergism becomes the predominant factor in determining the flammability of the treated cotton fabric even after multiple laundering cycles. The positive effect of TMM's providing a higher level of phosphorus-nitrogen synergism exceeds the negative effect of TMM's lower efficiency for bonding HFPO to cotton and its low laundering durability. Consequently, the cotton fabric treated with HFPO/TMM delivers superb flame retarding performance. In addition, the higher strength retention of the cotton fabric treated with HFPO/TMM is another advantage. TMM contains much higher levels of formaldehyde than DMDHEU, which must be considered as a major disadvantage for the HFPO/TMM system.

CONCLUSION

DMDHEU and TMM both function as the bonding agents for the hydroxy-functional organophosphorus flame retardant agent. DMDHEU is more effective for crosslinking cotton than TMM, thus cause higher fabric wrinkle resistance and higher fabric strength loss. DMDHEU is also more reactive for bonding HFPO to cotton than TMM, and the HFPO bound to cotton by DMDHEU is more durable to home laundering than that by TMM. Both DMDHEU and TMM also function as nitrogen providers for the flame retarding system, thus enhancing its flame retarding performance. TMM is significantly better nitrogen provider than DMDHEU for the flame retarding system. The cotton fabric treated with HFPO/TMM has significantly higher initial flame retarding properties than that treated with HFPO/DMDHEU. When the concentrations of the flame retarding organophosphorus compound and the crosslinker reach certain levels, the cotton fabric treated with HFPO/TMM maintain a higher level of flame retarding properties than that treated with HFPO/DMDHEU even after 12 home laundering cycles in spite of the fact that the phosphorus retention after laundering on the fabric treated with HFPO/DMDHEU is significantly higher than that treated with HFPO/TMM.

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CHAPTER 4

STATISTICAL ANALYSIS OF THE PERFORMANCE OF THE FLAME RETARDANT FINISHING SYSTEM CONSISTING OF A HYDROXY-FUNCTIONAL ORGANOPHOSPHORUS OLIGOMER AND THE MIXTURE OF DMDHEU AND MELAMINE-FORMALDEHYDE[1]

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ABSTRACT

In our previous research, we developed flame retarding systems for cotton based on a hydroxy-functional organophosphorus oligomer (HFPO) and a bonding agent, such as 1,2,3,4-butanetetracarboxylic acid (BTCA), dimethyloldihydroxyethyleneurea (DMDHEU) and trimethylolmelamine (TMM), which is able to form covalent bonding between HFPO and cotton. In this research, we used a factorial experimental design method to study the performance of flame retarding system based on HFPO and the mixture of DMDHEU and TMM. We found that an increase in the DMDHEU/(DMDHEU+TMM) ratio in the mixture increases amount of HFPO bound to cotton, increases the laundering durability of HFPO on cotton, and reduces the fabric tensile strength retention. DMDHEU and TMM also function as nitrogen-provider and enhance the flame retarding performance of the treated fabric due to phosphorus-nitrogen synergism. TMM is a more efficient nitrogen-provider than DMDHEU. The effect of reduced phosphorus-nitrogen synergism as a result of increasing the DMDHEU/ (DMDHEU+TMM) ratio outweighs that of improved bonding of HFPO. An increasing in HFPO concentration in a formula increases the amount of HFPO bound to cotton, whereas it reduces the percent retention of HFPO on the fabric and also reduces the fabric strength loss. Desirable performance of treated cotton fabric can be achieved by adjusting the concentrations of HFPO and the ratios of the two binders in a formula.

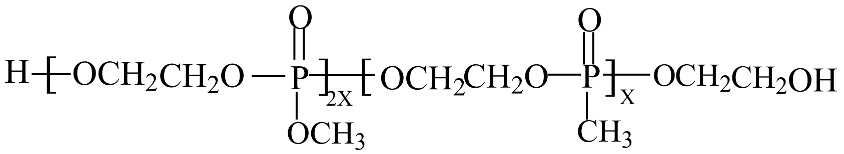
INDEX WORDS: Cotton, Flame retardant finishes, Trimethyloimelamine, Organophosphorus compound, Statistical analysis.

INTRODUCTION

Cotton either burns or smolders in the presence of oxygen and high temperatures [1]. Reducing the flammability of cotton is important for the fabrics used in apparel, home furnishing as well as those used as industrial fabrics. Several government regulations required to textile flammability are currently under consideration, which may affect 2-3 million bales of cotton fiber [2].

In the past several decades, a number of chemical treatment procedures have been developed to reduce the flammability of cellulosic substrates. However, only a few of them are still being practiced today. Currently, the durable flame retardant finishing systems for cellulosic fibers available to the industry include the “pre-condensate”/ammonia process and reactive organophosphorus chemicals [3, 4]. Both processes have certain limitations due to cost, need for special equipment, requirement of multiple after-washes, and other difficulties associated with the textile finishing operations [5].

In our previous research, we developed a nonformaldehyde flame retardant finishing system for cotton based on a hydroxy-functional organophosphorus oligomer (HFPO), such as the one shown in Scheme 4.1 (CA Register No. 70715-06-9), as the flame retardant agent and a polycarboxylic acid as the bonding agent [6-8].



$$H\!-\!\left[OCH_2CH_2O-\underset{OCH_3}{\overset{O}{\overset{\|}{P}}}\right]_{2x}\!\left[OCH_2CH_2O-\underset{CH_3}{\overset{O}{\overset{\|}{P}}}\right]_{x}\!-OCH_2CH_2OH$$

Scheme 4.1

We also developed the flame retardant finishing systems based on HFPO and a formaldehyde-based bonding agent, such as DMDHEU and TMM [9-12]. The use of DMDHEU with other phosphorus-containing alcohols was reported early in the literature [13]. In the present research, we studied the flame retardant system based on HFPO and the mixture of DMDHEU and TMM by using a factorial design method. We evaluated how the phosphorus content, percent phosphorus retention and LOI after different numbers of laundering cycles, and the strength retention of the treated cotton fabric are affected by the DMDHEU/(DMDHEU+TMM) ratio and the HFPO concentration so that the formulation of this finishing system can be optimized according to specific end uses.

EXPERIMENTAL

Materials

The fabric used was a desized, scoured, and bleached 40x40 cotton printcloth weighing 108 g/m^2 (Testfabrics Style 400). The hydroxy-functional organophosphorus oligomer with the commercial name of “Fyroltex HP” was supplied by Akzo Nobel, Dobbs Ferry, New York. DMDHEU with the commercial name of “Freerez 900” and trimethylolmelamine (TMM) with the trade name of “Aerotex M-3” were supplied by Noveon, Cleveland, Ohio. The catalyst based on NH_4Cl with the commercial name of “Catalyst RD” was supplied by Eastern Color & Chemical, Greenville, South Carolina.

Fabric Treatment and Home Laundering Procedures

The fabric was first immersed in a finish solution containing HFPO, mixture of DMDHEU and TMM, and the catalyst, then passed through a laboratory padder with two dips and two nips, dried at 90°C for 3 min, and finally cured in a Mathis curing oven at 165°C for 2.5 min. The weight of catalyst (Commercial product) in all formulas was 0.07% of that of (DMDHEU+TMM). All other concentrations (w/w, %) presented here were calculated based on weight of reagent (solid) and that of the bath. The wet pick-up of the cotton fabric was approximately 105±3%. After curing, the treated cotton fabric was subjected to different number of home laundering cycles with the use of "AATCC Standard Detergent 1993". The home laundering procedure was done according to AATCC Test Method 124-1996 ("Appearance of Fabrics After Repeated Home Laundering"). The water temperature for laundering was approximately 46°C.

Fabric Performance Evaluation

The limiting oxygen index (LOI) of the cotton fabric was measured according to ASTM Standard Method D2863-00. The tensile strength of the fabric was measured according to ASTM Standard Method D5035-95.

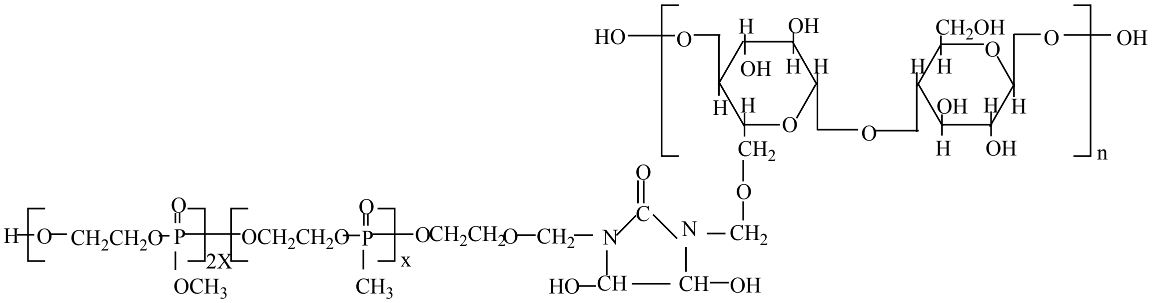
Determination of Phosphorus Concentration on the Treated Cotton Fabric

Approximately 2g of treated cotton fabric taken from different parts of a larger fabric specimen were ground in a Wiley mill into a powder to improve sample uniformity. 2 ml of concentrated H_2SO_4 were added to 0.1 g of cotton powder, and then 10 ml of 30% H_2O_2 was added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250ºC to digest the powder and to evaporate the water until dense SO_3 vapor is produced. The completely digested cotton sample as a clear solution was transferred to a 50-ml volumetric flask, and then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the phosphorus content. The percent phosphorus retention of the treated fabric after home laundering was calculated using the following formula: (P_{AL}/P_{BW}) x100%, where P_{AL} and P_{BW} is the phosphorus content on the fabric after laundering and that before washing, respectively.

RESULTS AND DISCUSSION

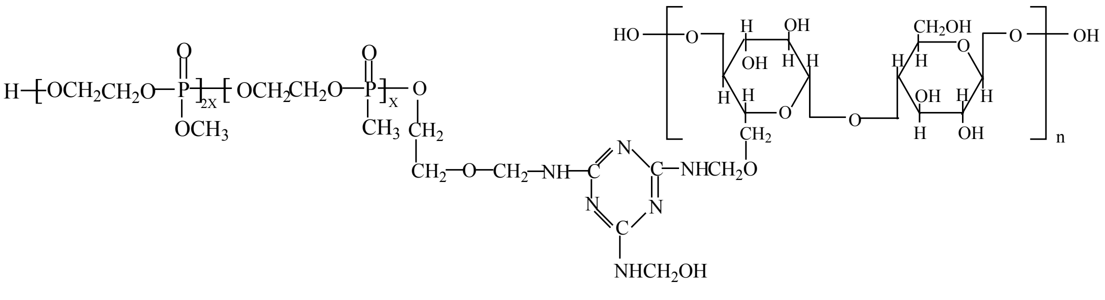
The Flame Retarding System and the Factorial Experimental Design Method

DMDHEU has four hemiacetal groups to react with the hydroxyl groups of cellulose (Scheme 4.2). The two hemiacetal groups derived from formaldehyde are significantly more reactive than those derived from glyoxal. In the presence of HFPO, these two hemiacetal groups are able to react with both hydroxyl groups of cotton cellulose and those of HFPO, thus forming a covalent bond between HFPO and cotton as shown in Scheme 4.2.



Scheme 4.2

The melamine-formaldehyde resin used in this study is a trifunctional reagent. When HFPO is present on the cotton fabric, TMM's three hemiacetal groups have the same reactivity towards the hydroxyl groups for cotton and HFPO, and form a linkage between cotton cellulose and HFPO (Scheme 4.3).



Scheme 4.3

Both DMDHEU and TMM functions as the binders for the flame retarding system. However, they have different reactivity, and the linkages between HFPO and cotton formed by the two binders have different durability to multiple laundering cycles. In this study, we applied a two-factor factorial experimental design method [14] to study how an HFPO/ (DMDHEU+TMM) formula influences the performance of the treated cotton fabric. The two factors used in this study, i.e., the HFPO concentration with three levels and the DMDHEU/ (DMDHEU+TMM) ratio with five levels, are presented in Table 4.1. The performance of the treated cotton fabric was evaluated based on (1) phosphorus content (%) on fabric and percent phosphorus retention by the fabric after home laundering and tumble dry (HLTD); (2) LOI of the cotton fabric before wash and after laundering; and (3) the tensile strength of the treated fabric at the filling direction after one laundering cycle. Duplicated tests were performed for each testing procedure.

Table 4.1. The factors and levels of a two-factor factorial experimental design method.

Factors	Levels				
	1	2	3	4	5
A: DMDHEU/(DMDHEU+TMM) ratios	0.00 (0/7)	0.29 (2/7)	0.57 (4/7)	0.86 (6/7)	1.00 (7/7)
B: HFPO concentrations (%)	16	32	48	-	-

The mathematical model used in the statistical analysis has a general polynomial form as shown in equation (1), where y_{ijk} is the response variable, μ is the overall mean, α_i is the effect of the i^{th} level of DMDHEU/(DMDHEU+TMM) ratio, β_j is the effect of the j^{th} level of HFPO concentration, $(\alpha\beta)_{ij}$ is the effect of the i^{th} level of DMDHEU/(DMDHEU+TMM) ratio combined with the j^{th} level of HFPO concentration (the interaction term), and ε_{ijk} is the residual error term.

$$y_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + \varepsilon_{ijk} \qquad (1)$$

The SAS® program was used in the statistics analysis to process the data. The statistical analysis was performed in the form of "analysis of variance" (ANOVA). This analysis included the F-test (overall model significance) and its associated probability (p-value) for studying the most influential factor affecting the performance of the treated cotton fabric. The F-test for interaction on phosphorus content, LOI, and tensile strength shows there is no interaction between HFPO concentration and DMDHEU/(DMDHEU+TMM) ratio, therefore, the analysis of the effect of the DMDHEU/(DMDHEU+TMM) ratio and HFPO concentration on phosphorus content, LOI, and tensile strength is meaningful.

Effect of the DMDHEU/ (DMDHEU+TMM) Ratio on the Phosphorus Content and Phosphorus Retention

The cotton fabric was treated with HFPO at three concentration levels (16%, 32%, and 48%) combined with 7% (DMDHEU+TMM) at five different DMDHEU/(DMDHEU+TMM) ratios, then cured at 165ºC for 2.5 min. The phosphorus concentration (%) of the cotton fabric thus treated before wash and after 1, 10, 25, and 50 laundering cycles is shown in Table 4.2 and Table 4.3 respectively, which includes the results of the two replicated sets of testing.

The statistical analysis on the phosphorus content data of the treated fabric after different number of home laundering cycles is presented in Table 4.4. The data shows that the p-value is 0.3436 before wash, which is larger than the significance level ($\alpha = 0.05$), meaning that the

DMDHEU/ (DMDHEU+TMM) ratio has no effect on the phosphorus content on the treated cotton fabric before wash. This is because all the formulas contain the same HFPO

Table 4.2. The phosphorus content of the cotton fabric treated with HFPO (16%, 32%) combined with 7% (DMDHEU+TMM) at five different DMDHEU/ (DMDHEU+TMM) ratios (two duplicated testing results).

Factor B	16%					32%				
Factor A	Before wash	1 HLTD	10 HLTD	25 HLTD	50 HLTD	Before wash	1 HLTD	10 HLTD	25 HLTD	50 HLTD
0.00 (0/7)	2.41	1.90	1.59	1.43	1.41	4.55	2.88	2.30	2.04	1.70
	2.38	1.89	1.58	1.42	1.38	4.58	2.86	2.28	2.26	1.68
0.29 (2/7)	2.43	1.92	1.60	1.44	1.34	4.58	3.03	2.45	2.21	2.00
	2.42	1.93	1.61	1.45	1.36	4.56	3.00	2.48	2.18	2.02
0.57 (4/7)	2.39	1.97	1.66	1.48	1.32	4.53	3.15	2.63	2.33	2.12
	2.36	1.96	1.68	1.50	1.36	4.56	3.16	2.61	2.36	2.10
0.86 (6/7)	2.38	1.92	1.70	1.54	1.53	4.47	3.43	2.99	2.80	2.66
	2.36	1.90	1.69	1.58	1.56	4.50	3.40	2.98	2.80	2.68
1.00 (7/7)	2.44	1.95	1.79	1.63	1.47	4.42	3.52	3.06	2.82	2.75
	2.48	1.96	1.81	1.66	1.50	4.48	3.55	3.08	2.85	2.78

Table 4.3. The phosphorus content of the cotton fabric treated with 48% HFPO combined with 7% (DMDHEU+TMM) at five different DMDHEU/(DMDHEU+TMM) ratios (two duplicated testing results).

Factor B	48%				
Factor A	Before wash	1 HLTD	10 HLTD	25 HLTD	50 HLTD
0.00 (0/7)	6.28	3.30	2.61	2.03	1.58
	6.28	3.28	2.58	2.00	1.60
0.29 (2/7)	6.24	3.56	2.65	2.03	1.77
	6.26	3.58	2.68	2.06	1.80
0.57 (4/7)	6.30	3.96	3.14	2.41	1.79
	3.29	4.00	3.10	2.38	1.80
0.86 (6/7)	6.27	4.43	3.47	2.95	2.27
	6.28	4.45	3.50	2.98	2.28
1.00 (7/7)	6.27	4.58	3.73	3.15	2.53
	6.27	4.56	3.69	3.18	2.58

concentration at each DMDHEU/(DMDHEU+TMM) level, therefore the phosphorus concentration on the fabric before wash is not related to the ratio of the two binders in those formulas. The p-value decreases to 0.0171 after one laundering cycle, which is smaller than the significance level ($\alpha=0.05$). Therefore, we can reject the null hypothesis and conclude that the DMDHEU/(DMDHEU+TMM) ratio has a significant effect on the phosphorus content on treated fabric after laundering. An increase in the DMDHEU content in the (DMDHEU+TMM) mixture evidently increases the percent phosphorus retention of the fabric after one laundering cycle as shown in Table 4.2 and Table 4.3. In our previous research, we found that DMDHEU is a more efficient reagent than TMM to bound HFPO to cotton [11], therefore an increase in DMDHEU/(DMDHEU+TMM) ratio results in more HFPO bound to the fabric.

Table 4.4. The statistical analysis of the effect of DMDHEU/(DMDHEU+TMM) ratio on the phosphorus content of the treated cotton fabric.

Laundering Conditions	Sum Square of Error	Mean Square of Error	F Value	Pr > F Value
Before Wash	0.002	0.002	1.01	0.3436
After 1 HLTD	0.65	0.65	9.00	0.0171
After 10 HLTD	0.72	0.72	15.95	0.0040
After 25 HLTD	0.73	0.73	14.40	0.0053
After 50 HLTD	0.71	0.71	15.21	0.0045

We notice that p-value decreases from 0.0171 after one laundering cycle to 0.0040 after 10 laundering cycles. Thus, the data indicate that the effects on the phosphorus content by varying the DMDHEU/(DMDHEU+TMM) ratio becomes more profound as the number of the home laundering cycle increases. The fabric treated using a formula with higher DMDHEU

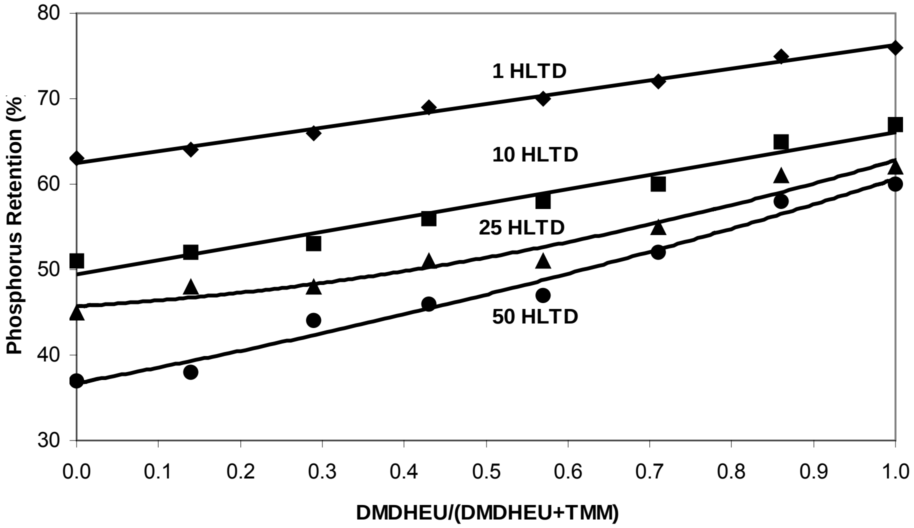


Figure 4.1. The phosphorus content (after 1, 10, 25, and 50 laundering cycles) of the cotton fabric treated with 32% HFPO and the combination of DMDHEU and TMM and cured at 165ºC for 2.5 min.

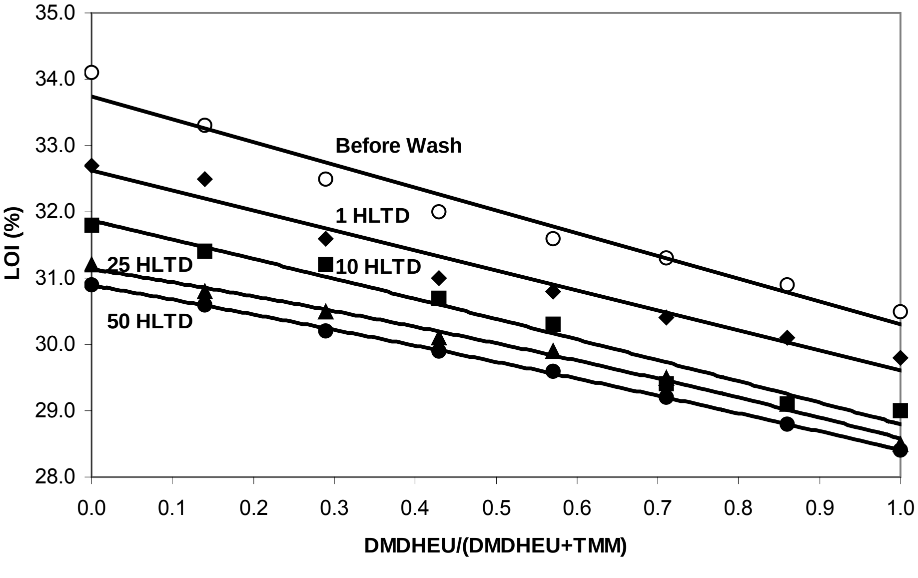


Figure 4.2. The LOI (before wash and after 1, 10, 25, and 50 laundering cycles) of the cotton fabric treated with 32% HFPO and the combination of DMDHEU and TMM and cured at 165ºC for 2.5 min.

content has higher laundering durability. The p-value after 25 and 50 laundering cycles are 0.0053 and 0.0045, respectively, which are all very close to that after 10 launderings.

To illustrate the effect of varying the DMDMDH/(DMDHDU+TMM) ratio on the phosphorus retention and the laundering durability of the treated fabric, we plotted the percent phosphorus retention of the cotton fabric treated 32% HFPO in combination with 7% (DMDHEU+TMM) after different numbers of home laundering cycles against the DMDHEU/(DMDHEU+TMM) ratio in Figure 4.1. The fabric treated with 32% HFPO and 7% TMM [DMDHEU/(DMDHEU+TMM)=0] retained 63% of the phosphorus after one laundering cycle. When the fabric is treated using 7% DMDHEU [DMDHEU/(DMDHEU+TMM)=1], the phosphorus retention increases to 80%. After 50 laundering cycles, the phosphorus retention of the fabric treated with 7% TMM is 37%, whereas it increases to 62% for the fabric treated with 7% DMDHEU. The effect of varying the DMDHEU/(DMDHEU+TMM) ratio on the phosphorus retention becomes more significant as the number of laundering cycle increases, thus indicating the bonding formed by DMDHEU between HFPO and cotton is more durable to the laundering that that formed by TMM.

The data presented here also show that the dependency of the phosphorus content on the DMDHEU/(DMDHEU+TMM) ratio is also affected by the HFPO concentration. At 16% HFPO, the phosphorus content on the fabric after one laundering cycle increases only slightly from 1.90 to 1.95% and the phosphorus retention remains 79% as the DMDHEU/(DMDHEU+TMM) ratio is increased from 0/7 to 7/7 (Table 4.2). When the HFPO concentration is increased to 32%, the phosphorus content increases from 2.89 to 3.54% and the phosphorus retention increases from 62 to 79% in the same DMDHEU/(DMDHEU+TMM) ratio range (Table 4.2). Evidently, the effect of varying the DMDHEU/(DMDHEU+TMM) ratio on the phosphorus concentration after laundering becomes more significant as the HFPO concentration increases. At the relatively low HFPO concentration (16%), the number of hemiacetal groups of DMDHEU and TMM is far greater than the number of hydroxyl groups of HFPO, therefore most of the HFPO molecules form two covalent linkages with DMDHEU and TMM, thus improving their retention on the fabric after laundering. As a result, the percent phosphorus retention on the fabric after laundering is less sensitive to the DMDHEU/(DMDHEU+TMM) ratio. As the HFPO concentration is increased, the relative amount of HFPO forming two covalent bonds decreases, and consequently, the percent phosphorus retention after laundering has a significant dependency on the types of binder used, as shown in the data presented in Table 4.2 and 4.3 respectively.

Effect of DMDHEU/(DMDHEU+TMM) Ratio on the LOI

The LOI of the cotton fabric treated HFPO at the three concentration levels combined with (DMDHEU+TMM) at five different DMDHEU/(DMDHEU+TMM) ratios before wash and after 1, 10, 25 and 50 laundering cycles is shown in Table 4.5 and Table 4.6. The two-factorial experimental design method was used to analyze the effect of the DMDHEU/(DMDHEU+TMM) ratio on the LOI of the treated cotton fabric before wash and after different number of laundering cycles (Table 4.7). The p-value is <0.0001 for the treated fabric before wash (Table 4.7). This indicates that the DMDHEU/(DMDHEU+TMM) ratio has a profound effect on the flame retarding performance of the treated fabric before wash. The LOI of the cotton fabric treated with 32% HFPO and 7% (DMDHEU+TMM) before wash and after multiple washes is plotted against the ratio of DMDHEU/(DMDHEU+TMM) (Figure 4.2). All the HFPO/(DMDHEU+TMM) finish solutions used to treat the cotton fabric in this study contain the same HFPO concentrations (32%) and the same total concentration of DMDHEU and TMM

(7%). The significantly higher LOI values of the fabric treated with the same concentrations of HFPO and (DMDHEU+TMM) but smaller DMDHEU/(DMDHEU+TMM) ratios [larger TMM/(DMDHEU+TMM) ratios] are attributed to the different effectiveness of DMDHEU and

Table 4.5. The LOI of the cotton fabric treated with HFPO (16%, 32%) combined with 7% (DMDHEU+TMM) at five different DMDHEU/(DMDHEU+TMM) ratios (two duplicated results).

Factor B Factor A										
	Before wash	1 HLTD	10 HLTD	25 HLTD	50 HLTD	Before wash	1 HLTD	10 HLTD	25 HLTD	50 HLTD
0.00 (0/7)	32.1 31.8	31.5 31.8	30.2 30.0	29.8 30.0	29.1 28.8	34.1 33.8	32.7 32.8	31.8 32.0	31.2 31.0	30.9 30.8
0.29 (2/7)	31.0 31.2	29.9 29.8	29.1 28.8	28.3 28.6	28.0 28.2	32.1 32.2	31.6 31.8	31.2 31.5	30.5 30.8	30.2 30.0
0.57 (4/7)	30.4 30.8	29.1 29.5	28.3 28.5	27.3 27.0	26.4 26.6	31.6 31.8	31.4 31.6	30.5 30.8	29.9 30.1	29.6 29.8
0.86 (6/7)	29.3 29.0	27.6 27.8	26.9 26.8	25.9 26.1	26.2 25.8	30.9 30.6	31.3 31.1	29.1 28.8	29.1 28.8	28.8 28.6
1.00(7/7)	29.0 28.8	27.3 26.9	26.7 26.5	25.8 26.0	25.8 26.0	29.8 30.0	29.8 29.6	28.7 28.6	28.7 28.5	28.4 28.0

Table 4.6. The LOI of the cotton fabric treated with 48% HFPO combined with 7% (DMDHEU+TMM) at five different DMDHEU/(DMDHEU+TMM) ratios (two duplicated results).

Factor B Factor A	48%				
	Before wash	1 HLTD	10 HLTD	25 HLTD	50 HLTD
0.00 (0/7)	35.0 35.2	34.3 34.6	33.2 32.8	31.0 31.2	30.3 30.6
0.29 (2/7)	34.4 34.6	33.6 33.2	32.1 32.5	29.9 29.8	28.3 28.0
0.57 (4/7)	34.0 33.8	32.6 32.9	31.7 31.6	30.3 30.2	28.5 28.6
0.86 (6/7)	33.5 33.3	31.9 31.6	31.3 31.0	30.6 30.8	28.5 28.3
1.00 (7/7)	32.2 31.8	31.0 31.2	30.6 30.8	29.6 29.8	28.3 28.0

Table 4.7. The statistical analysis of the effect of DMDHEU/(DMDHEU+TMM) ratio on the LOI of the treated cotton fabric.

Laundering Conditions	Sum Square of Error	Mean Square of Error	F Value	Pr > F Value
Before wash	17.34	17.34	111.51	< 0.0001
After 1 HLTD	18.03	18.03	86.81	< 0.0001
After 10 HLTD	14.11	14.11	119.72	< 0.0001
After 25 HLTD	10.40	10.40	18.62	0.0026
After 50 HLTD	10.14	10.14	37.23	0.0003

TMM in enhancing the performance of this flame retarding system. Both DMDHEU and TMM functions as a nitrogen provider to enhance the flame retarding performance due to phosphorus-nitrogen synergism. However, TMM provides a higher level of phosphorus-nitrogen synergism than DMDHEU, as discovered in our previous research [11]. Consequently, the fabric treated with a lower DMDHEU/(DMDHEU+TMM) ratio [higher TMM/(DMDHEU+TMM) ratio] demonstrates a higher LOI as shown in Figure 4.3.

The p-value for the treated fabric is still less than 0.0001 after 1 and 10 laundering cycles. The p-values after 25 and 50 laundering cycles are 0.0026 and 0.0003, respectively. Since all the p-values are less than significance level $\alpha = 0.05$, we can reject the null hypothesis and conclude that the DMDHEU/(DMDHEU+TMM) ratio has a significant effect on the LOI of the treated cotton fabric before wash and after multiple laundering cycles. The correlation between the LOI and the ratios of DMDHEU/(DMDHEU+TMM) and TMM/(DMDHEU+TMM) of the treated cotton fabric after 25 laundering cycle is illustrated in Figure 4.4. As we discussed above, DMDHEU is a more effective binder for HFPO. Increasing the DMDHEU/(DMDHEU+TMM) ratio increases amount of HFPO bound to cotton also increases

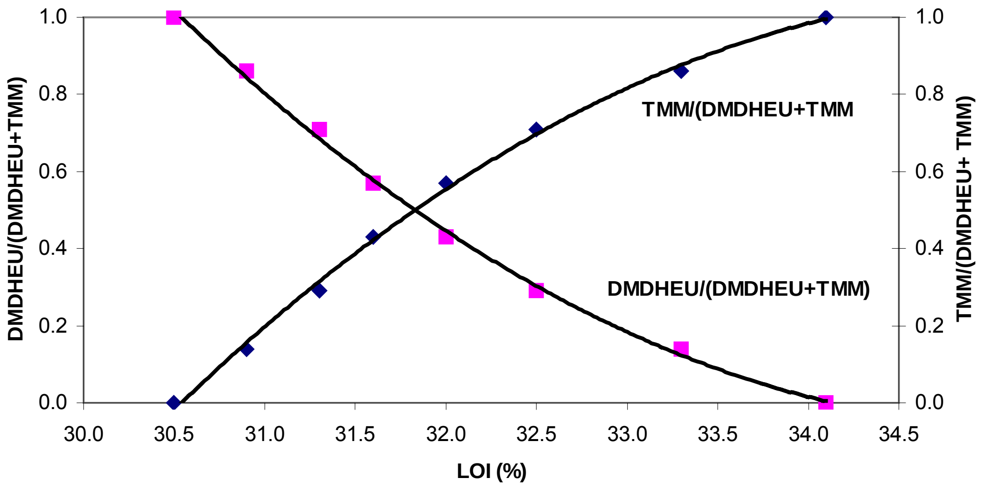


Figure 4.3. The correlations between the LOI and the ratios of DMDHEU/(DMDHEU+TMM) and TMM/(DMDHEU+TMM) of the cotton fabric treated with 32% HFPO and the combination of DMDHEU and TMM at different ratios and cured at 165ºC for 2.5 min (before wash).

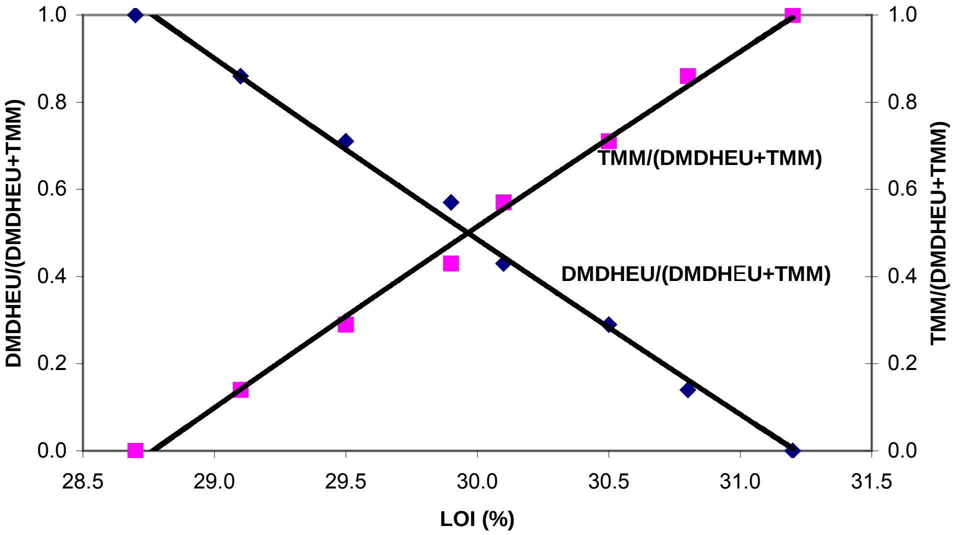


Figure 4.4. The correlations between LOI and the ratios of DMDHEU/(DMDHEU+TMM) and TMM/(DMDHEU+TMM) of the cotton fabric treated with 32% HFPO and the combination DMDHEU and TMM at different ratios and cured at 165ºC for 2.5 min (after 25 laundering cycles).

the laundering durability of HFPO on cotton. The lower LOI values for the fabric treated with higher DMDHEU/(DMDHEU+TMM) ratios after multiple laundering cycles indicate that the effect of reduced phosphorus-nitrogen synergism due to the increasing quantity of DMDHEU in the (DMDHEU+TMM) mixture of outweighs that of improved bonding of HFPO to cotton and improved laundering durability of HFPO on cotton. The synergism provided by DMDHEU and TMM appears to be the predominant factor in influencing the flame retarding performance of the HFPO/(DMDHEU+TMM) system.

Effect of the DMDHEU/(DMDHEU+TMM) Ratio on the Tensile Strength

The tensile strength at the filling direction of the cotton fabric treated with HFPO at three concentrations and (DMDHEU+TMM) at five different ratios and the statistical analysis of the fabric tensile strength data are shown in Tables 4.8 and 4.9, respectively. The p-value is 0.0002, far less than significant level $\alpha = 0.05$ (Table 4.9). Thus, we conclude that the tensile strength of the treated cotton fabric is also significantly affected by the DMDHEU/(DMDHEU+TMM) ratio. At the 32% HFPO level, the fabric tensile strength decreases from 14.5 to 10.7 kg as the DMDHEU/(DMDHEU+TMM) ratio increases from 0/7 to 7/7 (Table 4.8).

In our previous research on the cotton fabric treated by DMDHEU, we found that the fabric loss is due to cellulose depolymerization caused by the catalyst and the crosslinking of cellulose molecules [15]. Since all the HFPO/(DMDHEU+TMM) solutions used to treat the fabric contain the same catalyst concentration (0.5%), the fabric strength loss attributed to cellulose depolymerization should be independent of the DMDHEU/(DMDHEU+TMM) ratio. We also found that DMDHEU is a more efficient cross-linking agent for cotton than TMM [11].

Table 4.8. The tensile strength of the cotton fabric treated with HFPO (16%, 32%, and 48%) combined with 7% (DMDHEU+TMM) at five different DMDHEU/(DMDHEU+TMM) ratios (two duplicated testing results).

Factor B / Factor A	16%	32%	48%
0.00 (0/7)	12.7/13.0	14.5/14.0	15.8/15.6
0.29 (2/7)	12.6/12.2	14.3/13.8	14.7/15.0
0.57 (4/7)	11.3/10.8	13.6/13.0	13.7/13.2
0.86 (6/7)	11.2/10.6	12.5/12.3	12.4/12.0
1.00 (7/7)	10.9/10.0	10.7/10.8	12.4/12.6

Table 4.9. The statistical analysis of the effect of DMDHEU/(DMDHEU+TMM) ratio on the tensile strength of the treated cotton fabric.

Wash condition	SSE	MSE	F value	Pr > F value
After 1 HLTD	13.5	13.5	38.9	0.0002

Therefore, the increase in the fabric strength loss as a result of a higher DMDHEU/(DMDHEU+TMM) ratio at all three HFPO concentrations shown in Table 4.8 is attributed to the increase in the amount of crosslinking formed on the fabric. The tensile strength of the cotton fabric is plotted against the ratios of DMDHEU/(DMDHEU+TMM) and TMM/(DMDHEU+TMM) in Figure 4.5. The data presented here clearly demonstrate the dependency of the tensile strength of the treated fabric on the ratios of the two binders (Table 4.9).

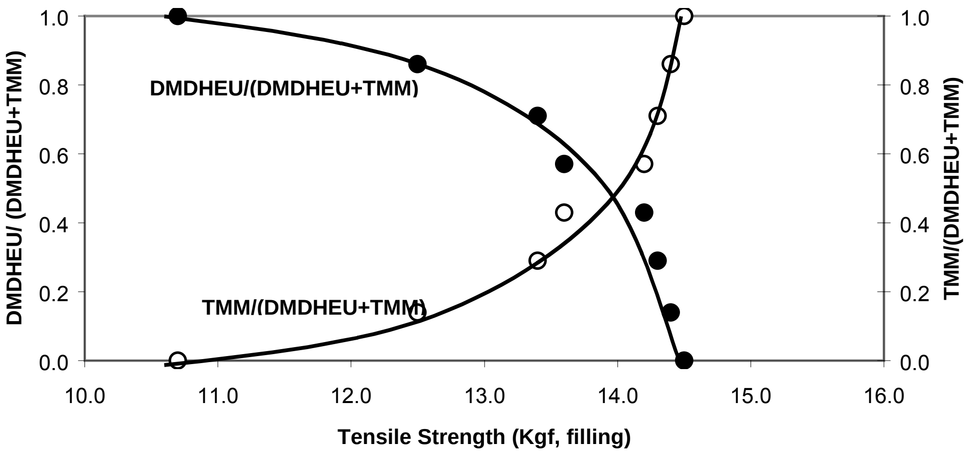


Figure 4.5. The correlations between the tensile strength at the filling direction and the ratios of DMDHEU/(DMDHEU+TMM) and TMM/(DMDHEU+TMM) of the cotton fabric treated with 32% HFPO and the combination of DMDHEU and TMM at different ratios and cured at 165ºC for 2.5 min.

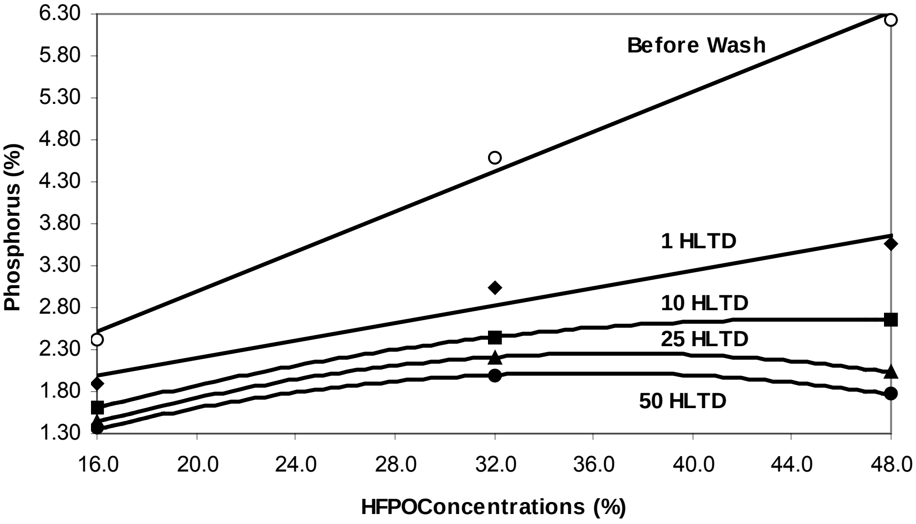


Figure 4.6. The phosphorus content of the cotton fabric treated with 7% binders with a DMDHEU/(DMDHEU+TMM) ratio of 0.29 (2/7) in combination with HFPO at different concentrations (before wash, after 1, 10, 25, and 50 laundering cycles).

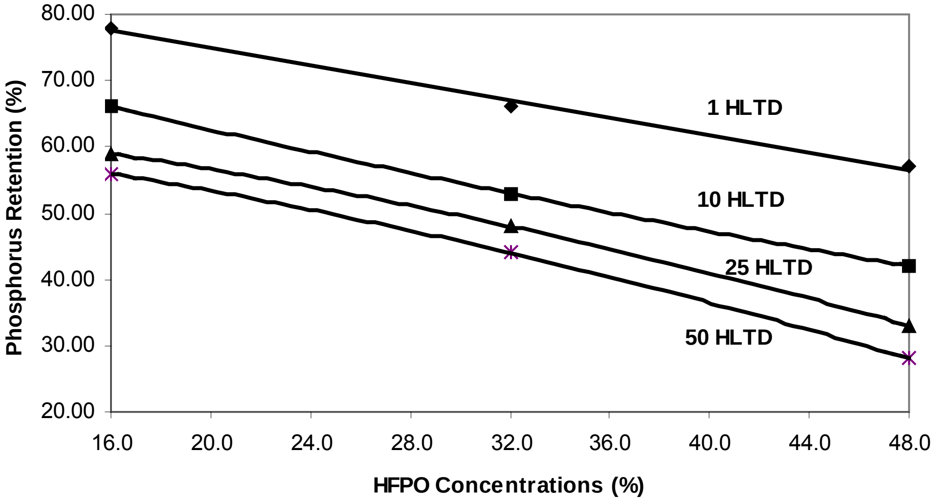


Figure 4.7. The percent phosphorus retention of the cotton fabric treated with 7% (DMDHEU+TMM) with a DMDHEU/(DMDHEU+TMM) ratio of 0.29 (2/7) in combination with HFPO at different concentrations (after 1, 10, 25, and 50 laundering cycles).

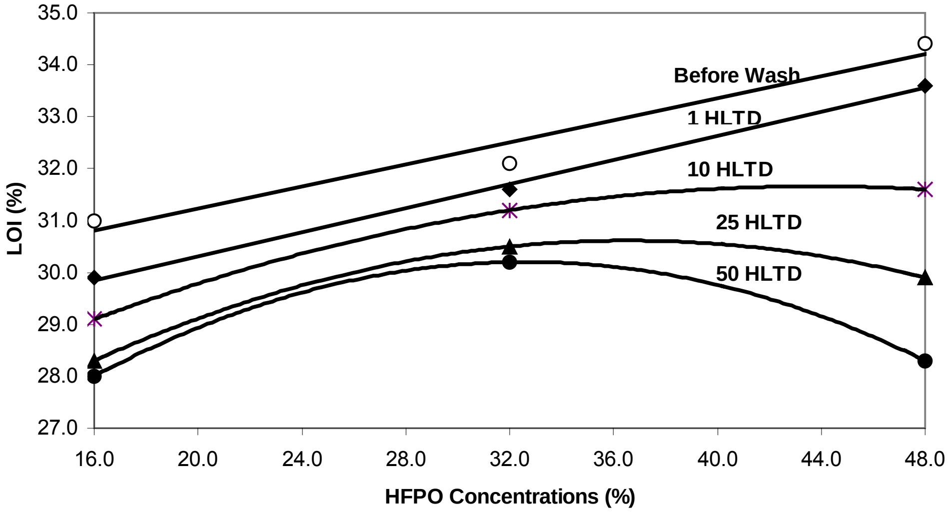


Figure 4.8. The LOI of the cotton fabric treated with 7% (DMDHEU+TMM) with a DMDHEU/(DMDHEU+TMM) ratio of 0.29 (2/7) in combination with HFPO at different concentrations (before wash, after 1, 10, 25, and 50 laundering cycles).

Effect of the HFPO Concentrations on the Phosphorus Content, LOI and Tensile Strength

The statistical analysis of the phosphorus content, LOI and tensile strength affected by the HFPO concentration is shown in Table 4.10. The p-values for phosphorus content, LOI and tensile strength after different number of laundering cycles are all well below the significance level ($\alpha = 0.05$). Thus, the HFPO concentrations have a statistically significant effect on all the parameters of the treated fabric.

Table 4.10. The statistical analysis of effect of HFPO concentration on LOI, phosphorus content and tensile strength of the treated cotton fabric.

Wash condition	P%			LOI (%)			Tensile strength (Kgf, filling)		
	SSE	F value	Pr > F value	SSE	F value	Pr > F value	SSE	F value	Pr > F value
Before wash	29.92	192.47	< 0.0001	-	-	-	-	-	-
After 1 HLTD	33.12	159.51	< 0.0001	10.34	149.31	<0.0001	10.61	30.57	0.0006
After 10 HLTD	31.32	265.88	< 0.0001	5.27	116.60	<0.0001	-	-	-
After 25 HLTD	20.45	36.31	0.0003	2.55	49.98	0.0001	-	-	-
After 50 HLTD	7.06	25.91	0.0009	0.82	17.71	0.0030	-	-	-

The cotton fabric was treated with HFPO at three concentration levels and 7% (DMDHEU+TMM) with a 0.29 (2/7) DMDHEU/(DMDHEU+TMM) ratio. The phosphorus content and percent phosphorus retention of the treated fabric after 1, 10, 25, and 50 laundering cycles are presented in Figures 4.6 and 4.7, respectively. One observes that the phosphorus content on the treated fabric after different number of laundering cycles increases as the HFPO concentration increases (Figure 4.6). However, the data presented here also clearly demonstrate that the percent phosphorus retention decreases as the HFPO concentration increase (Figure 4.7).

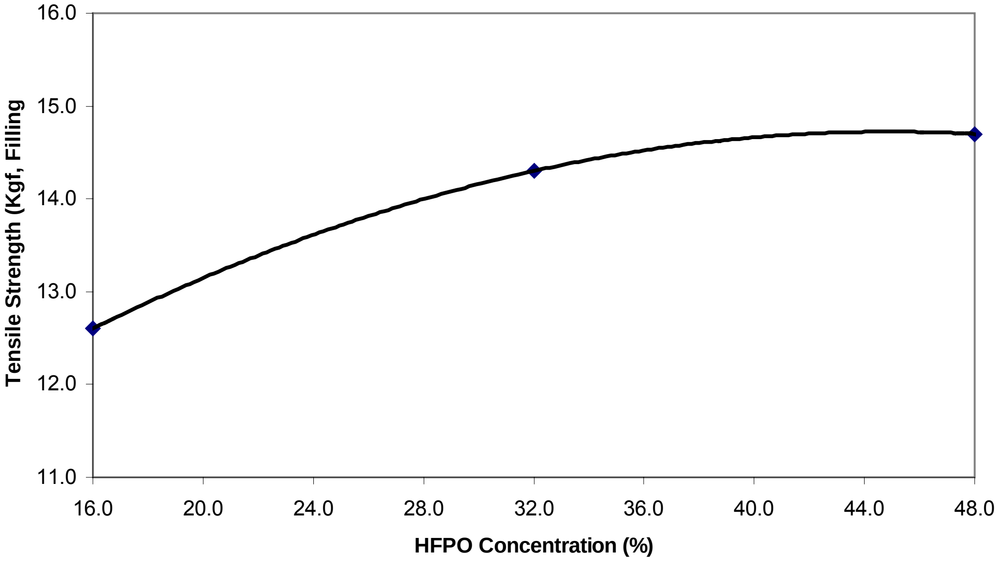


Figure 4.9. The tensile strength of the cotton fabric treated with 7% (DMDHEU+TMM) with a DMDHEU/(DMDHEU+TMM) ratio of 0.29 (2/7) in combination with HFPO at different concentrations.

The percent phosphorus retention decreases from 78 to 57% (a 28% decline) as the HFPO concentration increases from 16 to 48% after one laundering cycle, and it decreases from 56% to 28% (a 50% decline) in the same HFPO concentration range after 50 laundering cycles (Figure 4.7). The data presented in Figure 4.7 show that the effect of the HFPO concentration on the percent phosphorus retention on the fabric become more profound as the number of laundering cycles increases. When the amount of HFPO relative to that of (DMDHEU+TMM) becomes high, the number of the hemiacetal groups of DMDHEU may be inadequate for bonding the HFPO to cotton, thus reducing the percent phosphorus retention on the fabric as shown in Figure 4.7. At a relatively low HFPO/(DMDHEU+TMM) ratio, both hydroxyl groups of HFPO molecule may able to react with the binders, and thus being bound to cotton with two covalent bonds. Consequently, the laundering durability of the HFPO thus bound to cotton is improved. As the HFPO/(DMDHEU+TMM) ratio increases, more HFPO is bound to cotton by single linkage, thus diminishing its laundering durability.

The LOI of the cotton fabric treated with HFPO and 7% (DMDHEU+TMM) with a DMDHEU/(DMDHEU+TMM) ratio of 0.29 (2/7) is plotted against the concentration in Figure 4.8. The LOI of the treated fabric before wash and after one wash increases as the HFPO concentration increases (Figure 4.8). When the number of laundering cycle increases to 25 and 50 cycles, however, the LOI of the treated fabric increases from 28.3 and 28.0 at the 16% HFPO concentration level to 30.5 and 30.2 at the 32% HFPO concentration level, and then decreases to 29.9/28.3, respectively, at the 48% HFPO concentration level (Figure 4.8). The data shown here are another indication of the reduced laundering durability of the treated fabric at exceedingly high HFPO/(DMDHEU+TMM) ratio.

Presented in Figure 4.9 is the tensile strength of the cotton fabric treated with HFPO and 7% (DMDHEU+TMM) as a function of HFPO concentrations. The fabric strength at the filling direction increases from 12.6 to 14.7 kg as the HFPO concentration increases from 16 to 48%. As we discussed before, the hydroxyl groups of cellulose and those of HFPO compete to react with the binders. More DMDHEU and TMM form crosslinking on the cotton fabric as the HFPO concentration decreases, thus causing more fabric loss due to the increasing amount of crosslinking.

CONCLUSION

The statistical analysis of the performance of the cotton fabric treated with HFPO/(DMDHEU+TMM) using a two-factorial experimental design method reveals the following:

(1) Because of the different functionality and reactivity of DMDHEU and TMM, the DMDHEU/(DMDHEU+TMM) ratio in a HFPO/(DMDHEU+TMM) formula has a profound effect on the bonding of HFPO to cotton, the laundering durability of the HFPO bound to cotton and the strength retention of the treated fabric. An increase in the DMDHEU content in the mixture of the two binders increases amount of HFPO bound to cotton, increases the laundering durability of HFPO on cotton, and reduces the fabric tensile strength retention. DMDHEU and TMM also function as nitrogen-provider and enhance the flame retarding performance of the treated fabric due to phosphorus-nitrogen synergism. Because TMM is a significantly more efficient nitrogen-provider than DMDHEU, an increase in the DMDHEU/(DMDHEU+TMM) ratio reduces the flame retarding performance of the treated cotton fabric. The effect of reduced phosphorus-nitrogen synergism as a result of increasing the DMDHEU/(DMDHEU+TMM) ratio outweighs that of improved bonding of HFPO to cotton and improved laundering durability of HFPO on cotton due to the increasing the DMDHEU content in the mixture.

(2) An increasing in HFPO concentration in a formula decreases the amount of HFPO bound to cotton, whereas it reduces the percent retention of HFPO after laundering and the laundering durability of the treated fabric. An increasing in HFPO concentration also decreases fabric strength loss.

(3) Since the flame retarding performance and the strength of the cotton fabric treated with the HFPO/(DMDHEU+TMM) system are determined by the HFPO concentration, the total

concentrations of the total binders as well as the ratio of the two binders, the desirable performance of the treated cotton fabric can be achieved by adjusting the concentrations of the three components in a formula.

ACKNOWLEDGEMENT

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CHAPTER 5

PHOSPHORUS-NITROGEN SYNERGISM FOR COTTON FABRIC TREATED WITH AN ORGANOPHOSPHORUS FLAME RETARDANT FINISHING SYSTEM[1]

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[1] Wu, W, and Yang, CQ. 2004. Submitted to Polymer Degradation and Stability.

ABSTRACT

Both DMDHEU and trimethylolmelamine (TMM) are nitrogen providers for an organophosphorus-based flame retardant finishing system to enhance the flame resistance of cotton by means of phosphorus-nitrogen synergism. The synergistic role of nitrogen in enhancing flame resistance has been studied for cotton. We found that TMM was a more effective nitrogen provider than DMDHEU to improve the flame resistance through phosphorus-nitrogen synergism. The mechanism of phosphorus-nitrogen synergism has been investigated by studying the thermal decomposition of treated cotton cellulose. The interaction between phosphorus and nitrogen alters the thermal decomposition path: the interaction of phosphorus-nitrogen retards the thermal decomposition of cellulose by depolymerization, and contributes to the dehydration process, thus reducing levoglucosan and its volatilization, increasing the amount of solid char, and substantially improving the flame resistance of treated cotton fabric. The nitrogen and phosphorus contents have a different influence on the dehydration temperature. The extent of dehydration, not the dehydration temperature has a profound effect on the flame resistance of the treated cotton.

INDEX WORDS: Cotton, DMDHEU, Flame retardant finishes, Phosphorus-nitrogen synergism, Reactive organophosphorus chemicals, Trimethylolmelamine, Thermal decomposition.

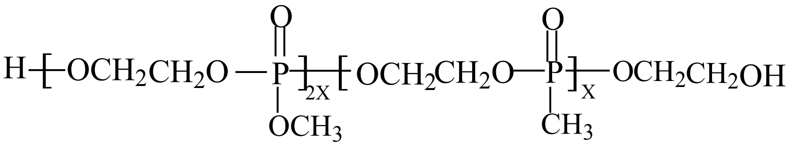
INTRODUCTION

The enhancement of the flame resistance of phosphorus flame retardants on cellulose by nitrogen resins were first recognized in the 1940 era [1]. One important feature of the action of phosphorus-based flame retardants on textile fabrics is the reported improvement in flame retardancy which occurs in the presence of compounds containing nitrogen. This is believed to arise as a result of phosphorus-nitrogen (P-N) synergism. Phosphorus-nitrogen synergism is defined as an effect greater than that predicted on the basis of the additive effect of individual phosphorus components. The enhancing effect of a non-flame retardant additive on a flame retardant system is also termed synergism [2].

Some published work on the quantitative basis of the interaction of phosphorus and nitrogen in cellulose flame retardancy was reviewed. It was found [3] that the synergistic effect is not a function of any specific phosphorus/nitrogen ratio, but the increasing amount of nitrogen-containing reagents at fixed phosphorus ratios regularly improve the flame resistance. It was also found that [4-5] the chemical structure of nitrogen-containing compounds used had a significant effect on its synergistic interaction. It was generally recognized that melamine-formaldehyde was an effective synergist for urea-phosphate; however, there were controversial results on the synergism of dimethyloldihydroxyethyleneurea (DMDHEU) [6-8]. Although there are some hypotheses on the mechanistic aspects of phosphorus-nitrogen synergism, the manner by which the phosphorus-nitrogen interaction influences the thermal decomposition of cellulose has not been studied in detail.

Our previous research showed [9] that both trimethylolmelamine (TMM) and

DMDHEU function as nitrogen providers for the flame retardant finishing system based on a reactive organophosphorus oligomer, such as the one shown in Scheme 5.1 (CA Registry No. 70715-06-9, abbreviated as “HFPO” here), thus enhancing its flame retardancy. We also found that TMM is a more efficient nitrogen provider than DMDHEU for the system. The cotton fabric treated with HFPO/TMM has significantly higher initial LOI than that treated with HFPO/DMDHEU when the same concentration of TMM and DMDHEU are used.



$$H\left[OCH_2CH_2O-\overset{O}{\overset{\|}{\underset{\underset{OCH_3}{|}}{P}}}\right]_{2X}\left[OCH_2CH_2O-\overset{O}{\overset{\|}{\underset{\underset{CH_3}{|}}{P}}}\right]_{X}OCH_2CH_2OH$$

Scheme 5.1

In this research, both TMM and DMDHEU were used as nitrogen providers for the HFPO flame retardant finishing system. We quantitatively evaluated the flame resistance of cotton at different phosphorus and nitrogen levels, compared the synergistic effect of those nitrogen-containing reagents, and investigated the mechanism of phosphorus-nitrogen synergism by studying the thermal decomposition process of treated cotton cellulose.

EXPERIMENTAL

Materials

The fabric used was a desized, scoured, and bleached cotton printcloth weighing 108g/m^2 twill weave (Testfabrics Style 400). The hydroxy-functional organophosphorus oligomer (HFPO) with the commercial name of “Fyroltex HP®” was supplied by Akzo Nobel Chemicals, Dobbs Ferry, New York. DMDHEU with the commercial name of “Freerez 900” and TMM with the trade name of “Aerotex M-3” were supplied by Noveon, Cleveland, Ohio.

Fabric Treatment

The fabric was first immersed in a finish solution containing flame retardant, TMM or DMDHEU, then passed through a laboratory padder with two dips and two nips, dried at 90°C for 3 min, and finally cured in a Mathis curing oven at 165°C for 2.5 min. Both the concentrations of DMDHEU and TMM were based on 100% solid. The wet pick-up of the cotton fabric was approximately 105±3%.

LOI Measurement

Limiting oxygen index (LOI) of the cotton fabric was measured according to ASTM D2863-00.

Determination of Phosphorus Concentration on the Treated Cotton Fabric

Approximately 2 g of treated cotton fabric taken from different parts of a larger fabric specimen were ground in a Wiley mill to a powder to improve sample uniformity. Then, 2 ml of concentrated H_2SO_4 were added to 0.1 g of cotton powder. 10 ml of 30% H_2O_2 was added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250ºC to digest the powder and to evaporate the water until dense SO_3 vapor was produced. The completely digested cotton sample as a clear solution was transferred to a 50-ml volumetric flask, and then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the phosphorus content.

Determination of Nitrogen Concentration on the Treated Cotton Fabric

The nitrogen content on cotton fabric was determined by Kjeldahl digestion followed by titration of distilled ammonia.

Thermal Analysis

Approximately 1g of treated cotton fabric taken from different parts of a larger fabric specimen was ground in a Wiley mill to a powder to improve sample uniformity. Thermal decomposition was carried out on approximately 10 mg samples under nitrogen flow (30cm^3/min) by thermogravimetry (TG) at heating rates of 10^{o}C/min and differential scanning calorimetry (DSC) at 5^{o}C/min using a Mettler Toledo thermal analyzer.

RESULTS AND DISCUSSION

Preliminary investigations have been carried out to examine the function of selected nitrogen-containing reactants in flame retardancy. The TMM and DMDHEU have been used as crosslinking agents for cotton, and are reasonable choices for use in flame retardant finishes. The cotton fabric was treated with TMM or DMDHEU alone at different concentrations. LOI of the cotton fabric thus treated is presented in Figure 5.1. The LOI of the cotton fabric treated with TMM or DMDHEU increased as the nitrogen content on fabric was increased. The DMDHEU-treated fabric with 4.94% nitrogen had LOI of 22.6, whereas TMM-treated fabric only had LOI of 19.4 when the nitrogen content was 4.54% (LOI of control is 17.8). Both TMM and DMDHEU can increase LOI of treated cotton fabric. However, DMDHEU treated fabric had a higher LOI value than that of TMM when the same amount of nitrogen content was on the fabric.

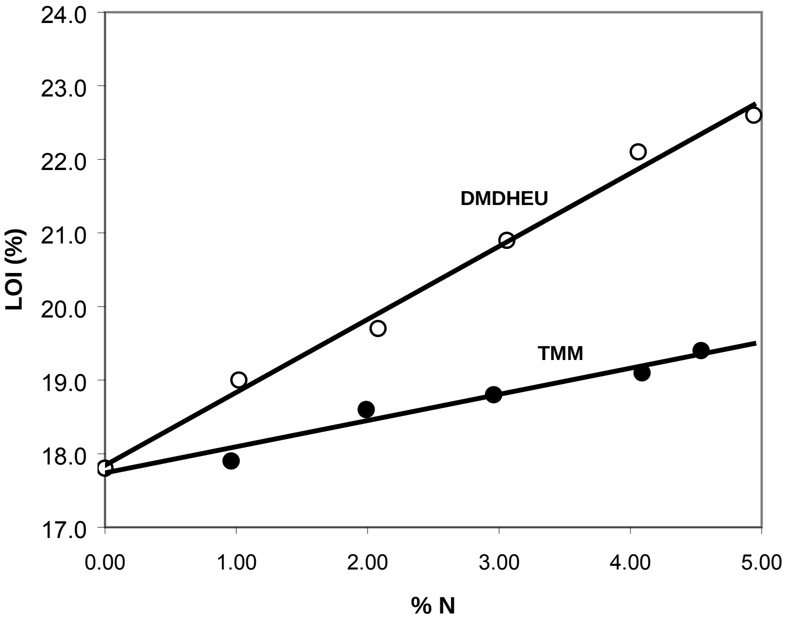


Figure 5.1. LOI vs nitrogen content of cotton fabric treated with different nitrogen-containing reactants.

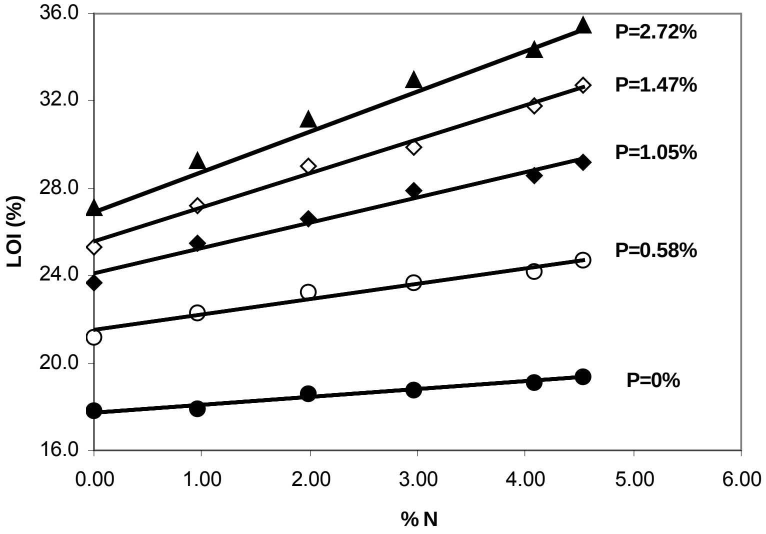


Figure 5.2. LOI vs nitrogen content at fixed phosphorus levels for HFPO/TMM treated cotton fabric.

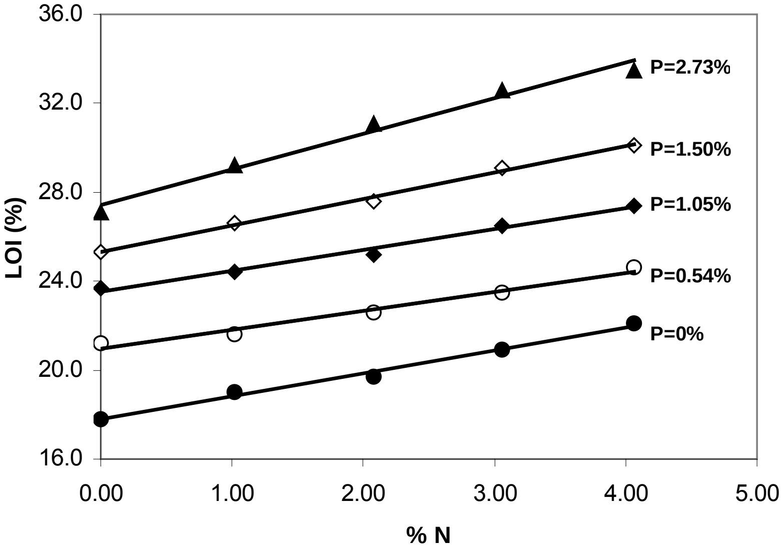


Figure 5.3. LOI vs nitrogen content at fixed phosphorus levels for HFPO/DMDHEU treated cotton fabric.

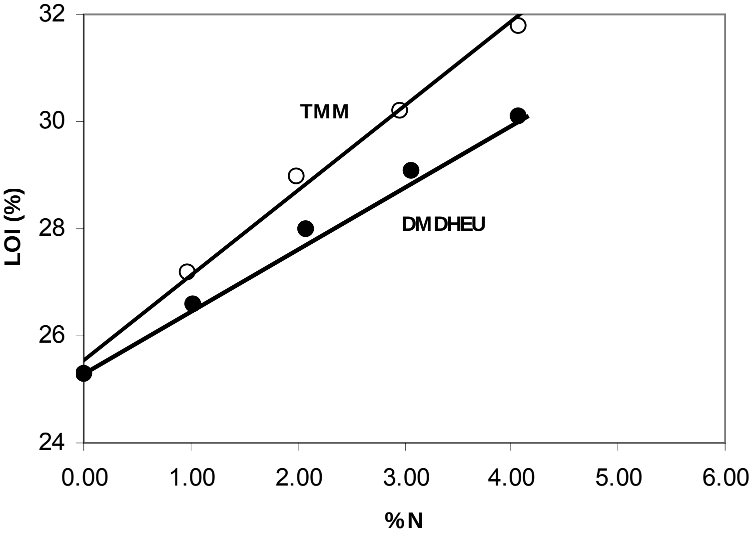


Figure 5.4. LOI vs nitrogen content at fixed phosphorus levels for different nitrogen-containing reactants treated cotton fabric.

The cotton fabric was treated with HFPO/TMM or HFPO/DMDHEU, and both finish systems were studied in detail at predetermined phosphorus levels, with nitrogen contents varying around 5%. LOI values of treated fabric are plotted against the nitrogen content at increasing specific phosphorus levels in Figure 5.2 and Figure 5.3, respectively. One observes that LOI is a linear function of nitrogen content at a given phosphorus level, as seen by the series of straight lines. We noticed that the LOI of fabric treated with HFPO only changed from 21.2 to 27.1 as the phosphorus content increased from 0.58% to 2.72%. In the presence of nitrogen, the flammability of treated cotton fabric is significantly different. The LOI of the fabric treated with HFPO/TMM increased from 27.1 to 34.5, whereas the LOI of HFPO/DMDHEU treated fabric increased from 27.1 to 33.5 when the nitrogen content was increased from 0 to 4.0%. At zero nitrogen and 2.72% phosphorus, LOI of treated fabric is 27.1, an increase of 9.3 above the control of 17.8, and at 4% nitrogen as DMDHEU, LOI is 21.7, and an increase of 3.9 above the control of 17.8. By additivity, this would product that at 4% nitrogen as DMDHEU plus 2.72% phosphorus, we would expected to get LOI of 3.9+9.3+17.8 =31.0, but in fact the measures LOI is 33.5, the measured LOI is much higher than the expected one in HFPO/DMDHEU system; Similarly, for HFPO/TMM flame retardant finishing system, the expected LOI is 1.3+9.3+17.8=28.4, nevertheless, the measured LOI is 34.5, the measured LOI is also much higher than that of expected LOI. Both HFPO/TMM and HFPO/DMDHEU had the same phosphorus content (2.72%); the data presented here indicate that both TMM and DMDHEU can enhance the flame resistance of treated fabric. An effect greater than that predicted on the basis of additives of individual phosphorus components is called synergism [2]. TMM and

DMDHEU by themselves can only marginally increase the LOI value (Figure 5.1), however, they can provide phosphorus-nitrogen synergism to the flame retardant finishing system, therefore significantly enhancing the flame resistance of treated fabric. The data also show that both TMM and DMDHEU are good synergistic agents for flame retardant agent HFPO.

Shown in Figure 5.4 are the LOI values of cotton fabric treated with HFPO/TMM or HFPO/DMDHEU at a fixed phosphorus content (1.50%) and an increasing amount of nitrogen content. We observed again that the LOI value of treated fabric increased as the nitrogen content was increased. However, the LOI of HFPO/TMM treated fabric increased from 25.3 to 31.8, whereas the LOI of HFPO/DMDHEU treated fabric only increased from 25.3 to 30.1 when the nitrogen concentration was increased from 0 to 4.0%. We found an approximately 2 unit lower LOI of HFPO/DMDHEU treated fabric compared to that of HFPO/TMM treated fabric at the same phosphorus and nitrogen content. To achieve the same level of flame resistance (LOI value), a smaller amount of nitrogen of TMM is needed than that of DMDHEU. The data presented here demonstrate that TMM is a more efficient nitrogen provider; because the cotton fabric treated HFPO/TMM has a higher LOI than that treated with HFPO/DMDHEU as the same amount of phosphorus and nitrogen content.

The LOI values of cotton fabric treated with HFPO/TMM or HFPO/DMDHEU were plotted as a function of phosphorus content at increasing specific nitrogen levels (Figure 5.5 and Figure 5.6 respectively). Without TMM and DMDHEU, the LOI of treated cotton fabric increased when the phosphorus content are less than 2.0%. As the phosphorus content

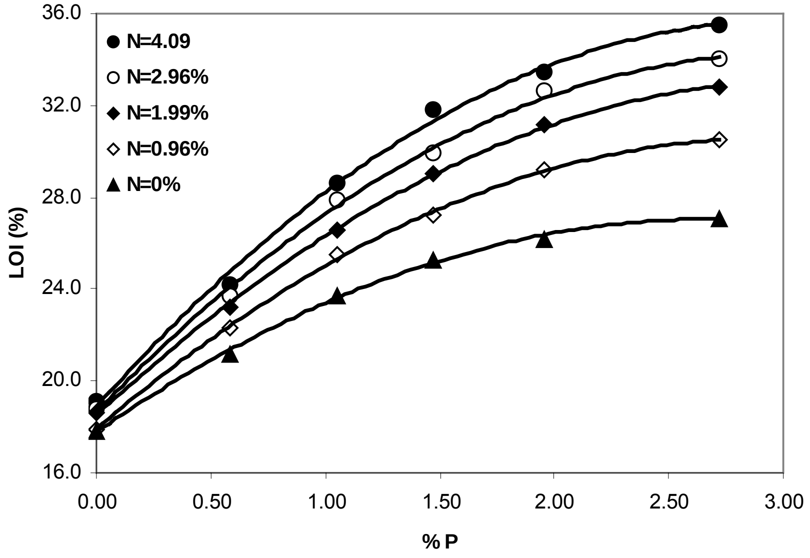


Figure 5.5. LOI vs phosphorus content at fixed nitrogen levels for HFPO/TMM treated cotton fabric.

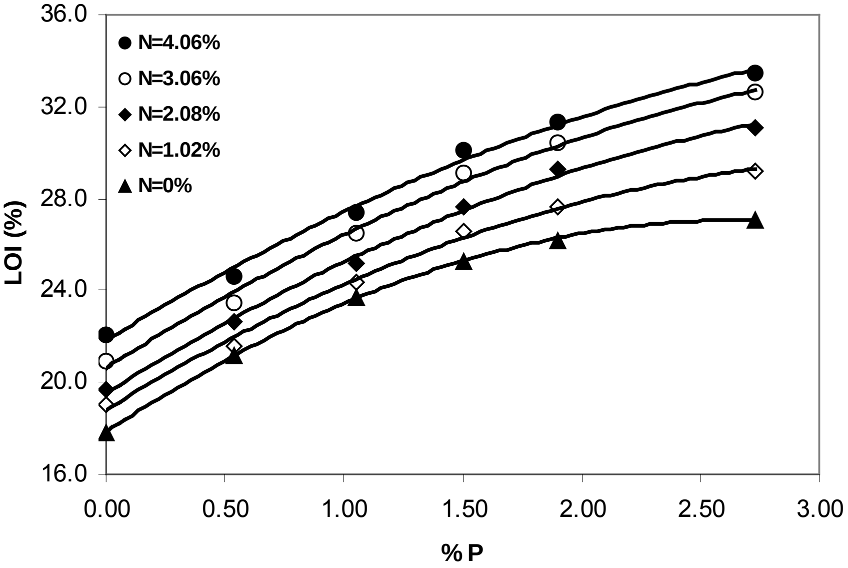


Figure 5.6. LOI vs phosphorus content at fixed nitrogen levels for HFPO/DMDHEU treated cotton fabric.

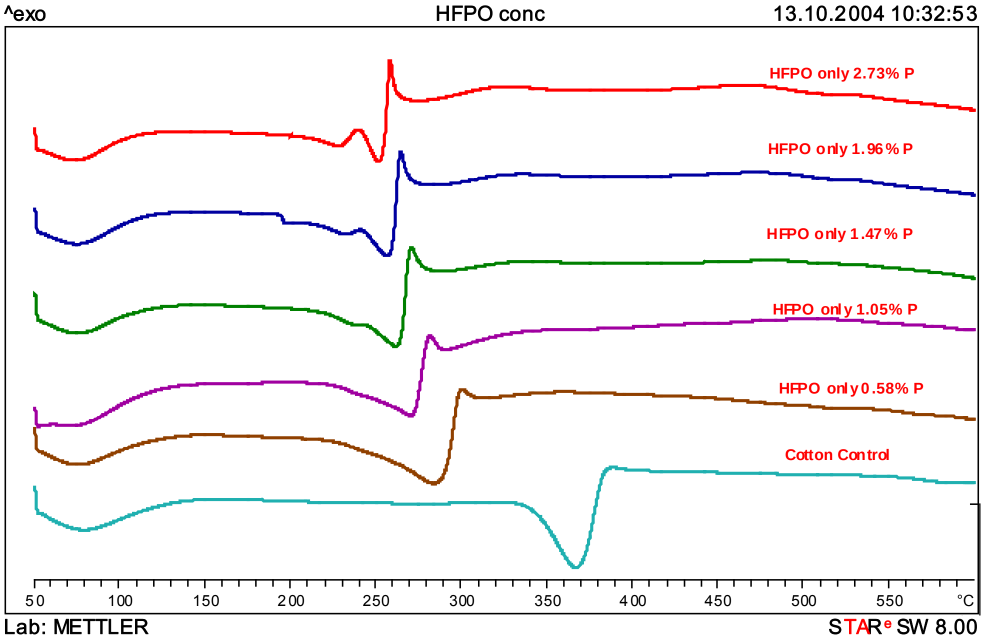


Figure 5.7. DSC curves of cotton fabric treated with HFPO at different concentrations.

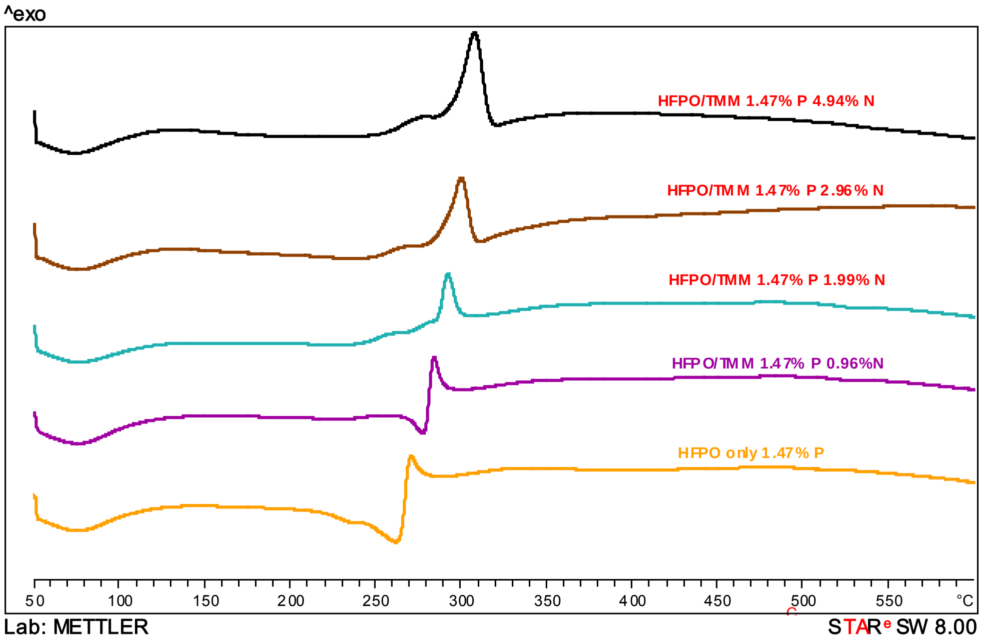
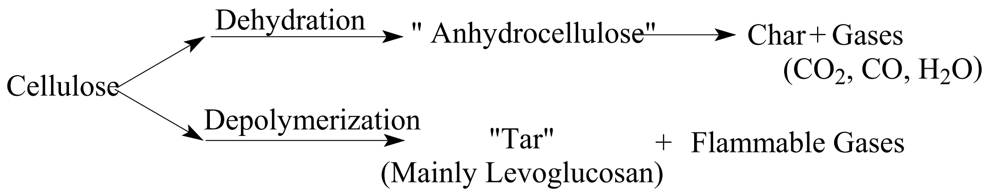


Figure 5.8. DSC curves of cotton fabric treated with 9.9% HFPO in combination with TMM with different concentrations.

further increased from 2.00% to 2.73%, the LOI of both treated fabric remained practically unchanged. Nevertheless, in the presence of the nitrogen-containing reactants, the LOI of treated fabric always increased as the phosphorus content was increased from 0 to 2.73%, with a substantial change noticed between 0.00 and 0.96% nitrogen on the HFPO/TMM treated fabric. The divergent character of these relationships further indicates a synergistic interaction between nitrogen and phosphorus in HFPO/TMM and HFPO/DMDHEU system.

Shown in Figure 5.7 are DSC curves of the cotton fabric treated with HFPO only at different concentrations. The DSC curves show a strong endothermic followed by an exothermic peak. Thermal decomposition of cellulose is an extremely complex chemical process. Two competitive pathways have been proposed in the literature [10-11] for the process, as shown in Scheme 5.2. If the dehydration of cellulose prevails, evolution of CO_2, H_2O and CO with formulation of solid char is mainly observed. If depolymerization occurs more extensively than dehydration, volatilization of tar mostly composed of levoglucosan is observed.



Scheme 5.2

It is generally accepted [12-14] that the endotherm is mainly due to depolymerization of cellulose with formation of levoglucosan and its evaporation, whereas the exotherm is due to dehydration of cellulose with the formation of char. The nadir of endothermic peak, which is correspondent to depolymerization of cellulose shifted from

365°C to 250°C as the phosphorus content was increased from 0 to 2.73%. Furthermore, the exothermic peak, which is related to dehydration of cellulose, is also shifted from 300°C to 260°C when the phosphorus content was changed from 0.58% to 2.73%. The thermal decomposition occurs between 250-310°C depending upon the amount of phosphorus compound present. At the same time, we also found that the exothermic peak area increased as the phosphorus content increased. That means the dehydration of cellulose occurs extensively as the phosphorus content on fabric was increased; therefore, the amount of char formation was significantly increased, and the amount of levoglucosan and its volatilization were dramatically reduced. The DSC curves shown in Figure 5.7 also indicate a small exothermic peak whose temperature seems to vary with the amount of phosphorus content. A logical interpretation would seem to be in terms of a phosphorylation occurring at approximately 240°C. For the HFPO treated fabric, the thermal decomposition takes place by the following pathway: phosphorylation, then followed by depolymerization and dehydration occurring between 250°C and 310°C, depending upon the amount of phosphorus compound present.

Figure 5.8 shows the DSC curves of cotton fabric treated with HFPO at a specified phosphorus level (1.47%) in combination of TMM at different concentrations. One observes that the endothermic peak disappeared gradually, and the exothermic peak area was dramatically increased. That means that the depolymerization of cellulose, which corresponds to the formation of levoglucosan and its evaporation, was significantly reduced, and the dehydration of cellulose became dominant during the thermal degradation process

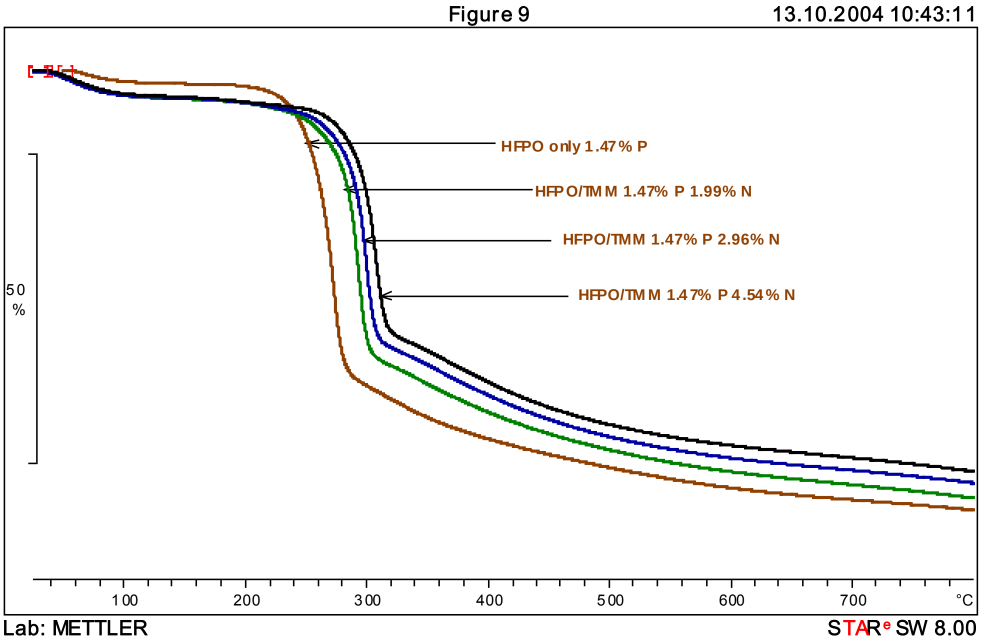


Figure 5.9. TGA curves of cotton fabric treated with 9.9% HFPO in combination with TMM with different concentrations.

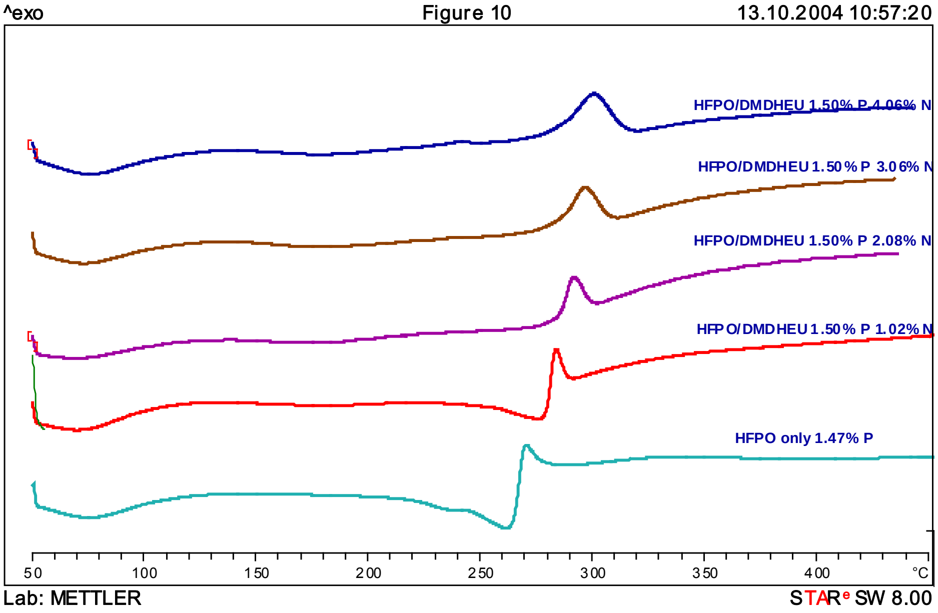


Figure 5.10. DSC curves of cotton fabric treated with 9.9% HFPO in combination with DMDHEU with different concentrations.

in the presence of phosphorus and high content of nitrogen, which is in agreement with the larger char formation in thermogravimetric analysis (Figure 5.9). Without the nitrogen, even at a high phosphorus level (2.73% phosphorus) there was still a strong depolymerization peak, nevertheless, in the presence of 2.96% nitrogen, the fabric treated with 1.47% phosphorus has no depolymerization peak. Compared to the thermal decomposition of the phosphorus-only treated fabric, the interaction of phosphorus-nitrogen significantly alters the pyrolytic process of cellulose. The interaction of phosphorus-nitrogen retards the thermal decomposition of cellulose by the depolymerization, and contributes to the dehydration process, thus reducing the levoglucosan and its evaporation, and increasing the amount of solid char. We also observed that the dehydration temperature shifted to a higher temperature as the nitrogen content was increased in the presence of phosphorus (Figure 5.8). However, the TGA curves in Figure 5.8 show the amount of char formation increased as the nitrogen content was increased. The presence of nitrogen does not decrease the dehydration temperature, but rather, increasing the decomposition temperature, and also increasing the amount of solid char. This results are a bit surprising and might go against the traditional condensed-phase mechanism, which usually is considered to be that, the flame retardant alters the pyrolytic path of the substrate, decreases the decomposition temperature, and reduces substantially the amount of flammable gases produced by favoring the formation of carbonaceous char [2]. A reasonable interpretation here is that the nitrogen is forming a salt with the phosphorus acid formed from the phosphorus ester and buffering the acids, thus reducing the catalytic acid effect of the phosphorus acids, and therefore shifting the dehydration toward a higher temperature, eventually, even though the reaction is slowed down, it does finally create the char. Another piece of evidence to support this interpretation is that the temperature of the presumed phosphorylation of cellulose by the phosphorus component of the finish, indicated by the small exothermic peak in DSC curves (Figure 5.8), shifted from 240^{o}C to approximately 270^{o}C as the nitrogen content was increased from 1.99% to 4.94%. We hypothesize that neutralizing or buffering of the phosphorus acids by nitrogen reagent reduces the catalytic acid effect of the phosphorus acid, thus making the phosphorylation take place at a higher temperature when both phosphorus and nitrogen are present in the flame retardant finish system.

DSC and TGA curves of cotton fabric treated with HFPO at a specified phosphorus level in combination of DMDHEU at different concentrations are shown in Figure 5.10 and Figure 5.11 respectively. For HFPO/DMDHEU treated cotton fabric, the thermal decomposition of cellulose followed the same pyrolytic process as that of the HFPO/TMM system. The phosphorus-nitrogen interaction significantly reduces the depolymerization process, in favor of the dehydration decomposition process during the thermal decomposition. This substantially decreases the formation of levoglucosan and amount of flammable gases and increases the amount of solid char, thus improving the flame resistance. Similarly, the dehydration occurs at a higher temperature when the nitrogen content was increased.

The DSC curves of cotton fabric treated with a specified TMM level in combination of HFPO at different concentrations are shown in Figure 5.12. Once again, the endothermic peak, which is related to formation of levoglucosan and its evaporation, disappeared in the presence of 3.0% nitrogen and more than 0.58% phosphorus. This indicated that the amount

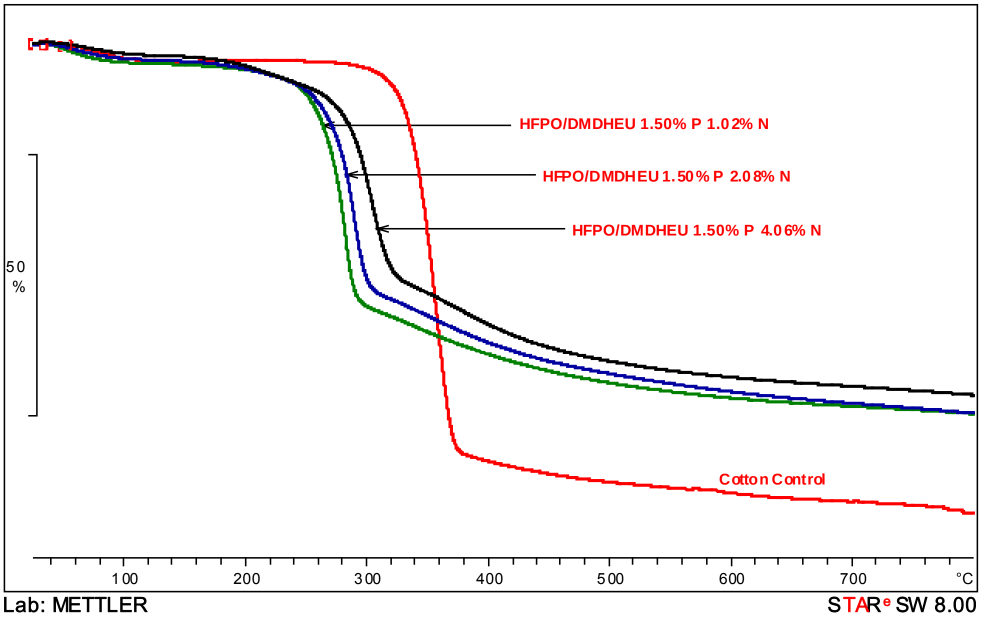


Figure 5.11. TGA curves of cotton fabric treated with 9.9% HFPO in combination with DMDHEU with different concentrations.

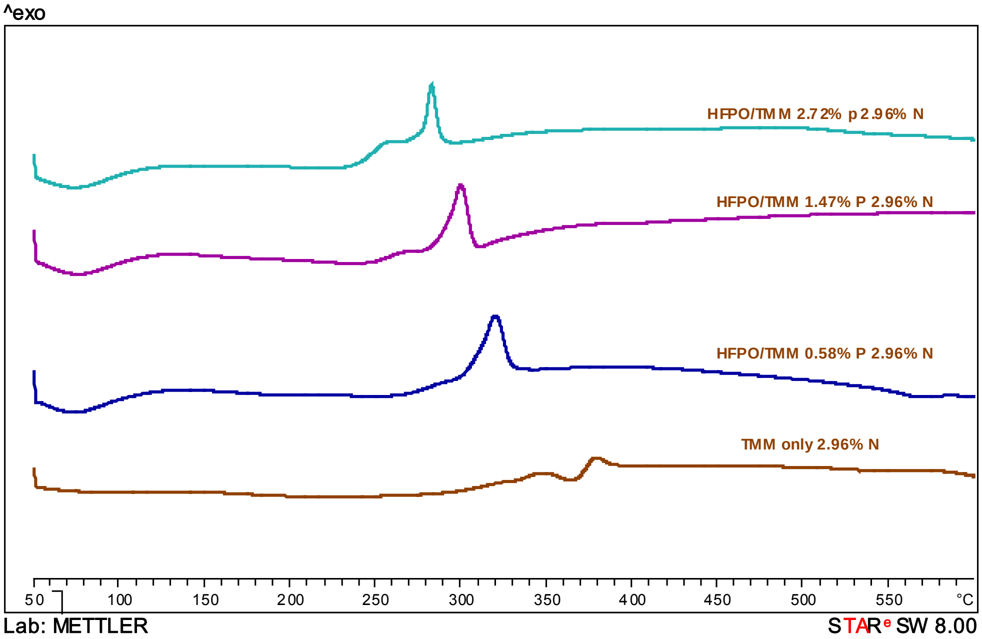


Figure 5.12. DSC curves of cotton fabric treated with 9% TMM in combination with HFPO with different concentrations.

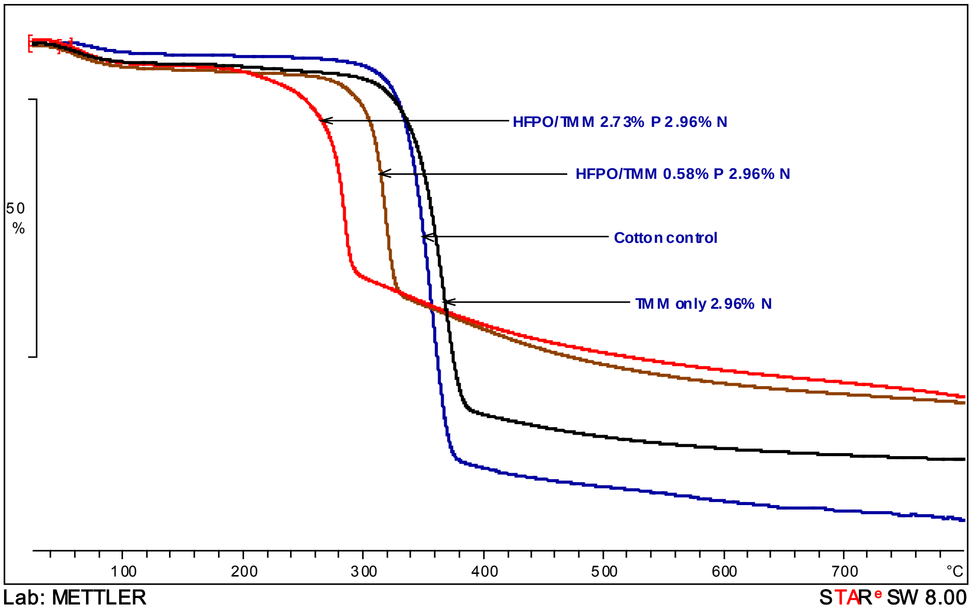


Figure 5.13. TGA curves of cotton fabric treated with 9% TMM in combination with HFPO with different concentrations

of levoglucosan and its flammable gases were significantly reduced when both nitrogen and phosphorus are present. The TGA results shown in Figure 5.13 are consistent to the DSC analysis. The data presented here clearly demonstrate that the phosphorus-nitrogen interaction retards the thermal decomposition of cellulose by depolymerization, and contributes to the dehydration process, thus reducing the levoglucosan and its evaporation, increasing the amount of solid char, and significantly enhancing the flame resistance of cotton fabric. At fixed nitrogen level, the more the phosphorus content, the lower the dehydration temperature, the higher the amount of solid char, and the better is the flame resistance performance of the treated fabric. However, as the phosphorus content increased, the exothermic peaks shifted to a lower temperature, whereas the exothermic peaks shifted

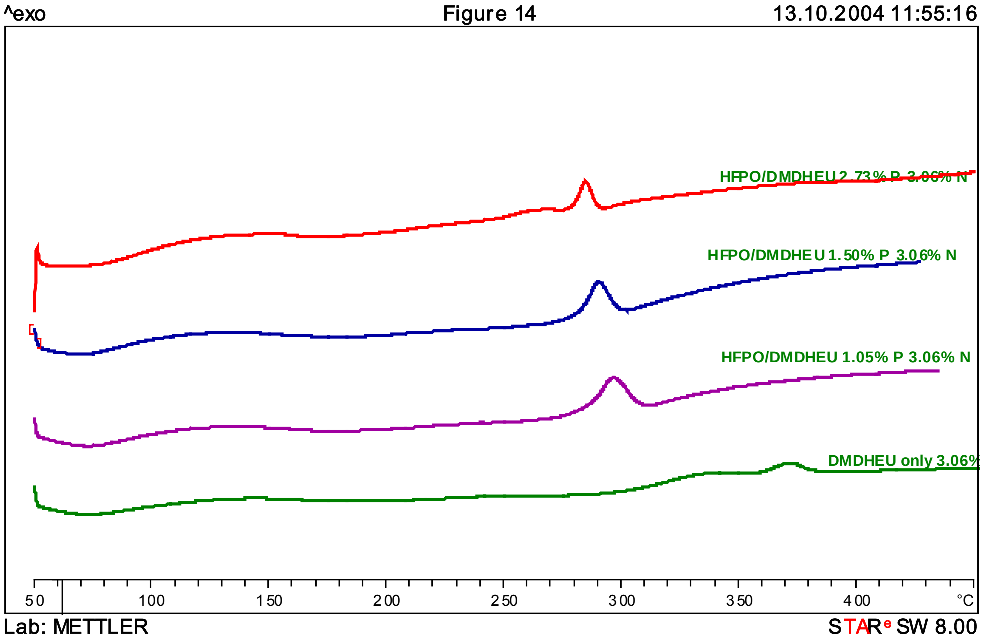


Figure 5.14. DSC curves of cotton fabric treated with 22.5% DMDHEU in combination with HFPO with different concentrations.

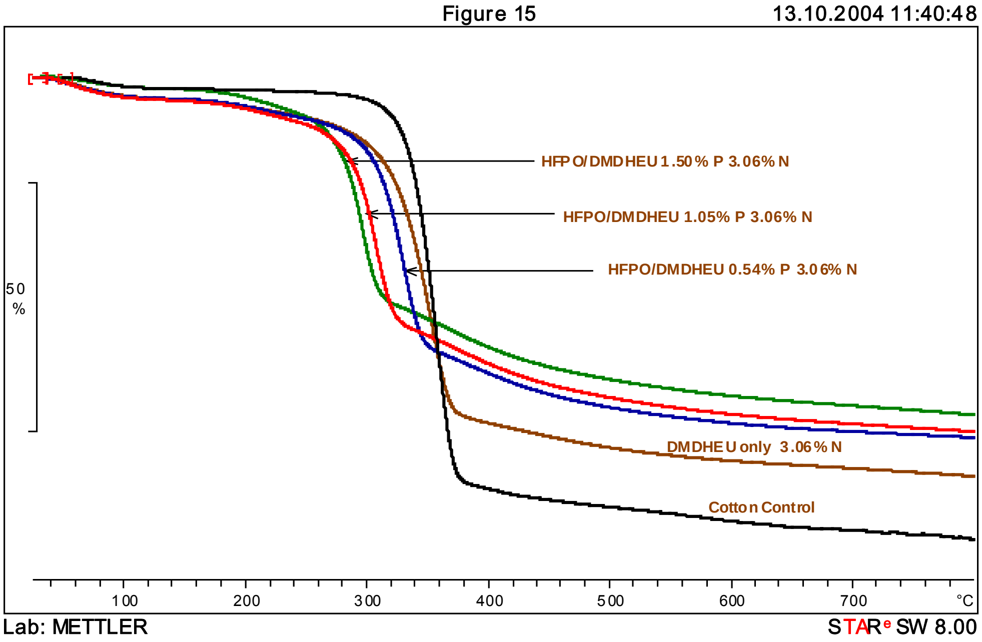


Figure 5.15. TGA curves of cotton fabric treated with 22.5% DMDHEU in combination with HFPO with different concentrations.

to higher temperature as the nitrogen content was increased at a fixed phosphorus level (Figure 5.8). Again, it might be hypothesized that the nitrogen is forming a salt with the phosphorus acids and buffering them thus reduce the catalytic acid effect of the phosphorus acid. At a fixed level of nitrogen, the nitrogen can only consume a fixed amount of the phosphorus acids. When the phosphorus content was increased, an excess amount of phosphorus acids existed, and the catalytic acid effect of the phosphorus acids also increased. The observation that phosphorylation occurs at 250^{o}C instead of 270^{o}C is another piece of evidence that more phosphorus acids existed when the phosphorus content was increased. For both different phosphorus levels at a fixed nitrogen content and different nitrogen contents at a fixed phosphorus level, dehydration takes place at either higher or lower temperature as the nitrogen or phosphorus content increased, however, the solid char amount always increased, and the flame resistance also improved. We might say that the extent of dehydration, not the dehydration temperature has the most significant effect on the amount of char. Therefore, the extent of dehydration has a profound effect on flame resistance. The DSC and TGA curves of the cotton fabric treated with HFPO at different concentrations, in combination with DMDHEU at a fixed level, are in Figure 5.14 and Figure 5.15 respectively. Similar decomposition results were observed as the phosphorus content increased at fixed nitrogen content, and a similar phosphorus-nitrogen interaction occurs in the HFPO/DMDHEU finish system.

The DSC curves of cotton fabric treated with HFPO only, and HFPO/TMM or HFPO/DMDHEU at the same phosphorus and nitrogen content are shown in Figure 5.16.

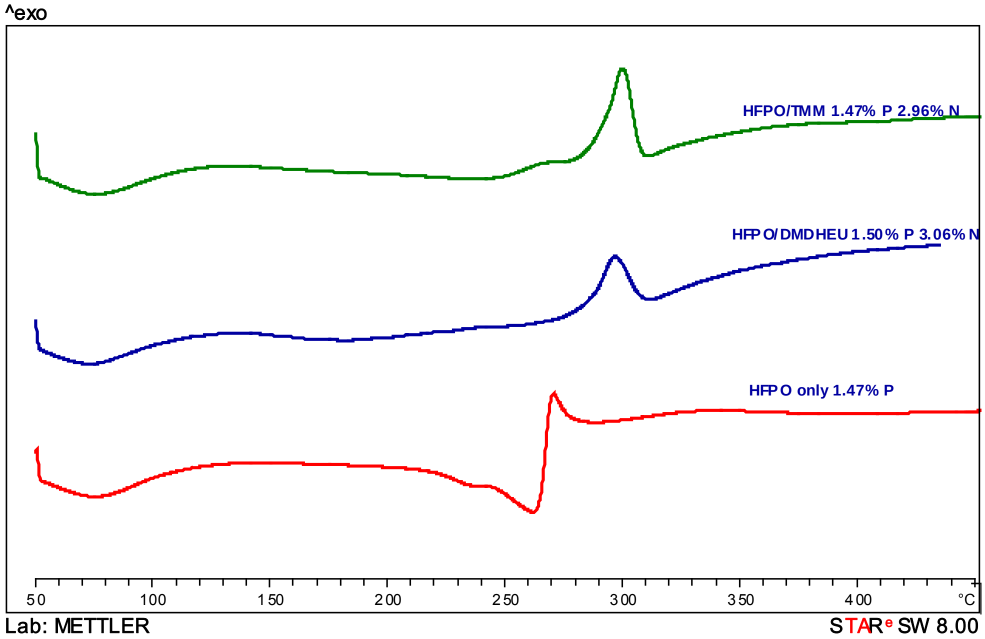


Figure 5.16. DSC curves of cotton fabric treated with 9.9% HFPO in combination with TMM or DMDHEU at the same content nitrogen.

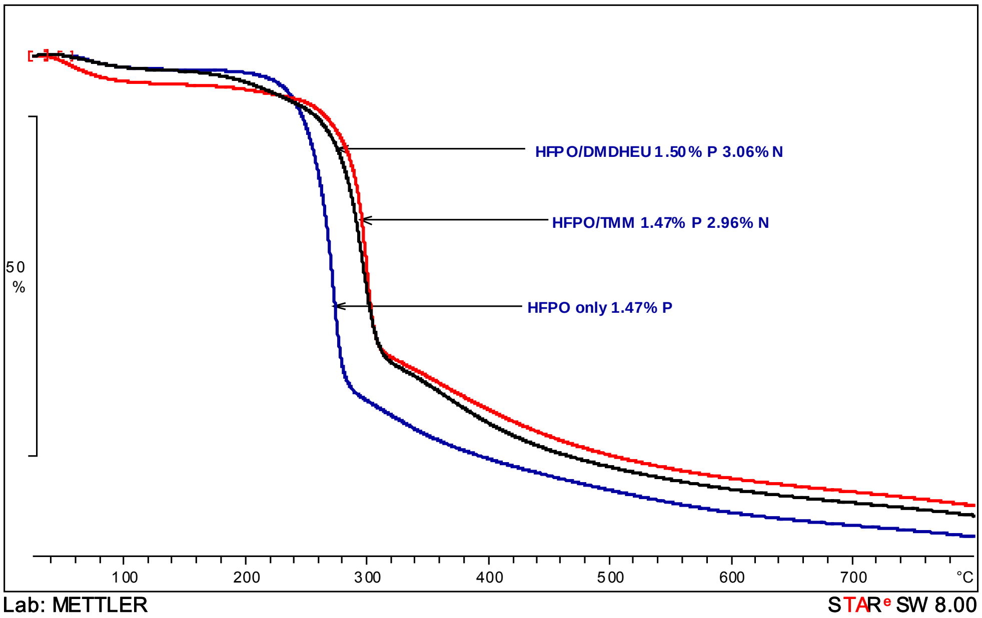


Figure 5.17. DSC curves of cotton fabric treated with 9.9% HFPO in combination with TMM or DMDHEU at the same content nitrogen.

The LOI of cotton fabric treated with 1.47% phosphorus of HFPO only is 25.3; however, the LOI of cotton fabric treated with 1.47% phosphorus and 2.99% nitrogen of TMM or DMDHEU is 29.9 and 28.8 respectively. Obviously, both TMM and DMDHEU can enhance the flame resistance of treated fabric by means of phosphorus-nitrogen synergism. We noticed that with both HFPO/TMM and HFPO/DMDHEU treated fabrics, the endothermic peaks, which correspond to formation of levoglucosan and its evaporation have disappeared, and the exothermic peaks, which are related to the dehydration of cellulose have become dominant during the thermal decomposition. We also observed that the dehydration temperature of HFPO/TMM treated fabric is somewhat higher than that of HFPO/DMDHEU treated fabric perhaps because of the stronger basicity of TMM. Meanwhile, the exothermic peak area of the HFPO/TMM treated fabric is larger than that of HFPO/DMDHEU treated fabric, which means the dehydration of cellulose is more extensive on HFPO/TMM treated fabric than that of HFPO/DMDHEU. This is another piece of evidence that the extent of dehydration, not the dehydration temperature has a profound influence on the flame resistance. Further confirmation of this interpretation is given by the TGA curves (Figure 5.17). Although the HFPO/TMM treated cotton decomposes at a higher temperature, the HFPO/TMM treated fabric showed a higher amount of char, and thus a better flame resistance.

CONCLUSION

Both TMM and DMDHEU finishes by themselves can increase the flame resistance of cotton fabric, DMDHEU to a greater degree. TMM and DMDHEU are good nitrogen providers to the organophosphorus-based flame retardant finishing system, and therefore enhancing the flame resistance performance of cotton fabric by means of phosphorus-nitrogen synergism. TMM is found to be a more efficient synergistic agent than DMDHEU. The interaction between phosphorus and nitrogen alters the thermal decomposition path. The phosphorus-nitrogen interaction inhibits the thermal decomposition of cellulose by depolymerization, and contributes to the dehydration process, thus reducing levoglucosan formation and evaporation, increasing the amount of solid char, and substantially improving the flame resistance of treated cotton fabric. The nitrogen and phosphorus content have a different influence on the dehydration temperature. The extent of dehydration, not the dehydration temperature is observed to have the significant effect on the flame resistance.

ACKNOWLEDGMENT

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CHAPTER 6

A COMPARATIVE STUDY OF DIFFERENT REACTIVE ORGANOPHOSPHORUS FLAME RETARDANT AGENTS FOR COTTON[1]

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[1] Wu, W. and Yang, CQ. Submitted to Polymer Degradation and Stability.

ABSTRACT

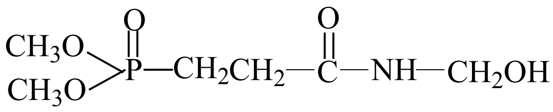
N-methylol dimethyl-phosphonopropionamide (MDPA) has been one of the most commonly used durable flame retardant agents for cotton. New flame retardant finishing systems based on a hydroxy-functional organophosphorus oligomer (HFPO) and bonding agent, such as dimethyloldihydroxyethyleneurea (DMDHEU), trimethylolmelamine (TMM), and a mixture of DMDHEU and TMM are currently developed. In this research, we investigated the covalent bonding, flame resistance as well as the physical properties of those two flame retardant finishing systems: MDPA/TMM, and HFPO with TMM and a mixture of DMDHEU and TMM (1:1) as the bonding agent. We found that MDPA by itself can be bound to cotton cellulose via its N-methylol group. The presence of TMM improves the amount of MDPA bound to cotton (approximately a 25% increase in phosphorus retention at 8% TMM level). The bonding agent, such as TMM or DMDHEU, is necessary for HFPO to be bound to cotton, and the amount of HFPO bound to cotton is determined by the type and concentration of the bonding agent. The amount of the flame retardant agent bound to cotton is significantly higher for the HFPO system than that for the MDPA system when equal moles of the phosphorus and N-methylol group are used. The content of N-methylol groups also substantially affects the laundry durability of the treated fabric. The type of catalyst plays a significant role in influencing the bonding of flame retardant agents and cotton. We also found that the MDPA/TMM treated fabric has a higher initial LOI than that of the HFPO/TMM treated fabric due to the nitrogen content in the MDPA molecule, which can improve the flame resistance by means of phosphorus-nitrogen synergism. The flame resistance of cotton is identical for both the HFPO and MDPA system when there are same amount of the phosphorus and nitrogen on the fabric. The fabric treated with MDPA/TMM and HFPO/TMM showed the similar LOI after 1, 10, and 25 laundering cycles. Both

HFPO/TMM and MDPA/TMM treated fabric remained at a low level of the WRA. The tensile strength loss of the treated fabric did not increase as the TMM concentration was increased, however, the fabric stiffness significantly increased when a high TMM concentration was used. MDPA/TMM treated fabric showed higher dimensional change during the laundering cycles and higher formaldehyde release level.

INDEX WORDS: Cotton, Crosslinking, Flame retardant finishes, DMDHEU, Trimethylol melamine, Reactive organophosphorus chemicals.

INTRODUCTION

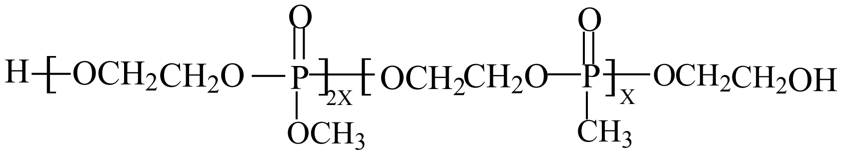
Cotton and cellulosic substrates in general, are combustible textile fibers. Flame retardant finishing is highly desirable for those fibers to improve life safety [1]. It is not surprising that most efforts in the field of flame retardancy were made on modifying the flame resistance properties of cotton fibers since cotton is the most commonly used of textile fibers. In the past several decade lots of procedures have been developed to overcome the flammability of cellulosic substrates [2-5]. Among those flame retardant chemistries, reactive phosphorus ester, such as N-methylol dimethyl phosphosphonopropionamide (MDPA) and its commercial versions with the trade name of "Pyrovatex CP New", has been one of the most commonly used durable flame retardant agents for cotton since it was introduced in 1968 [6-8]. The structure of MDPA is shown in Scheme 6.1 (CA Registry No. 20120-33-6). Several researches on reactive phosphorus chemistry have been done in past several years. MDPA may bond to the cellulose molecules via N-methylol group in the presence of bonding agent and an acidic catalyst, therefore making the flame retardant finishing system durable to home laundry [9], and MDPA can confer acceptance flame retardancy for cotton [10-11]. The MDPA finish functions as a condensed-phase retardant and promotes char formation [12]. The effect of MDPA finishes flame retardancy, strength loss, and color fastness have been studied, there are several limitations and, in many cases, undesirable facets associated with this finishing technique [13-14].



$$(CH_3O)_2\overset{O}{\overset{\|}{P}}-CH_2CH_2-\overset{O}{\overset{\|}{C}}-NH-CH_2OH$$

Scheme 6.1

In our previous research, we developed a flame retardant finishing system for cotton based on a hydroxy-functional organophosphorus oligomer (abbreviated as "HFPO" here) with the commercial name of "Fyroltex HP", shown in Scheme 6.2 (CA Registry No. 70715-06-9,), and a bonding agent, such as DMDHEU and TMM [15-18].



$$H\left[OCH_2CH_2O-\overset{\overset{O}{\|}}{\underset{\underset{OCH_3}{|}}{P}}\right]_{2x}\left[OCH_2CH_2O-\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{P}}\right]_{x}-OCH_2CH_2OH$$

Scheme 6.2

The objective of this research was to investigate the bonding of those reactive organophosphorus compounds to cotton and to compare the laundering durability of those compounds after they are bound to the cotton fabric. We studied the bonding of MDPA to cotton with and without the presence of TMM. We used TMM and mixture of DMDHEU and TMM (1:1) as the bonding systems for HFPO. We also evaluated the effects of different catalysts on the bonding of those two different flame retardant finishing systems. Meanwhile, we evaluated the flame resistance performance and the physical properties as well as the amount of formaldehyde release on the cotton fabric treated with those two different flame retardant finishing systems.

EXPERIMENTAL

Materials

The fabric used was a 3/1 twill weave 100% cotton fabric weighing 242 g/m^2. MDPA with the commercial name of "Pyrovatex CP New®" and HFPO with the commercial name of "Fyroltex HP®" were supplied by Ciba Specialty Chemicals, High Point, North Carolina, and Akzo Nobel, Dobbs Ferry, New York, respectively. DMDHEU with the commercial name of "Freerez 900" and TMM with the trade name of "Aerotex M-3" were supplied by Noveon, Cleveland, Ohio. The NH_4Cl-based catalyst with the commercial name of "Catalyst RD" was supplied by Eastern Color & Chemical, Greenville, South Carolina. Phosphoric acid was a reagent grade chemical supplied by Aldrich Chemical, Wisconsin. The $MgCl_2$-based “activated” catalyst with the commercial name of “Catalyst 531” was supplied by Omnova Solutions, Chester, South Carolina.

Fabric Treatment and Home Laundering Procedures

The fabric was first immersed in a finish solution containing flame retardant, TMM or mixture of DMDHEU&TMM (1:1), and a catalyst, and then passed through a laboratory padder with two dips and two nips, dried at 90°C for 3 min, and finally cured in a Mathis curing oven at 165°C for 2.5 min. The weight of catalyst H_3PO_4 was 2% of the bath. The weight of Catalyst RD was 2% of that of TMM or of the mixture of DMDHEU and TMM. All other concentrations (w/w, %) presented here were calculated based on the weight of reagent (solid) and that of the bath. The wet pick-up of the cotton fabric was approximately 80±3%. After curing, the treated cotton fabric was subjected to different numbers of home laundering cycles with the use of “AATCC Standard Detergent 1993”. The home laundering procedure was done according to AATCC Test Method 124-1996 (“Appearance of Fabrics After Repeated Home Laundering”). The water temperature for laundering was approximately 46°C.

Fabric Performance Evaluation

The limiting oxygen index (LOI) of the cotton fabric was measured according to ASTM D2863-00. The vertical flammability of the cotton fabric was measured according to ASTM D6413-99. The tensile strength of the fabric was measured according to ASTM D5035-95. The conditional wrinkle recovery angle (WRA) was measured according to AATCC Test Method 66-1996. The stiffness of fabric was measured according to ASTM D6828-02, and the formaldehyde release from the fabric was measured according to AATCC Test Method 112-1998.

Determination of Phosphorus Concentration on the Treated Cotton Fabric

Approximately 2g of treated cotton fabric taken from different parts of a larger fabric specimen were ground in a Wiley mill into a powder to improve sample uniformity. Then, 2 ml of concentrated H_2SO_4 were added to 0.1 g of cotton powder. 10 ml of 30% H_2O_2 was added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250ºC to digest the powder and to evaporate the water until dense SO_3 vapor is produced. The completely digested cotton sample as a clear solution was transferred to a 50-ml volumetric flask, and then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the phosphorus content. The phosphorus retention of the treated fabric was calculated using the formula $(P_{AL}/P_{BW})\times 100\%$, where, P_{AL} is the phosphorus content on the fabric after laundering, and P_{BW} is the phosphorus content on the fabric before wash.

Elemental Analysis

The concentrations of carbon, hydrogen, and nitrogen of the samples were analyzed with a PE 240C C, H, N analyzer. Approximately 2 mg of a sample was first combusted, then separated by chemical chromatography, and measured by a thermal conductivity detector to determine the C, H, and N concentrations.

RESULTS AND DISCUSSION

Both the theoretical and the measured values of the phosphorus, carbon, hydrogen and nitrogen content of the commercial products of MDPA and HFPO are presented in Table 6.1. The measured phosphorus concentration of HFPO is 19.56% whereas the theoretic value is 20.58% (Table 6.1). Based on those values, the purity of HFPO is determined to be 95.0%

assuming that all the phosphorus in the product came from the active ingredient shown in Scheme 6.2. The measured values of both carbon and hydrogen contents of HFPO are higher than the corresponding theoretical value due to the impurities in the commercial product. Based on the measured and theoretical values of the phosphorus content of MDPA presented in Table 6.1, the purity of MDPA is determined to be 75.4% assuming all the phosphorus in the product came from MDPA shown in Scheme 6.1. The ratios of the theoretical value to measured value of the nitrogen, carbon and hydrogen content of MDPA is 80.3, 76.9 and 82.0%, respectively.

Table 6.1. Elemental concentration of HFPO and MDPA

Samples	P%		N%		O%		H%	
	TH[1]	Me[2]	TH[1]	Me[2]	TH[1]	Me[2]	TH[1]	Me[2]
HFPO	20.58	19.56	0	0	29.20	29.92	5.97	6.06
MDPA	18.67	14.70	8.43	6.77	43.37	33.35	8.43	6.90

Note: 1: Theoretical; 2: Measured

Table 6.2. Phosphorus retention of cotton fabric treated with MDPA of different concentrations, cured at 165^{o}C for 2.5 min, after 1 HLTD cycle.

MDPA Concentration (%)	8	16	24	32	40	48
Phosphorus Retention (%)	51	52	51	51	52	52

The cotton fabric was treated with MDPA of different concentrations with phosphoric acid as the catalyst, cured at 165ºC for 2.5 min, and finally subjected to one laundering cycle to remove the MDPA not bound to cotton. The phosphorus content of the cotton fabric thus treated

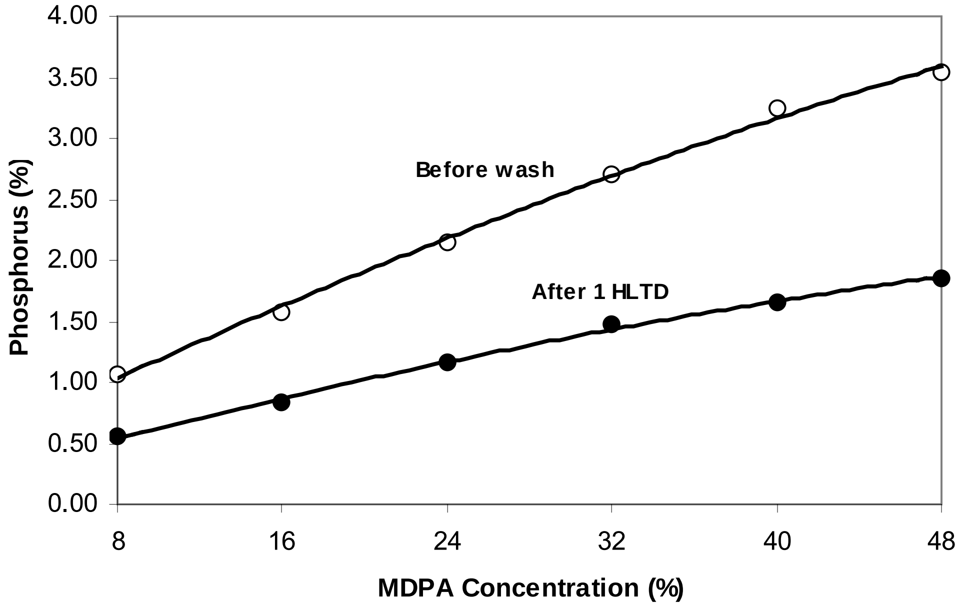


Figure 6.1. Phosphorus content of the cotton fabric treated with MDPA of different concentrations and cured at 165°C for 2.5 min (before and after 1 HLTD cycle).

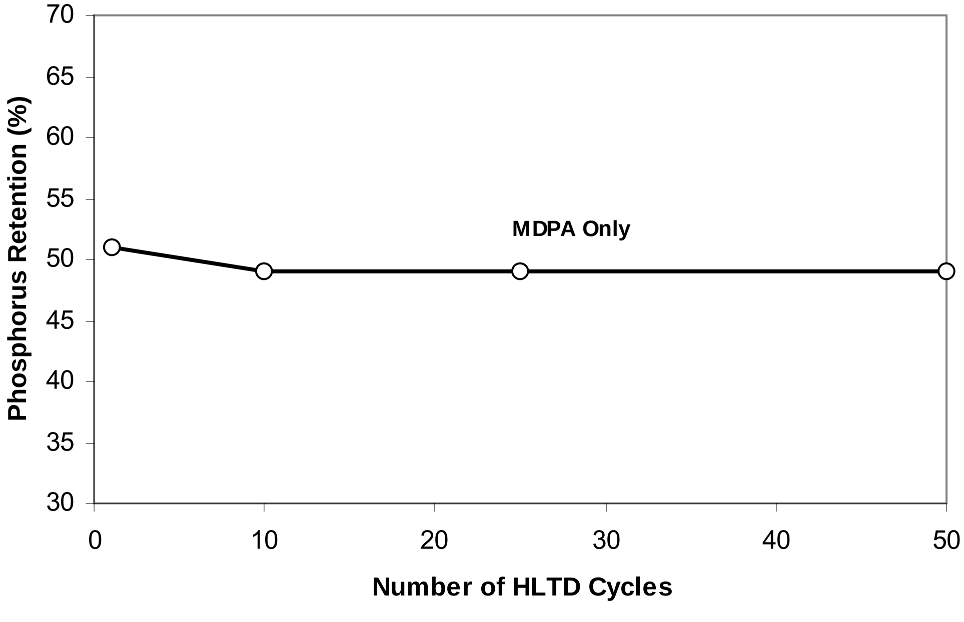
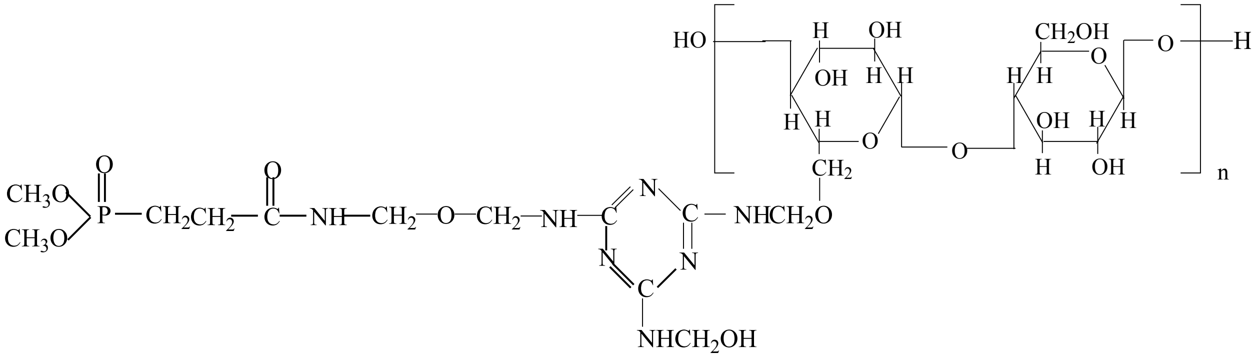


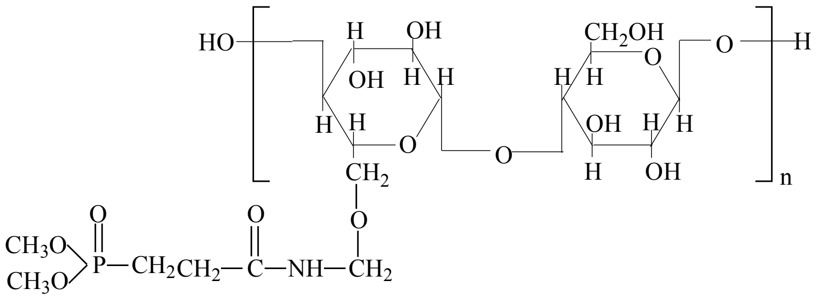
Figure 6.2. Phosphorus retention of cotton fabric treated with 45% MDPA only and cured at 165°C for 2.5 min, as a function of the number of the HLTD cycles.

is presented as a function of the MDPA concentration in Figure 6.1, and the percent phosphorus retention of the MDPA-treated cotton fabric is shown in Table 6.2. The fabric treated with 8% MDPA had 1.07% phosphorus before laundering, and the phosphorus concentration decreased to 0.56% after one laundering cycle (Figure 6.1), which represented 51% of the phosphorus retention on the fabric after one laundering cycle (Table 6.2). It was reported in the literature that MDPA was bound to cotton cellulose by the reaction of TMM with both MDPA and cellulose shown in Scheme 6.3 [9].



Scheme 6.3

The data presented here, however, clearly indicate that MDPA reacts directly with cellulose through its N-methylol group, as shown in Scheme 6.4. The concentration of MDPA bound to cotton increased linearly as the concentration of the MDPA applied to the fabric was



Scheme 6.4

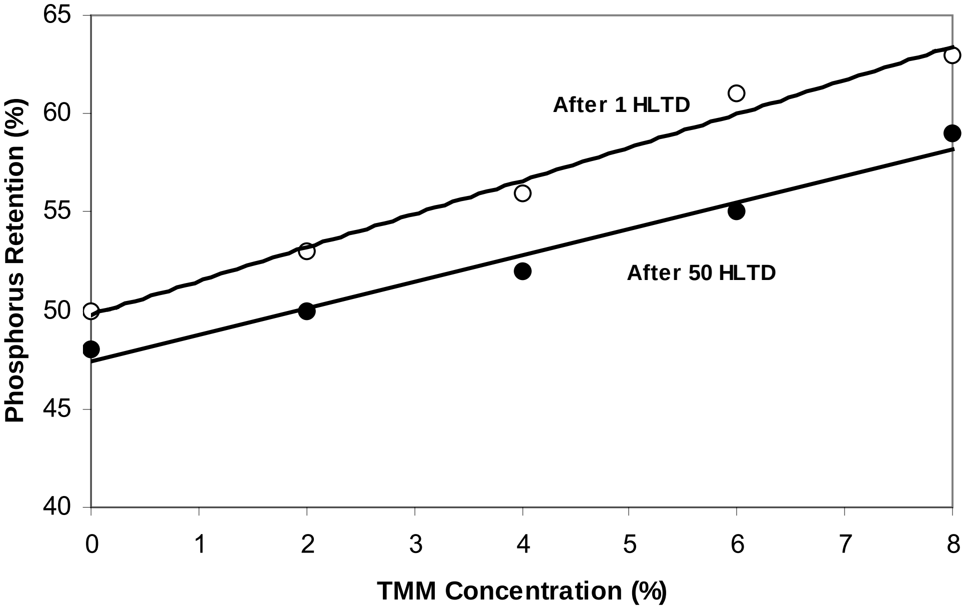


Figure 6.3. Phosphorus content of the cotton fabric treated with 45% MDPA, in combination of TMM with different concentrations and cured at 165°C for 2.5 min (after 1, 50 HLTD cycles).

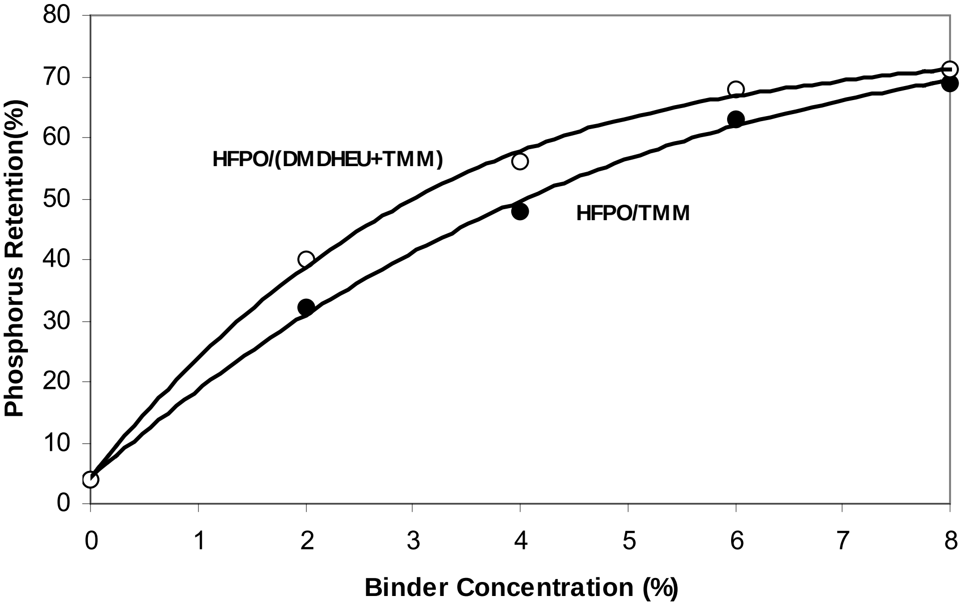


Figure 6.4. Phosphorus content of the cotton fabric treated with 32% HFPO, in combination of a binder with different concentrations and cured at 165°C for 2.5 min (after 1 HLTD cycle).

increased (Figure 6.1). The percent retention of phosphorus after one laundering cycle remained statistically unchanged (50-52%) as the MDPA concentration was increased from 8 to 48% (Table 6.2). The percent retention of MDPA on the fabric after one laundering cycle appears to be independent of the concentration of the MDPA applied to the fabric.

The cotton fabric was treated with 45% MDPA and cured at 165ºC for 2.5 min, and then subjected to 50 home laundering cycles. The percent phosphorus retention of the fabric thus treated is plotted against the number of home laundering cycles in Figure 6.2. The phosphorus retention of treated fabric was 51% after one laundering cycle, and it was 49% after 50 laundering cycles (Figure 6.2). The data presented here demonstrate that the MDPA bound to cotton through its N-methylol group is extremely durable to multiple home laundering.

Shown in Figure 6.3 is the phosphorus retention of the cotton fabric treated with 45% MDPA in combination with TMM at different concentrations and cured at 165ºC for 2.5 min after 1 and 50 laundering cycles. The amount of MDPA bound to cotton was increased from 50 to 63% (a 25% increase) when 8% TMM was present in the finish solution (Figure 6.3). Certain portions of the cellulosic hydroxyl groups, which are not accessible by the bulky MDPA molecules, can react with the N-methylol groups of TMM. Consequently, a portion of MDPA is bound to cotton by the TMM-bridge as shown in Scheme 6.3. It should be point out that such a portion approximately 20% of the total amount of MDPA bound to cotton is still relatively small even at a high TMM concentration (8%) in the finish solution.

The cotton fabric was treated with the combination of 32% HFPO and (DMDHEU+TMM) (1:1, w/w) or TMM at concentrations ranging from 2 to 8%, and then cured at 165ºC for 2.5 min. The phosphorus retentions of the fabric thus treated after 1 home laundering is presented as a function of the total binder concentration in Figures 6.4. The phosphorus retention of the treated fabric after one laundering cycle was close to 0% when no binder was used. Since HFPO does not have a reactive functional group to form a covalent bond with cellulose, it cannot be retained on the fabric without the use of a bonding agent, such as DMDHEU or TMM. When 2% (DMDHEU+TMM) or TMM was present in the finish solution, the phosphorus retention on treated fabric after one home laundering became 40 or 32%, respectively (Figure 6.4). The higher phosphorus retention for the fabric treated using (DMDHEU+TMM) the binders was due to the fact that DMDHEU is more effective in reacting with HFPO and cotton to for a "bridge" between them than TMM, as discussed in our previous research [15-17]. One observes that the phosphorus retention was increased as the binder concentration was increased (Figures 6.4). Because a bonding agent or the mixture of bonding agents were necessary for HFPO to be bound to cotton, the effectiveness and the concentration of the bonding agent play the most critical role in determining the amount HFPO bound to cotton.

One also observes that the difference in the phosphorus retention after home laundering became smaller as the binder concentration was increase to 6% and beyond (Figure 6.4). When 8% (DMDHEU+TMM) or TMM was used, the phosphorus retentions were 71% and 69% after one home laundering (Figure 6.4). After 50 launderings, the phosphorus retention of the fabric treated using 8% TMM became 41%, which was higher than that treated using (DMDHEU+TMM). At high concentration, TMM react with HFPO to form a crosslinked polymer network on the fabric shown in Scheme 6.5, thus improving the laundering durability of the HFPO bound to cotton.

The cotton fabric was treated with the combination of 45% MDPA and 8% TMM and the combination of 32% HFPO and 8% (DMDHEU+TMM) or TMM. The treated fabric was cured at 165ºC for 2.5 min and then subjected to different number of home laundering cycles. The percent phosphorus retention of the cotton fabric was shown against the number of laundering cycles (Figure 6.5). MDPA/TMM treated cotton had 2.29% phosphorus after one laundering cycle, which represented 63% of the phosphorus retention on fabric. The percent phosphorus of HFPO/TMM or (DMDHEU+TMM) treated cotton was 2.39% and 2.46% respectively after one laundering cycle, which was 69% and 71% phosphorus retention after one laundering cycle. Approximately 13% higher phosphorus retention on HFPO treated fabric after one laundering cycle than that MDPA treated fabric when 8% of TMM was used as a bonding agent.

MDPA can be bound to cotton cellulose via its own N-methylol group or by additional N-methylol groups (TMM), and N-methyloy bonding agent, such as DMDHEU or TMM, is necessary for HFPO to be bound to cotton. Thus, the amount of the bonding between MDPA-cotton and HFPO-cotton should be affected by the content of N-methylol groups in the finishing system. The cotton fabric was treated with 45% MDPA or 32% HFPO in combination of TMM with different concentrations, cured at 165ºC for 2.5 min. The retention of phosphorus in the fabric thus treated is presented as a function of the mole ratio of N-methylol/phosphorus in Figure 6.6 (after one laundering cycle). The mole ratio of N-methylol/phosphorus in MDPA is 1, 45% MDPA only treated cotton fabric has 51% phosphorus retention after one laundering cycle. Meanwhile, in the HFPO/TMM flame retardant finishing system, when the N-methylol/phosphorus mole ratio is 0.26 (TMM concentration 4.0%), the treated fabric has 49% phosphorus retention after one laundering cycle, which represented the same phosphorus retention as the MDPA treated fabric with 1.0 mole ratio of N-methylol/phosphorus. The cotton fabric treated with 45% MDPA and 8% TMM (1.52 mole ratio of N-methylol/phosphorus) had the phosphorus retention of 63% after one laundering cycle, to achieve the same phosphorus content, only 0.39 mole ratio of N-methylol/phosphorus (TMM concentration 6%) is required for

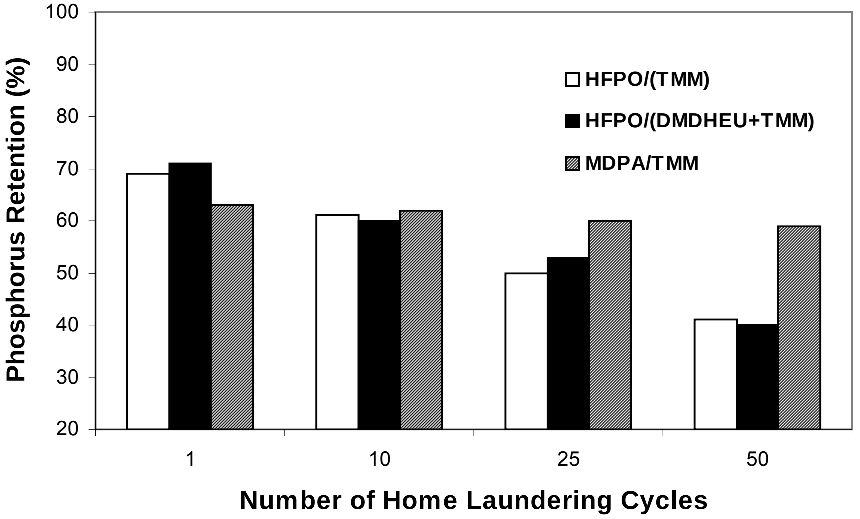


Figure 6.5. Phosphorus retention of the cotton fabric treated with 45% MDPA or 32% HFPO, in combination of 8% binder and cured at 165°C for 2.5 min, as a function of the number of the HLTD cycles.

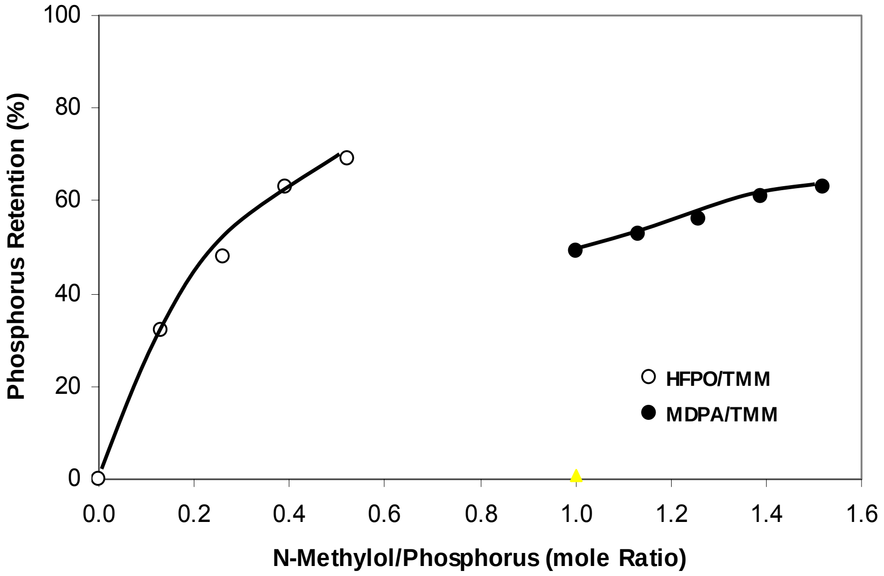
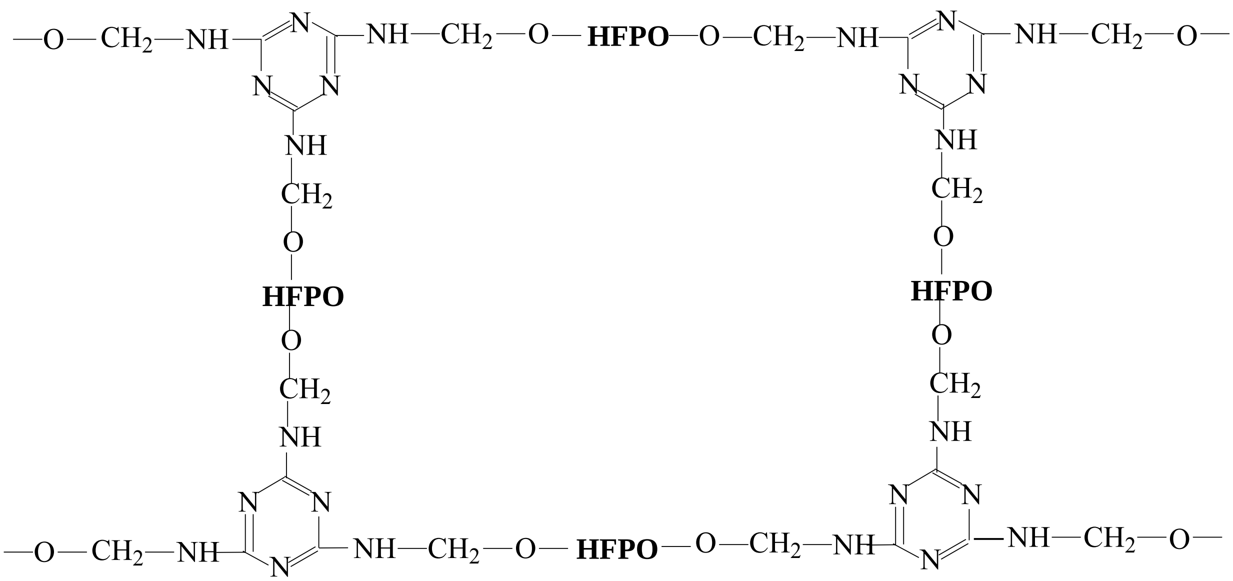


Figure 6.6. Phosphorus retention of cotton fabric treated with 45% MDPA, or 32% HFPO in combination of TMM with different concentrations, cured at 165°C for 2.5 min, as a function of mole ratio of N-methylol/phosphorus (after 1 HLTD cycle).



Scheme 6.5

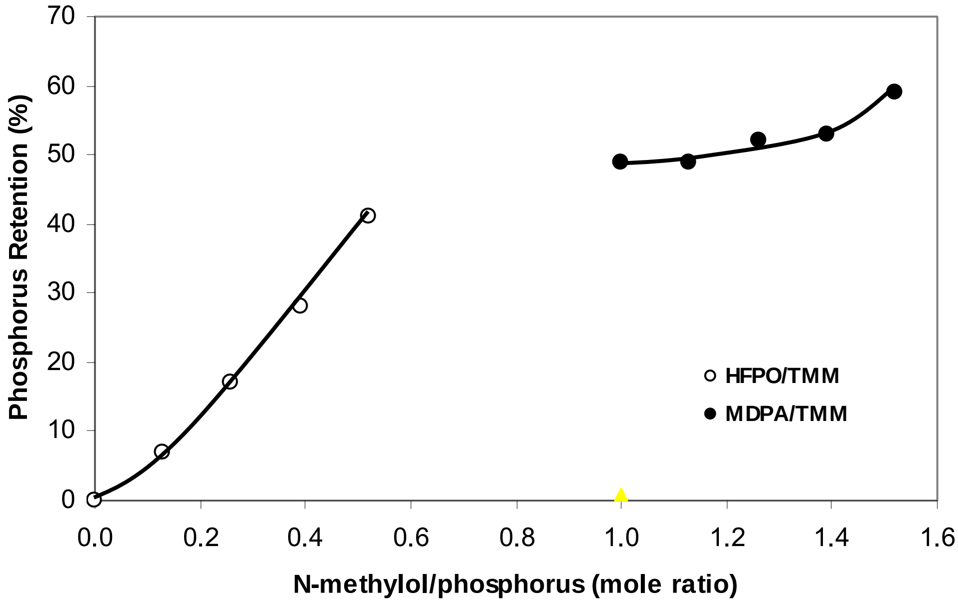


Figure 6.7. Phosphorus retention of cotton fabric treated with 45% MDPA, or 32% HFPO in combination of TMM with different concentrations, cured at 165°C for 2.5 min, as a function of mole ratio of N-methylol/phosphorus (after 50 HLTD cycles).

HFPO/TMM finishing system. When the mole ratio is increased to 1.0 in HFPO/TMM finishing system (TMM concentration 15.3%), the phosphorus retention of HFPO/TMM treated fabric is 78% after one laundering cycle, which is 53% higher than that of MDPA/TMM treated fabric. The data presented here demonstrate the amount of the flame retardant agent bound to cotton is significantly higher for the HFPO system than for MDPA system when the same content of N-methylol group was used in the system. In our previous research, we found that the HFPO/TMM mole ratio of the crosslinked polymeric network is 1.5 (Scheme 6.5) [17], assuming x=1 in Scheme 6.1, 1.0 mole HFPO contains 3.0 mole of phosphorus, and 1.0 mole TMM contains 3.0 mole of N-methylol group, so the phosphorus/N-methylol mole ratio of the crosslinked polymeric network is 1.5. One mole N-methylol group can bond 1.5 mole of phosphorus as HFPO to cotton. On the contrary, the mole ratio of phosphorus/N-methylol in MDPA system is 1, 1.0 mole N-methylol group can only bound 1.0 mole of phosphorus to cotton. This is the possible reason why HFPO was more effective to be bound to cotton cellulose than MDPA.

The phosphorus content on the fabric treated with 45% MDPA and 8%TMM after 50 laundering cycles was 2.06%, which represented 59% of the phosphorus retention on fabric, 6% decrease in phosphorus after 50 laundering cycles compared to after one laundering cycle (63% phosphorus retention in Figure 6.5). Meanwhile, the phosphorus content of cotton fabric treated with 32% HFPO and 8% of TMM or (DMDHEU+TMM) only has 1.42% and 1.32% of P after 50 laundering cycles, respectively, which was around 40% retention of the phosphorus, approximate 40% decrease in phosphorus after 50 laundering cycles compared to after one laundering cycle. The decrease in percent phosphorus content after multiple laundering cycles for HFPO system is substantially higher than that for MDPA system. This is an indication that the laundry durability of the MDPA/TMM treated fabric was significantly better than that of HFPO/TMM or (DMDHEU+TMM) treated fabric when 8% of bonding agent was used.

The cotton fabric was treated with 45% MDPA or 32% HFPO in combination with TMM at different concentrations, and cured at 165ºC for 2.5 min. The retention of phosphorus on the fabric thus treated after 50 laundering cycles is presented as a function of the mole ratio of N-methylol/phosphorus in Figure 6.7 (after 50 laundering cycles). The cotton fabric treated with N-methylol/phosphorus mole ratio of 1.0 (45% MDPA only) had 49% retention of phosphorus after 50 laundering cycles. And the fabric treated with 45% MDPA and 8% TMM (1.52 mole ratio of N-methylol/phosphorus) had the phosphorus retention of 59% (Figure 6.7). Meanwhile, in the HFPO/TMM flame retardant finishing system, when the mole ratio was 0.39 (TMM concentration is 6.0%), the treated fabric had 28% phosphorus retention after 50 laundering cycles. When the mole ratio was increased to 0.52 (50% N-methylol content as MDPA itself), the phosphorus retention of HFPO/TMM treated fabric was 41% after 50 laundering cycles (Figure 6.7). Approximately 20% higher retention of phosphorus was achieved when 50% more N-methylol content was used. The data demonstrate that the higher laundry durability of MDPA/TMM treated fabric is attributed to the greater content of N-methylol in MDPA system. Another possible reason is that more phosphorus got lost by hydrolysis during the laundering, since several units of phosphorus in the chain of the oligomer were bound to cotton by a single N-methylol unit in the HFPO system, whereas each phosphorus ester unit is bound by an N-methylol unit in the MDPA system.

We studied the effects of the catalyst type on the bonding formed between the flame retardant agents and cotton. The cotton fabric was treated with 45% MDPA and 6% TMM, or with 32% HFPO and 6% TMM or (DMDHEU+TMM) with different types of catalysts: H_3PO_4,

Table 6.3. The phosphorus retention and LOI of cotton fabric was treated 45% MDPA and 6% TMM, or 32% HFPO and 6% TMM/DMDHEU&TMM with different type of catalysts, cured at 165^{o}C for 2.5 min, after 1 HLTD cycle.

Catalyst Type	HFPO/TMM		HFPO/(DMDHEU+TMM)		MDPA/TMM	
	% P Retention	LOI (%)	% P Retention	LOI (%)	% P Retention	LOI (%)
H_3PO_4	55	32.3	61	32.0	61	33.3
NH_4Cl-Based	63	33.6	68	32.2	53	29.8
$MgCl_2$-Based	56	32.4	62	32.0	51	29.5

NH_4Cl-based and $MgCl_2$-based catalyst. The percent retention of phosphorus and LOI of the fabric thus treated after one laundering cycle is shown in Table 6.3. All H_3PO_4, NH_4Cl-based and $MgCl_2$-based catalyst can be used as a catalyst for both MDPA and HFPO finishing system. However, for MDPA finishing system, the use of H_3PO_4 as a catalyst got a 15% higher of phosphorus retention on cotton than that of NH_4Cl-based catalyst, and an approximately 20% higher of phosphorus retention on cotton than that of $MgCl_2$-based catalyst (Table 6.3). The LOI of the fabric reached its maximum when H_3PO_4 was used as a catalyst for MDPA system (Table 6.3). Although the use of NH_4Cl-based catalyst in HFPO/(DMDHEU+TMM) finishing system got the highest phosphorus retention, the LOI of treated cotton are very close for all those three different catalyst (Table 6.3). For HFPO/TMM finishing system, the use of NH_4Cl-based catalyst achieved an approximately 15% and 13% higher of phosphorus retention on cotton than that of H_3PO_4 and $MgCl_2$-based catalyst (Table 6.3). And also the use of NH_4Cl-based catalyst in HFPO/TMM finishing system, the highest LOI of treated cotton was obtained. Therefore, we can say that the catalyst type plays an important role in influencing the bonding of both of these flame retardant finishing systems. Evidently, H_3PO_4 is the optimum catalyst for the MDPA system, and the NH_4Cl-based catalyst is the best catalyst for the HFPO system.

The cotton fabric treated with 45% MDPA or 32% HFPO in combination with a bonding agent (TMM or the mixture of DMDHEU and TMM) at different concentrations and cured at 165ºC for 2.5 min. The LOI of the cotton fabric thus treated is plotted against the concentration of TMM or the mixture of DMDHEU and TMM in Figure 6.8 (before laundering). The LOI of the fabric treated with MDPA/TMM and that treated with HFPO/TMM or HFPO/(DMDHEU+TMM) increased as the concentration of the TMM or (DMDHEU + TMM) was increased. Since the phosphorus content of the treated fabric was the same (around 3.50%) before laundering, the increasing LOI of the fabric clearly indicate that the presence of TMM or the mixture of DMDHEU and TMM in both MDPA and HFPO system enhanced the flame resistance performance of the treated fabric. The positive effect of a non-flame retardant additive to a flame retardant agent is one of the two definitions for synergism [15]. The LOI of the fabric treated with MDPA/TMM increased from 36.5 to 41.8, whereas the LOI of HFPO/TMM treated fabric only increased from 30.8 to 36.3 when the concentration of the TMM was increased from 0 to 8%. The fabric treated with MDPA/TMM has a significantly higher LOI value than that of HFPO/TMM treated fabric (before laundering). Two parallel curves for both MDPA/TMM and HFPO/TMM system in Figure 6.8 indicate that both MDPA/TMM and HFPO/TMM system have the same effect of phosphorus-nitrogen synergism when there is the same amount of nitrogen on fabric. The higher LOI of the MDPA/TMM treated fabric is attributable to the nitrogen content in the MDPA molecule, which improves the flame resistance performance by means of phosphorus-nitrogen synergism.

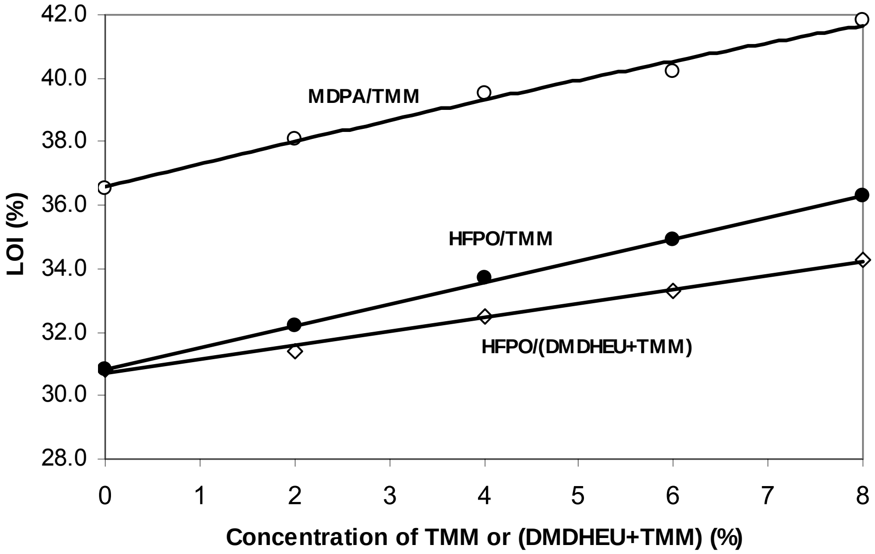


Figure 6.8. LOI of cotton fabric treated with 45% MDPA or 32% HFPO, in combination of TMM or the mixture of DMDHEU and TMM with different concentrations, cured at 165°C for 2.5 min (before wash).

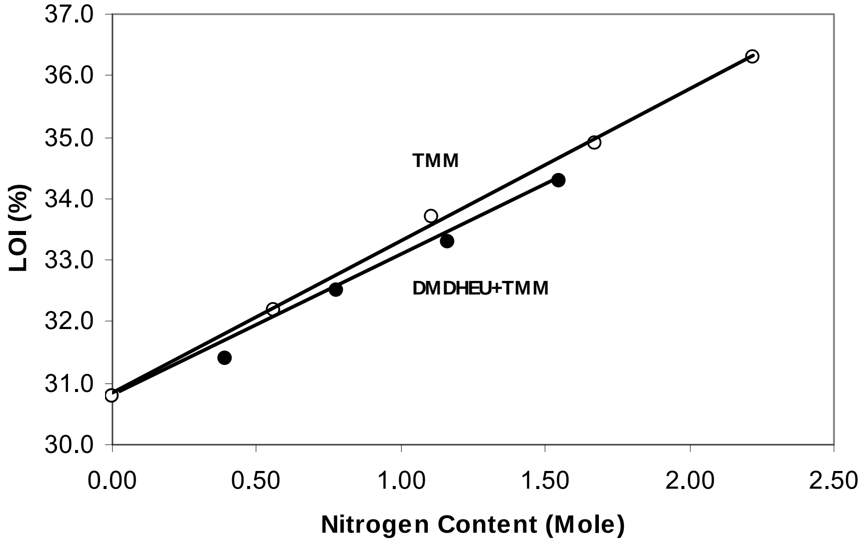


Figure 6.9. LOI of cotton fabric treated with 32% HFPO, in combination of TMM or the mixture of DMDHEU and TMM with different concentrations, cured at 165°C for 2.5 min, as a function of calculated nitrogen content on fabric (before wash).

We also noticed that LOI of HFPO/TMM treated fabric was higher than that of HFPO/(DMDHEU+TMM) treated fabric (Figure 6.8). It is quite reasonable, the nitrogen content of TMM is 39%, whereas DMDHEU contains 16% nitrogen, so the same concentration of the bonding agent was used, the nitrogen content of fabric treated with HFPO/TMM system is much higher than that of HFPO/(DMDHEU+TMM), therefore resulting in significant better flame resistance by means of phosphorus-nitrogen synergism. When the same content of nitrogen (calculated) is on the fabric, the fabric treated with HFPO/TMM system also had a higher LOI than that of HFPO/(DMDHEU+TMM) system (Figure 6.9). The nitrogen in TMM is possibly more efficient to enhance the flame resistance of cotton through phosphorus-nitrogen synergism.

Shown in Figure 6.10 is the LOI of the cotton fabric thus treated versus the mole ratio of nitrogen/phosphorus (before laundering). One observes that the LOI of HFPO/TMM treated fabric increased from 30.8 to 36.3 when the nitrogen/phosphorus mole ratio changed from 0 to 1.0 (TMM concentration from 0 to 8%). The flame resistance of HFPO/TMM treated fabric was improved when the mole ratio of nitrogen/phosphorus was increased. And the LOI of MDPA-only treated fabric (nitrogen/phosphorus mole ratio with 1.0) was 36.5, is identical to the LOI of the HFPO/TMM treated fabric with the nitrogen/phosphorus mole ratio of 1.0. The flame resistance of cotton is same for both the HFPO system and the MDPA system when there are the same amounts of the phosphorus and nitrogen on fabric. The LOI of the MDPA/TMM treated fabric increased when the TMM concentrations increased, and the curve of LOI versus the nitrogen/phosphorus mole ratio for MDPA/TMM system is on the same line of that HFPO/TMM treated fabric. Since both treated fabric have the same phosphorus content (3.50%, before laundering), this is another evidence to demonstrate that the higher LOI for the MDPA system is due to the nitrogen content in the MDPA structure.

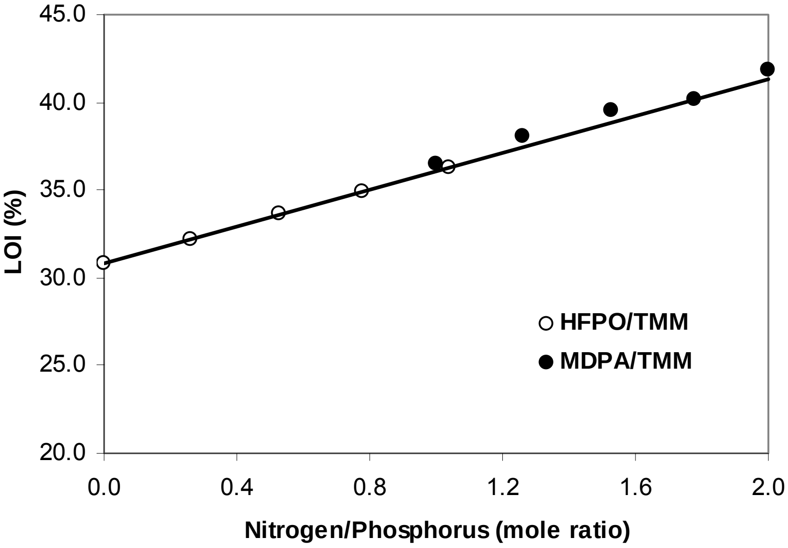


Figure 6.10. LOI of cotton fabric treated with 45% MDPA or 32% HFPO in combination of TMM or the mixture of DMDHEU and TMM with different concentrations, cured at 165°C for 2.5 min, as a function of mole ratio of nitrogen/phosphorus (before wash).

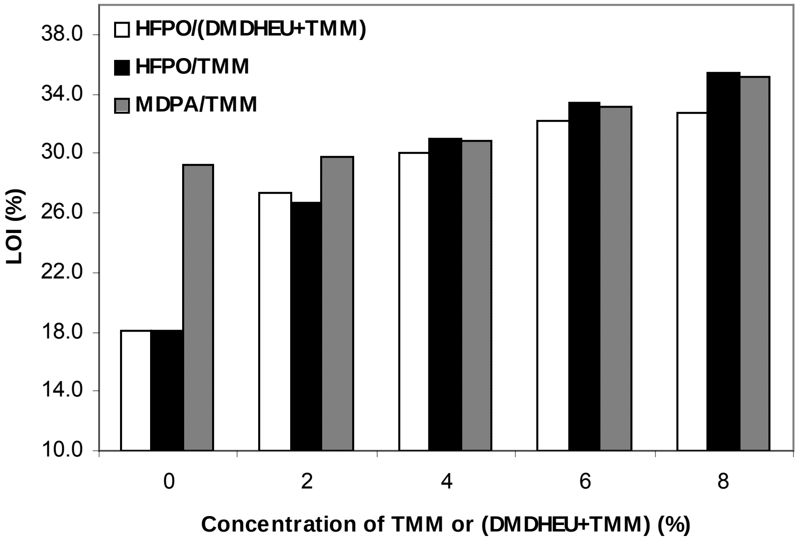


Figure 6.11. LOI of cotton fabric treated with 45% MDPA or 32% HFPO in combination of TMM or the mixture of DMDHEU and TMM with different concentrations, cured at 165°C for 2.5 min (after 1 HLTD cycle).

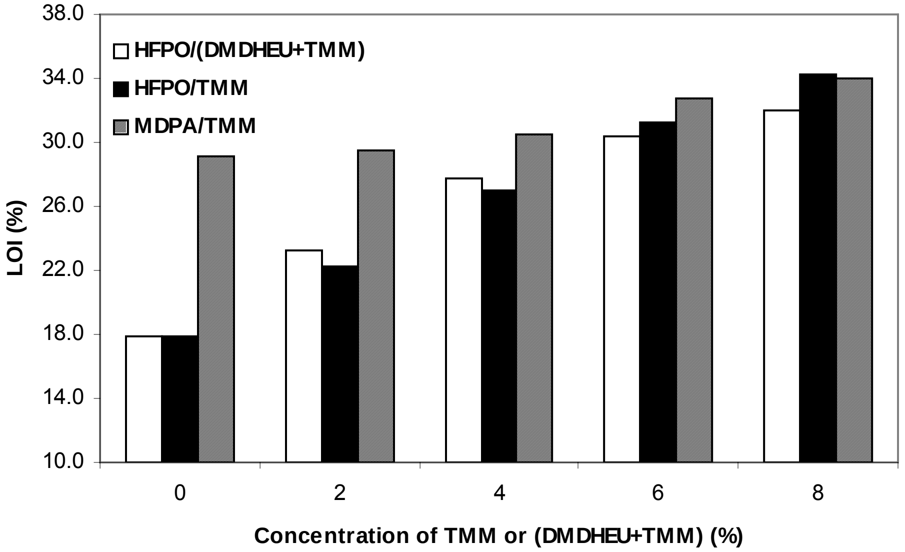


Figure 6.12.The LOI of the cotton fabric treated with 45% MDPA or 32% HFPO in combination of TMM or the mixture of DMDHEU and TMM with different concentrations, cured at 165°C for 2.5 min (after 25 HLTD cycles).

Table 6.4. Phosphorus content of cotton fabric treated with 32% HFPO, in combination with TMM or the mixture of DMDHEU and TMM of different concentrations, and cured at 165°C for 2.5 min.

TMM or (DMDHEU +TMM) (%)	Phosphorus (%)							
	HFPO/TMM				HFPO/(DMDHEU+TMM)			
	After 1 HLTD	After 10 HLTD	After 25 HLTD	After 50 HLTD	After 1 HLTD	After 10 HLTD	After 25 HLTD	After 50 HLTD
0	0.15	0.05	0.02	0.01	0.15	0.05	0.02	0.01
2	1.12	0.75	0.48	0.24	1.40	0.99	0.70	0.39
4	1.65	1.35	0.92	0.58	1.94	1.56	1.20	0.73
6	2.18	1.85	1.45	0.96	2.35	1.85	1.52	1.05
8	2.38	2.10	1.85	1.42	2.46	2.08	1.83	1.32

Table 6.5. Phosphorus content of cotton fabric treated with 45% MDPA in combination with TMM of different concentrations, and cured at 165^{o}C for 2.5 min.

TMM or (DMDHEU +TMM) (%)	Phosphorus (%)			
	MDPA/TMM			
	After 1 HLTD	After 10 HLTD	After 25 HLTD	After 50 HLTD
0	1.75	1.72	1.70	1.67
2	1.85	1.70	1.75	1.70
4	1.96	1.86	1.82	1.83
6	2.12	1.96	1.95	1.93
8	2.20	2.15	2.10	2.05

Note: The phosphorus content of fabric is 3.50% (before wash)

The LOI of the treated cotton fabric subjected to 1 and 25 home laundering cycles is presented as a function of the concentration of the TMM or the mixture of DMDHEU and TMM in Figure 6.11 and 6.12, respectively. The LOI of the fabric treated with MDPA/TMM was higher than that treated with HFPO/TMM or HFPO/(DMDHEU+TMM). However, the LOI difference between the fabric treated with MDPA/TMM and HFPO/TMM became smaller as the concentration of TMM or (DMDHEU+TMM) increased (Figure 6.11). Without the TMM, the MDPA treated fabric has the LOI of 29.3; whereas the HFPO treated fabric only has 18.1 (very close to control). When the TMM concentration increased to 8.0%, the LOI of fabric treated with MDPA was 35.1, the HFPO treated fabric had LOI of 35.4, marginally higher of LOI than that MDPA treated fabric due to the relatively higher phosphorus content of the fabric after one laundering cycle (Table 6.4 and 6.5 respectively). We also noticed that the LOI of the fabric treated with HFPO/TMM was lower than that treated with HFPO/(DMDHEU+TMM) when the bonding agent concentration was below 3.0% (Figure 6.11). When the bonding agent concentration increased to 4.0% and more, the LOI of the HFPO/TMM treated fabric was higher

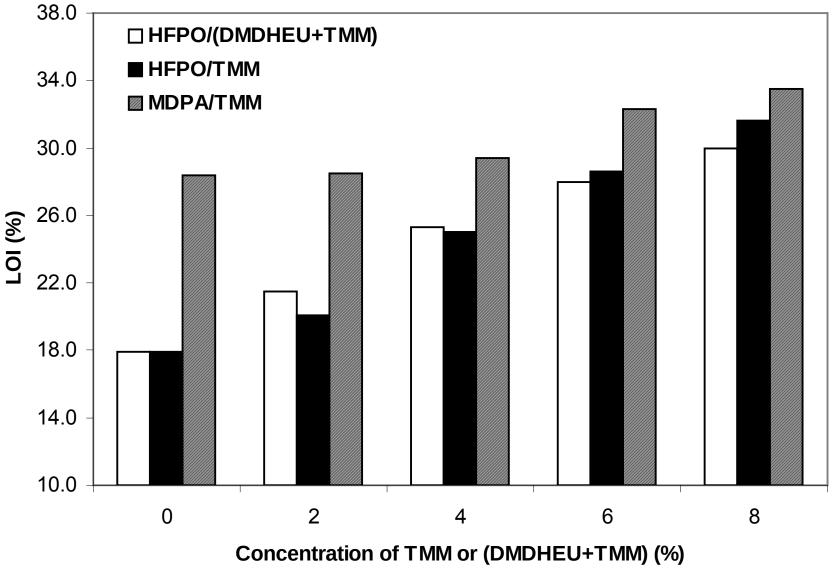


Figure 6.13.The LOI of the cotton fabric treated with 45% MDPA or 32% HFPO in combination of TMM or the mixture of DMDHEU and TMM with different concentrations, cured at 165°C for 2.5 min (after 50 HLTD cycles).

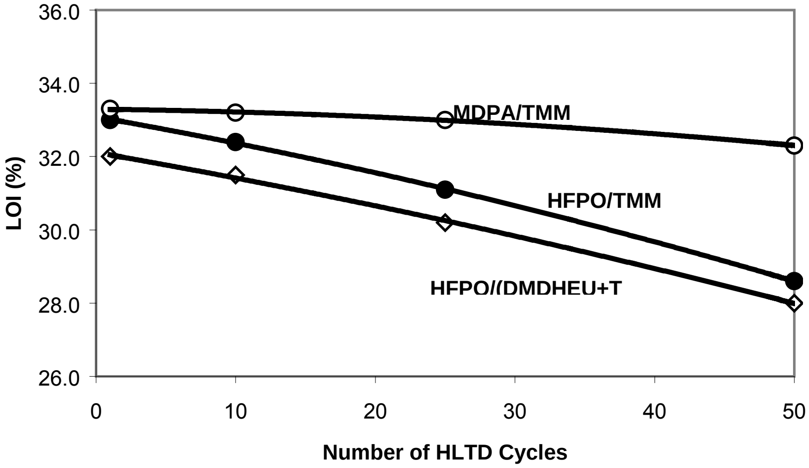


Figure 6.14. LOI of cotton fabric treated with 45% MDPA or 32% HFPO, in combination of 6% TMM or the mixture of DMDHEU and TMM, cured at 165°C for 2.5 min, as a function of the numbers of the HLTD cycles.

than that treated with HFPO/(DMDHEU+TMM) although the HFPO/(DMDHEU+TMM) treated fabric had higher phosphorus content (Table 6.4 and 6.5). TMM is a more efficient nitrogen provider; phosphorus-nitrogen synergism became more significant at higher TMM concentration [16]. The LOI of the cotton fabric treated with MDPA/TMM is higher than that HFPO/TMM or HFPO/(DMDHEU+TMM) treated fabric after 25 home laundering cycles (Figure 6.12). Similarly, the LOI difference between the fabric treated with MDPA/TMM and HFPO/TMM became smaller as the concentration of TMM or (DMDHEU + TMM) was increased. When 8% TMM was used, the LOI of HFPO/TMM treated fabric was 34.2, whereas the MDPA/TMM treated fabric had LOI of 34.0. After 25 laundering cycles, the HFPO/TMM treated fabric had a same flame resistance as that MDPA/TMM treated fabric.

After the treated fabric was subjected to 50 laundering cycles, the LOI of the cotton fabric treated with MDPA/TMM is obviously higher than that HFPO/TMM or HFPO/(DMDHEU+TMM) treated fabric (Figure 6.13). Since MDPA/TMM treated fabric was more durable to home laundering, higher phosphorus content was obtained on MDPA/TMM treated fabric even after 50 laundering cycles.

The data presented in Figure 6.14 show the LOI of the cotton fabric treated with 45% MDPA or 32% HFPO in combination with 6% TMM or (DMDHEU + TMM) after multiple laundering cycles. The fabric treated with MDPA/TMM showed a higher LOI value than that HFPO/TMM and HFPO/(DMDHEU+TMM) after multiple laundering cycles. When the TMM or (DMDHEU + TMM) concentration increased to 8%, the LOI of the cotton fabric thus treated versus the numbers of home laundering cycles is in Figure 6.15. Both MDPA/TMM and HFPO/TMM treated fabric showed the same LOI value after 1, 10, and 25 laundering cycles.

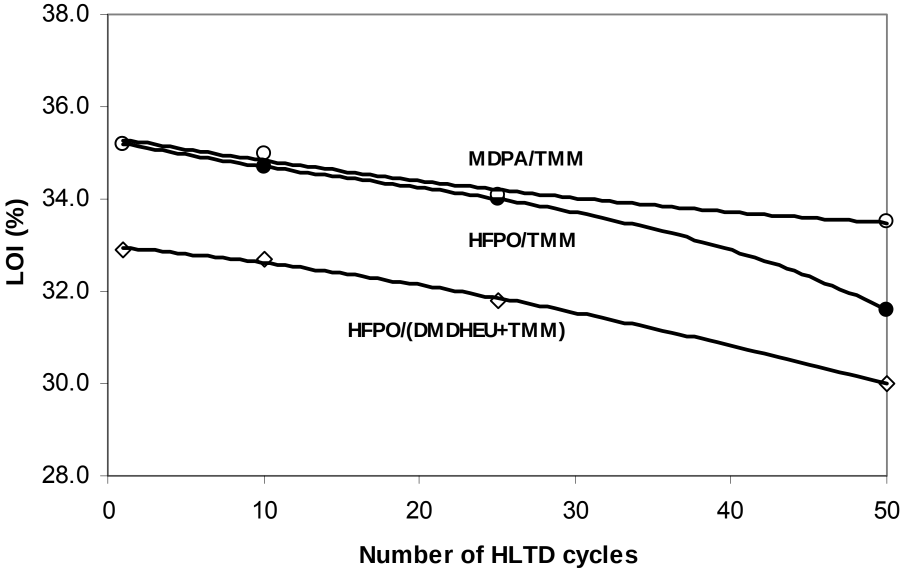


Figure 6.15. LOI of cotton fabric treated with 45% MDPA or 32% HFPO, in combination of 8% TMM or the mixture of DMDHEU and TMM, cured at 165°C for 2.5 min, as a function of the numbers of the HLTD cycles.

Table 6.6. Vertical flammability of cotton fabric treated with 32% HFPO, in combination with TMM or the mixture of DMDHEU and TMM with different concentrations, and cured at 165°C for 2.5 min.

TMM or (DMDHEU +TMM) (%)	Char length (mm)									
	HFPO/TMM					HFPO/(DMDHEU+TMM)				
	Before wash	After 1 HLTD	After 10 HLTD	After 25 HLTD	After 50 HLTD	Before wash	After 1 HLTD	After 10 HLTD	After 25 HLTD	After 50 HLTD
0	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-
4	59	70	81	82	>300	53	52	57	73	>300
6	48	46	60	87	85	52	62	75	75	81
8	48	60	60	63	73	56	65	68	63	63

The LOI difference drastically increased when the fabric was subjected to 50 laundering cycles because of the lower phosphorus content on the HFPO/TMM treated fabric.

The vertical flammability of the treated cotton fabric presented in Table 6.6 and 6.7 is consistent with LOI data shown in Figure 6.10-6.14, respectively. MDPA/TMM treated cotton fabric showed good flame resistance at any TMM concentration even after 50 laundering cycles, whereas the HFPO/TMM or HFPO/(DMDHEU+TMM) treated fabric had the satisfactory performance when the binder concentration is 6% or beyond.

Table 6.7. Vertical flammability of cotton fabric treated with 45% MDPA in combination with TMM of different concentrations, and cured at 165^{o}C for 2.5 min.

TMM or (DMDHEU +TMM) (%)	Char length (mm)				
	MDPA/TMM				
	Before wash	After 1 HLTD	After 10 HLTD	After 25 HLTD	After 50 HLTD
0	65	56	49	56	60
2	52	69	44	50	83
4	37	34	66	36	63
6	58	45	42	38	59
8	44	45	49	39	47

The WRA and tensile strength retention of the cotton fabric treated with 45% MDPA or 32% HFPO in combination with TMM or (DMDHEU+TMM) at different concentrations and cured at 165ºC for 2.5 min, as shown in Table 6.8, and 6.9, respectively. The WRA of the MDPA/TMM treated fabric remained statistically unchanged at 163-168^{o} (close to control 166^{o}) and tensile strength retention was in the 95-93% range when the TMM concentration was increased from 2.0% to 8.0%. TMM, a class of formaldehyde melamine resin, is the reaction product of melamine and formaldehyde at slight alkaline conditions (Scheme 6.6). It is able to self-condense between methylol and amine groups to form a polymer with methylene bridges [19], shown in Scheme 6.6, in addition to forming crosslinkages between cellulosic hydroxyl groups on cotton. The self-condensation also can take place between methylol groups to form a polymer under acidic conditions (Scheme 6.7) [20], therefore, to improve the wrinkle resistance of cellulosic materials.

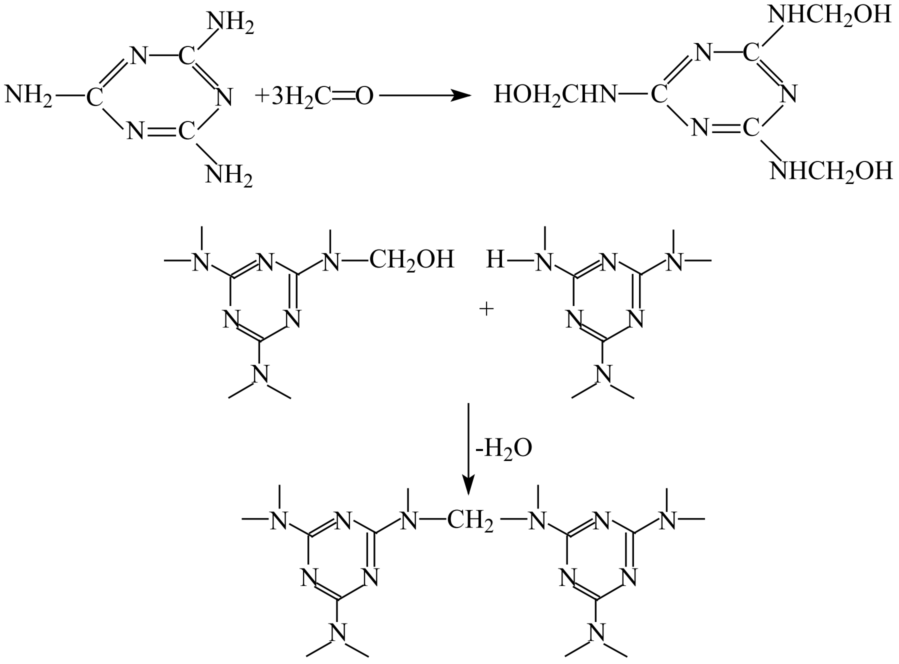
The fact that the WRA and strength loss of MDPA/TMM treated fabric remained at a low level and the WRA. The tensile strength loss of the treated fabric did not increase as the TMM concentration was increased; indicate that for MDPA/TMM system, there was no crosslinking among cellulose molecules even at high TMM concentration. For HFPO/TMM system, the WRA of the treated fabric increased from 163° to 180° and the tensile strength retention was at the 93-87% range when the TMM concentration was increased from 2.0% to 8.0%. The slightly increased WRA on HFPO/TMM treated fabric indicate the amount of crosslinking among cellulose molecules were small but significant at higher TMM concentration. The tensile strength loss was 87% of HFPO/TMM treated fabric when TMM concentration is 8.0% in HFPO system,

Table 6.8. WRA of cotton fabric treated with 45% MDPA or 32% HFPO, in combination with TMM or (DMDHEU + TMM) with different concentrations, and cured at 165°C for 2.5 min.

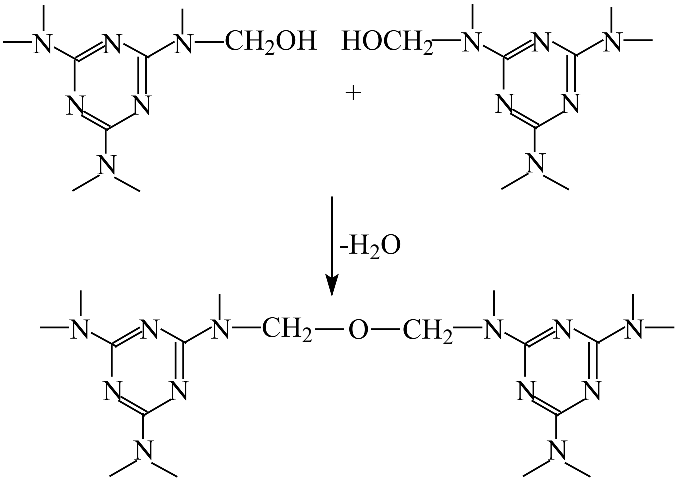
TMM or (DMDHEU+TMM) (%)	WRA (Degree, W + F)		
	HFPO/TMM	HFPO/(DMDHEU+TMM)	MDPA/TMM
0	163	163	164
2	167	215	163
4	165	228	165
6	171	235	164
8	180	240	168

Table 6.9. Tensile strength of cotton fabric treated with 45% MDPA or 32% HFPO, in combination with TMM or the mixture of DMDHEU and TMM with different concentrations, and cured at 165°C for 2.5 min.

TMM or (DMDHEU+TMM) (%)	HFPO/TMM		HFPO/(DMDHEU+TMM)		MDPA/TMM	
	Tensile strength (kgf)	T.S. retention (%)	Tensile strength (kgf)	T.S. retention (%)	Tensile strength (kgf)	T.S. retention (%)
0	43.3	99	43.3	99	43.3	90
2	40.9	93	38.1	87	40.9	95
4	40.8	93	36.0	82	40.8	94
6	39.5	89	35.8	81	41.2	94
8	38.3	87	34.4	78	38.3	93



Scheme 6.6



Scheme 6.7

which is consistent with that the WRA increase, i.e. cross-linking cellulose reduced the tensile strength of cotton fabric [21].

Nevertheless, the WRA of the HFPO/(DMDHEU+TMM) treated fabric notably increased from 166° to 238° and tensile strength retention reduced from 87% to 78% when the mixture of DMDHEU and TMM concentration was increased from 2.0% to 8.0%. The data show that a substantially higher amount of crosslinking is formed among cellulose molecules by DMDHEU in the HFPO/(DMDHEU+TMM) system.

The stiffness of the treated cotton fabric is presented in Figure 6.16. When the TMM or the mixture of DMDHEU and TMM concentration was 2.0%, the stiffness of the treated fabric was 220 grams, which is close to control. When the TMM or the mixture of DMDHEU and TMM concentration was increased to 4.0% or more, the stiffness of HFPO/TMM and HFPO/(DMDHEU+TMM) treated fabric was increased to around 550 grams. The substantially increased stiffness for the fabric as a result of an increase in TMM concentration indicates that TMM react with HFPO to form crosslinked polymeric network [17]. The MDPA/TMM treated

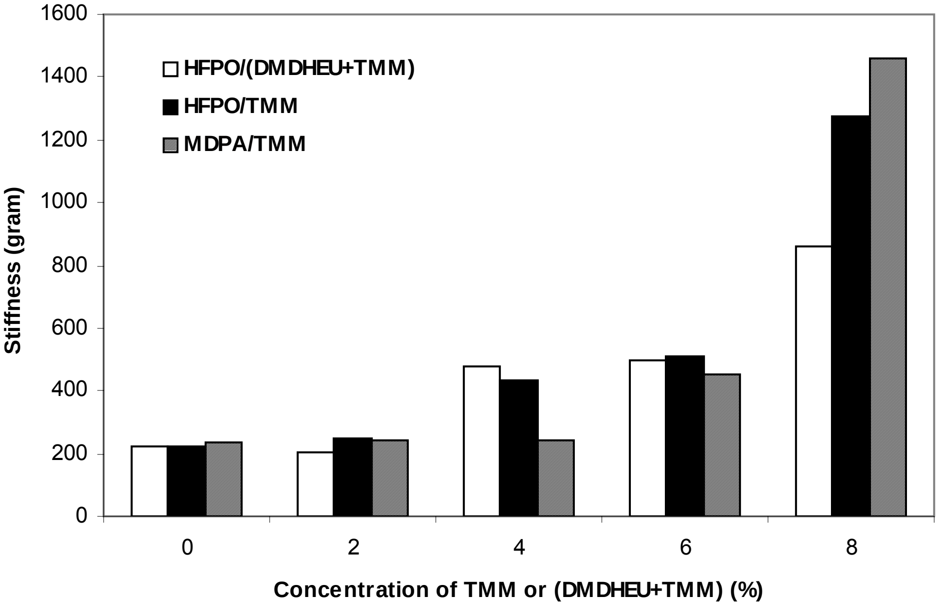


Figure 6.16. Stiffness of cotton fabric treated with 45% MDPA or 32% HFPO, in combination of TMM or (DMDHEU + TMM) with different concentrations, cured at 165°C for 2.5 min.

fabric has highest stiffness (1462 gram) when the TMM concentration was increased to 8%, which is double of that of HFPO/(DMDHEU+TMM) treated fabric. For HFPO system, we can further reduce the fabric stiffness by adjusting the HFPO/TMM or HFPO/(DMDHEU+TMM) ratio [17].

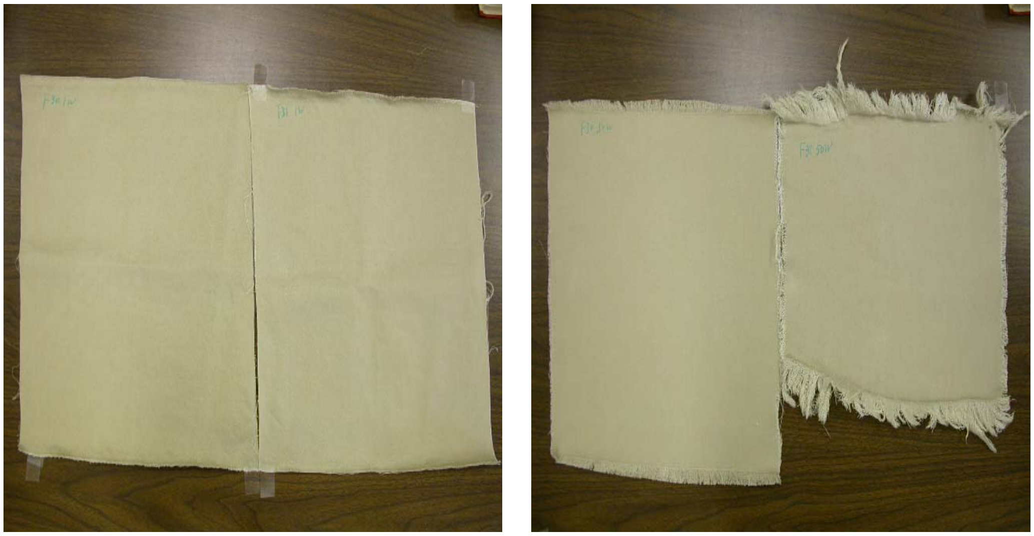
The cotton fabric was treated with 45% MDAP or 32% HFPO in combination with 6% TMM and cured at 165°C for 2.5 min. The dimensional change in the warp direction of treated fabric after multiple laundering cycles is shown in Table 6.10. The percent dimensional change of the fabric was calculated using the formula $(L_{AL}/L_{BW})\times 100\%$, where, L_{AL} is the length of the fabric after laundering, and L_{BW} is length of the fabric before washing.

Both MDPA and HFPO treated fabric give the satisfactory results after one laundering cycle with more than 97% dimensional retention. However, as the numbers of home laundering cycles increased, the cotton fabric treated with MDPA/TMM was prone to fraying and unravels at edge (Figure 6.17), the dimensional retention of the MDPA/TMM treated fabric is 82% after 10 laundering cycles, and is only 64% after 50 laundering cycles, whereas the HFPO treated fabric has 90% dimensional retention after 50 laundering cycles. Because we use the same laundering conditions, the higher yarn friction coefficient of MDPA/TMM treated fabric is the possible reason why the MDPA/TMM treated fabric frays more easily during the laundering cycles.

Table 6.10. Dimensional change in the warp direction of cotton fabric treated with 45% MDPA or 32% HFPO, in combination with 6% TMM, and cured at 165°C for 2.5 min after different numbers of HLTD cycles

Number of HLTD cycles	HFPO		MDPA	
	Length in warp direction (cm)	Dimensional retention (%)	Length in warp direction (cm)	Dimensional retention (%)
0	37.6	-	37.7	-
1	37.2	99	36.7	97
10	35.6	95	30.8	82
25	33.9	90	28.8	76
50	34.0	90	24.5	64

The amount of formaldehyde release of cotton fabric treated with 45% MDPA or 32% HFPO in combination with 6% TMM or the mixture of DMDHEU and TMM is presented in Table 6.11. The MDPA/TMM treated fabric has 8913 ppm formaldehyde release before wash, and is 7172 ppm after one laundering cycle. However, the cotton fabric treated with HFPO/(DMDHEU+TMM) has only 4513 and 3323 ppm formaldehyde release before and after one laundering cycle, respectively, which is substantially lower than that of MDPA/TMM treated fabric. For HFPO/TMM treated fabric, it has similar level of formaldehyde release as that of MDPA/TMM treated fabric. We noticed that HFPO itself had no formaldehyde content, and



HFPO/TMM MDPA/TMM HFPO/TMM MDPA/TMM

Before Wash **After 50 HLTD Cycles**

Figure 6.17. Dimensional change of MDPA/TMM and HFPO/TMM treated cotton (before and after 50 HLTD cycles)

Table 6.11. Formaldehyde level of the cotton fabric treated with 45% MDPA or 32% HFPO, in combination with 6% TMM, and cured at 165^{o}C for 2.5 min before and after one HLTD cycle.

Number of HLTD cycles	Formaldehyde (ppm)		
	HFPO/TMM	HFPO/(DMDHEU+TMM)	MDPA/TMM
0	8888	4513	8913
1	6493	3323	7172

MDPA had much a higher level of formaldehyde (1211 ppm in solution). The data indicate that for both HFPO/TMM and MDPA/TMM system, the major part of the formaldehyde release was attributed to the TMM in the systems.

During the fabric treatment and curing process, the MDPA/TMM finishing system has a strong unpleasant odor, whereas HFPO/TMM and HFPO/(DMDHEU+TMM) systems have not. The formaldehyde in MDPA and the by-product are the possible reason for this odor. This must be considered as a significant drawback of the MDPA/TMM system.

CONCLUSION

MDPA by itself can be bound to the cotton cellulose via its N-methylol group. The presence of TMM can improve the amount of MDPA bound to cotton (approximately a 25% increase in phosphorus at 8% TMM level). The percent retention of MDPA bound to cotton cellulose is independent of the MDPA concentration in the system. The bonding agent, such as TMM or DMDHEU, is necessary for the HFPO finishing system. The type and concentration of binder significantly affect the amount of HFPO bound to cotton. The amount of the flame retardant agent bound to cotton is significantly higher for the HFPO system than that for the MDPA system when the equal moles of the phosphorus and N-methylol group are used. The better laundry durability of MDPA/TMM treated fabric is attributed to the higher content of N-methylol in MDPA system. The H_3PO_4 is the optimum catalyst for MDPA system, and the NH_4Cl-based catalyst is the best catalyst for the HFPO system.

The MDPA/TMM treated fabric has a higher initial LOI than that of HFPO/TMM treated fabric due to the nitrogen content in the MDPA molecule, which enhances the flame resistance by means of phosphorus-nitrogen synergism. The flame resistance of cotton is identical for both the HFPO system and MDPA system when there is an equal amount of the phosphorus and nitrogen on the fabric. The fabric treated with MDPA/TMM and HFPO/TMM had similar LOI values after 1, 10, and 25 laundering cycles. The better flame resistance of the MDPA/TMM treated fabric is attributed to the higher phosphorus content of MDPA/TMM treated cotton after 50 laundering cycles.

Both the HFPO/TMM and MDPA/TMM treated fabric remained at a low level of WRA. The tensile strength loss of the treated fabric did not increase as the TMM concentration was increased. The fabric stiffness significantly increased when a high TMM concentration is used.

And MDPA/TMM treated fabric showed lower dimensional retention during the laundering cycles and higher formaldehyde release level.

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CHAPTER 7

CORRELATION BETWEEN VERTICAL BURNING TEST RESULTS AND LIMITING OXYGEN INDEX OF COTTON TREATED WITH ORGANOPHOSPHORUS FLAME RETARDANT FINISHES[1]

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[1] Wu, W, and Yang, CQ. 2003. Submitted to Fire and Materials.

ABSTRACT

The statistical models between char length and limiting oxygen index (LOI) have been developed on flame resistant cotton treated with a hydroxy-functional organophosphorus oligomer (HFPO) and a bonding agent: BTCA, DMDHEU, trimethylolmelamine (TMM) or mixture of DMDHEU and TMM. We found that the linear regression model is not appropriate to interpret the relationship between char length and LOI. The non-linear correlation between char length and LOI is meaningful to predict the char length of the cotton fabric treated with HFPO and a bonding agent at a specified LOI value. The use of different bonding systems for the flame retardant agent has no significant effect on the correlation between char length and LOI. And the use of fabrics with different thickness has a significant influence on this non-linear function between char length and LOI.

INDEX WORDS: BTCA, Cotton, Char length, DMDHEU, Limiting oxygen index, Trimethylolmelamine, Organophosphorus oligomer, Regression model, Statistical analysis.

INTRODUCTION

Since its introduction in 1966 by Fenimore and Martin [1-2], the limiting oxygen index (LOI) test has been widely used to provide information on a material's flammability in a given configuration and with a particular set of test conditions. Limiting oxygen index or critical oxygen index is defined as the minimum concentration of oxygen which allows a sample to sustain combustion under specified conditions in a candle-like fashion, and thus may be considered to measure the ease of extinction of a sample [3].

Limiting oxygen index test is easy to run and usually reproducible, it can be run on any solid or, with some equipment modification, even on a liquid. It has been formalized in the USA as ASTM 2863, the latest version being D2863-00 [4]. Lots of work has been done on the correlation between LOI and other fire test, and the LOI has been criticized, as having no relation to a "real" fire, particularly in view of the non-representative atmospheres used for combustion in the test [5-6].

The vertical test used for the Children's Sleepwear Standard (FF3-71) is performed on a vertical specimen that has been bone-dried [7]. Ignition is at the lower edge of the specimen with the burning configuration upwards, thus simulating conditions usually encountered in an apparel fire.

Both LOI and vertical test are intend to measure flammability, however, they are quite different in their mode of testing, the type of results gained, and the interpretation of these results. Some work have been done on the qualitative relationship between char length and LOI values. An LOI of 26 had been associated with a 5-inch char length in the vertical test for several flame retardant treated cotton fabrics [8]. A rule of thumb has been that fabrics with a LOI greater than 26 pass the vertical test and those with a LOI less than 24 fail. In the range of 24 to

26, fabrics will sometimes pass and sometimes fail the vertical test. And the weight, geometry, and air permeability are the major factors for influencing the vertical test results [9-10].

In order to obtain a quantitative relationship between the vertical test and LOI values, in this research, we statistically studied the relationship between the vertical test results and LOI values on cotton fabric treated with a hydroxy-functional organophosphorus oligomer (HFPO) and a bonding agent: 1,2,3,4-Butanetetracarboxylic acid (BTCA), DMDHEU, trimethylolmelamine (TMM), or mixture of DMDHEU and TMM. We analyzed the (1) different bonding systems factor; and (2) fabric weight factor on the relationship between char length and LOI values.

EXPERIMENTAL

Materials

The fabric used were used in this study: (1) a desized, scoured, and bleached 40x40 cotton printcloth weighing 108 g/m^2 (Testfabrics Style 400); and (2) a 100% cotton weave fabric weighing 246 g/m^2 supplied by Milliken, Spartanburg, South Carolina. The hydroxy-functional organophosphorus oligomer with the commercial name of “Fyroltex HP” was supplied by Akzo Nobel Chemical Inc., Dobbs Ferry, New York. DMDHEU with the commercial name of “Freerez 900” and methylolated melamine formaldehyde resin with the trade name of “Aerotex M-3” were supplied by Noveon, Inc, Cleveland, Ohio. The catalyst with the commercial name of “Catalyst RD” was supplied by Eastern Color & Chemical Co., Greenville, South Carolina. BTCA, NaH_2PO_2 were reagent-grade chemicals supplied by Aldrich Chemical, Wisconsin

Fabric Treatment and Home Laundering Procedures

The fabric was first immersed in a finish solution containing HFPO, different kind of bonding agents, such as BTCA, DMDHEU, TMM, or mixture of DMDHEU and TMM, and a catalyst, then passed through a laboratory padder with two dips and two nips, dried at 90°C for 3 min, and finally cured in a Mathis curing oven at a specified temperature. The wet pick-up of the plain cotton fabric was approximately 105±3%, and the wet pick-up of the twill cotton fabric was approximately 80±3%. After curing, the treated cotton fabric was subjected to different number of home laundering cycles with the use of "AATCC Standard Detergent 1993". The home laundering procedure was done according to AATCC Test Method 124-1996 ("Appearance of Fabrics After Repeated Home Laundering"). The water temperature for laundering was approximately 46°C.

Fabric Performance Evaluation

The limiting oxygen index (LOI) of the cotton fabric was measured according to ASTM Standard Method D2863-00. The vertical flammability of the cotton fabric was measured according to ASTM Standard Method D 6413-99.

RESULTS AND DISCUSSION

The cotton twill fabric was treated with HFPO and BTCA with different concentrations, then cured at 185ºC for 2 min, and subjected to different home laundering cycles. The limiting oxygen index (LOI) and char length thus treated are shown in Table 7.1. The limiting oxygen index and char length of the cotton twill fabric treated with HFPO/DMDHEU, HFPO/TMM, and HFPO/(DMDHEU+TMM) are presented in Table 7.2-7.4 respectively, and the LOI and char length of cotton plain fabric treated with HFPO/TMM are shown in Table 7.5. One observes that

Table 7.1. LOI and char length of 100% cotton twill fabric treated with HFPO and BTCA with different concentrations, cured at 185°C for 2 min, after different number of HLTD cycles.

LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)
29.8	108	29.6	78	30.0	99	28.2	131	24.1	150
29.9	95	29.8	85	32.4	87	31.4	80	24.7	136
29.9	95	28.2	128	28.9	116	28.7	122	25.6	133
29.9	102	26.6	103	32.3	103	27.6	114	26.3	138
29.8	100	26.5	104	28	89	27.4	102	26.5	144
27.2	114	30.9	85	32.8	79	26.3	105	26.9	119
27.5	108	25.4	213	28.6	110	30.7	110	26.9	133
27.6	96	26.2	125	27.7	98	29.1	135	29.1	117
27.5	108	30.1	74	34.3	66	27.9	134	29.2	92
27.6	112	26.9	110	33.7	80	27.6	140	29.2	99
29.9	83	27.8	118	29.3	92	26.7	120	29.2	124
29.9	81	31.7	76	31.1	70	30.9	90	29.2	97
29.9	79	27.8	129	31.8	88	30.2	92	29.2	97
29.9	94	27.0	119	27.5	97	28.1	86	26.6	138
29.9	110	25.6	136	30.5	78	30.2	105	26.9	115
30	97	30.9	96	30.1	85	29.7	77	26.9	136
29.9	106	27.0	127	28.6	102	29.6	80	26.8	135
29.9	87	27.1	90	28.3	114	30.9	90	27.0	143
27.5	125	26.0	132	38.1	40	27.2	127	26.5	169
27.7	108	32.2	75	26.8	97	27.1	115	29.4	94
27.8	110	29.2	114	38.6	71	27.2	106	29.6	78
27.7	117	30.0	104	28.6	121	27.6	106	29.8	85
27.6	134	27.3	110	30.9	66	28.3	106	28.2	128
27.6	135	25.2	173	33.8	67	28.9	106	26.6	103
27.7	113	33.6	66	28.1	102	29.0	85	26.5	104
27.3	112	30.7	84	29.7	117	29.1	88	29.8	108
29.4	94	32.0	92	35.3	58	29.2	88	29.9	95
29.9	95	27.2	114	27.5	108	29.9	81	29.9	110
29.9	102	27.5	108	27.6	112	29.9	79	27.5	125
29.8	100	27.6	96	29.9	83	29.9	94	27.7	108
27.8	110	30.0	97	27.6	135	31.9	72	26.8	105
27.7	117	29.9	95	27.8	110	31.9	85	29.9	87
27.6	134	29.9	106	27.7	113	32.1	90	27.3	112
30.4	78	29.8	112	29.7	102	30.1	65	29.5	114
31.2	112	29.2	121	28.9	107	29.9	85	29.0	112
30.9	114	28.4	101	28.9	113	30.9	115	28.5	115
30.0	128	27.6	129	29.0	94	30.5	118	26.7	148
30.2	122	29.4	98	29.6	117	29.5	112	26.1	149
30.7	108	29.6	77	29.0	126	32.7	84		

Table 7.2. LOI and char length of 100% cotton twill fabric treated with HFPO and DMDHEU with different concentrations, cured at 165^{o}C for 2.5 min, after different number of HLTD.

LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)
30.0	73	29.4	98	30.2	82	30.2	84	29.6	100
29.9	93	29.6	77	30.0	77	30.2	100	29.7	71
30.1	115	29.7	102	29.3	87	31.3	46	29.5	76
29.7	90	28.9	107	29.3	84	31.0	102	29.6	78
29.7	83	28.9	113	28.3	95	29.0	45	27.7	108
29.7	93	29.0	94	27.4	103	29.7	88	29.2	74
30.0	84	29.6	117	27.2	106	28.9	84	29.1	85
29.7	96	29.0	126	30.6	78	30.4	73	29.3	80
30.5	66	30.1	65	29.9	100	29.1	95	30.2	92
30.4	78	29.9	85	29.6	98	29.3	109	29.6	132
31.2	112	30.9	115	30.9	112	31.0	115	29.9	125
30.9	114	30.5	118	31.0	112	31.2	110	29.9	126
30.0	128	29.5	112	32.3	106	31.9	124	29.6	87
30.2	122	32.7	84	32.0	111	30.5	107	30.9	98
30.7	108	29.5	114	32.7	84	32.7	93	29.9	82
29.8	112	29.0	112	29.6	87	30.4	83	29.9	96
29.2	121	28.5	115	30.9	98	30.9	119	29.7	100
28.4	101	26.1	148	27.6	129	28.3	117	27.5	117
27.6	129	26.7	149	29.5	114	29.5	123	29.9	102

Table 7.3. LOI and char length of 100% cotton twill fabric treated with HFPO and TMM with different concentrations, cured at 165^{o}C for 2.5 min, after different number of HLTD cycles.

LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)
31.0	107	33.2	85	33.5	50	30.2	43	36.5	55
30.8	97	32.2	90	30.5	38	29.0	36	34.3	48
35.6	67	29.4	100	29.6	93	28.0	38	33.1	63
34.4	68	31.5	111	34.5	79	26.9	124	33.2	77
34.0	68	29.9	98	35.8	78	33.4	89	34	90
32.9	75	30.8	83	28.3	98	34.6	89	29.6	77
32.9	100	31.8	75	33.6	86	31.1	82	30.2	110
30.3	105	30.3	89	34.3	81	31.6	94	31.2	72
31.3	87	34.4	68	36.8	79	33.3	102	28.4	169
33.5	74	29.9	99	35	91	31.4	78	29.4	100
35.6	67	30.8	83	34.0	68	32.9	75	31.5	111
26.9	168	27.8	78	31.8	75				

Table 7.4. LOI and char length of 100% cotton twill fabric treated with HFPO and mixture of DMDHEU and TMM with different concentrations, cured at 165^{o}C for 2.5 min, after different number of HLTD cycles.

LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)
34.7	70	28.1	111	28.5	75	28.9	77	29.8	98
32.6	85	27.3	132	28.5	65	28.3	49	29.3	84
31.8	96	28.0	125	28.4	88	26.7	164	29.2	88
30.0	80	27.8	127	29.5	80	27.2	118	30.0	77
28.5	75	27.2	121	28.9	77	28.3	49	26.3	155
28.2	79	26.7	179	27.3	132	30.8	73	26.8	123
28.5	65	26.7	164	27.8	127	27.2	118	25.9	170
28.4	88	27.2	118	27.7	121	29.5	128	30.2	88
29.5	80	29.5	128	26.7	179	32.4	79	31.8	83
28.9	77	28.5	75	26.7	164	32.8	73	30.2	84
28.3	49	28.2	79	31.0	70	30.0	100	30.5	93
30.8	73	27.3	132	32.5	64	30.2	95	26.9	130
34.5	75	28.0	125	32.5	66	28.3	90	28.2	94
32.5	75	34.5	75	32.9	63	28.2	85	26.1	123
32.4	79	35.1	82	28.2	85	29.1	81	26.5	177
29.9	100	34.8	77	30.0	100	28.5	90	34.5	75
30.0	100	32.5	79	30.8	89	27.6	86	35	80
34.5	75	33.1	90	30.3	95	25.8	148	35.6	70
35	76	32.8	86	34.1	75	29.7	102	32.5	79
32.5	79	29.8	100	33.9	82	28.3	102	33.1	88
32.9	80	29.7	98	32.3	79	29.0	98	33.5	76
29.9	100	29.4	102	32.0	90	32.9	98	29.9	100
29.4	108	28.9	102	29.1	106	32.3	96	28.9	112
34.1	75	32.3	79	29.1	106	32.2	90	30.3	95
34.3	82	32.4	90	29.7	98	34.8	77	33.2	75
33.7	94	32.8	93	33.4	76	34.1	83	32.9	85
34.0	89	33.0	95	33.2	65	34.0	66	33.0	73
34.2	71	29.0	77	33.1	82	32.8	81	32.9	76
34.3	77	29.7	95	33.2	65	32.9	70	32.8	80
34.8	65	29.5	101	34.1	71	33.1	82	32.7	85
31.3	99	29.9	98	34.0	77	33.0	73	33.0	75
31.8	100	30.2	90	34.8	65	31.8	76	29.8	86
32.6	86	34.2	69	32.0	73	31.6	83	29.6	91
30.4	80	30.0	77	28.0	94	26.8	150	31.9	79
31.2	78	29.5	84						

Table 7.5. LOI and char length of 100% cotton plain fabric treated with HFPO and TMM with different concentrations, cured at 165°C for 2.5 min, after different number of HLTD cycles.

LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)
29.8	132	28.9	118	28.3	110	27.2	150	31.9	90
30.2	100	29.8	105	29.0	108	28.5	125	29.0	110
31.0	107	28.9	101	28.9	146	28.9	150	28.8	103
30.8	97	29.5	78	29.3	129	29.0	105	28.1	110
27.5	127	28.9	118	28.3	110	27.2	150	33.0	100
27.1	135	28.9	101	28.9	146	28.9	150	31.5	68
29.8	132	29.5	78	29.3	129	28.5	105	30.7	87
28.9	64	29.8	83						

when the LOI is 24.1, the char length is close to 150 mm. When the LOI increased to 35.6, the char length is decreased to 67 mm. The increase of LOI will accordingly decrease the char length. Our concern here is to quantitatively measure the relationship between char length and LOI. Is there a linear correlation or a non-linear function between char length and LOI? In order to solve this concern, SAS® program was used in the statistical analysis. The statistical analysis was performed in the form of "analysis of variance" (ANOVA). This analysis include the regression model for interpreting the correlation between char length and LOI, the F-test (overall model significance) and its associated probability (p-value) for studying the effect of both flame retardant finishing system factor and fabric factor on the correlation between char length and LOI.

The Pearson linear correlation coefficient and Spearman linear correlation coefficient of char length and LOI are shown in Table 7.6. Both parameter (Pearson) and non-parameter (Spearman) linear correlation coefficients of char length and LOI are approximately -0.64, it indicates that the linear relationship between char length and LOI is not strong. With the

Table 7.6. The Pearson and Spearman linear correlation coefficients between char length and limiting oxygen index (LOI).

	Pearson (parameter) correlation coefficient	Spearman (non-parameter) correlation coefficient
Char length vs LOI	- 0.6359	- 0.6481

Table 7.7. Linear regression parameter estimates for flame retardant cotton.

Variable	Degree of freedom	Parameter estimate	Standard Error	t-value	Pr > t
Intercept	1	298.9244	10.3326	28.93	< 0.0001
LOI	1	-6.6808	0.3436	-19.45	< 0.0001

assistance of SAS® program, we developed a linear regression model between char length and LOI. From the SAS output, the parameter estimates are shown in Table 7.7. The linear statistical model is expressed in Equation (1), where CL refers to char length.

$$CL = 298.92 - 6.68 * LOI \qquad (1)$$

Equation (1) gives an R^2 of 0.4044, thus indicating that only approximately 40% of the total variability of char length is associated with the variability of the independent variable LOI within the frame-work of the equation. Obviously, the R^2 of 0.4044 is too low, this is an evidence of that the relationship between char length and LOI is not linear. We also added a term of $(LOI)^2$ to the regression model, and obtained the following linear model:

$$CL = 929.73 - 48.16 * LOI + 0.68\,(LOI)^2 \qquad (2)$$

R^2 for equation (2) is 0.4341, is not significant improved, only less than 50% of the total char length can be interpreted by the independent variable of LOI within the linear regression model, that is not enough.

To achieve an appropriate linear regression model $Y=\beta_0+\beta_1X_1+\cdots\beta_nX_n+\varepsilon_i$, it is necessary to make the following assumptions on the residuals ε_i: (1) ε_1, ε_2, $\cdots\varepsilon_n$ are independent; (2) ε_1, ε_2,

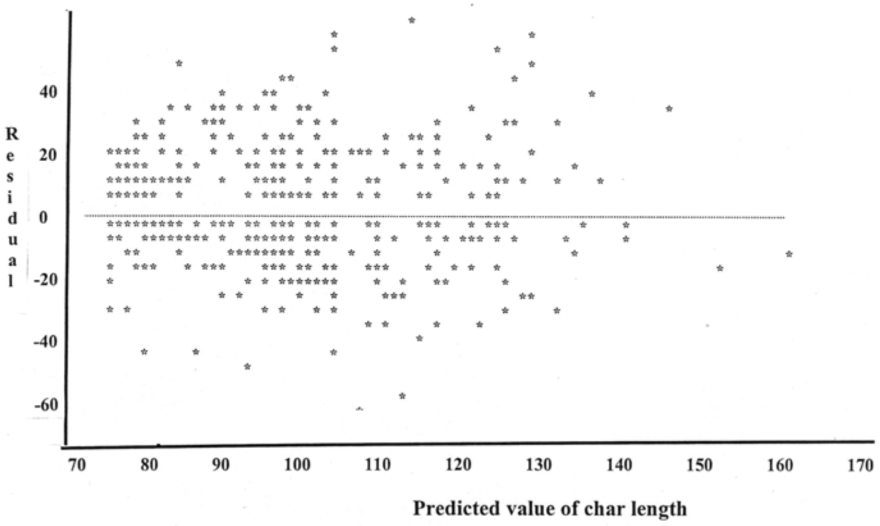

Figure 7.1. Plot of the residual vs. predicted value of char length

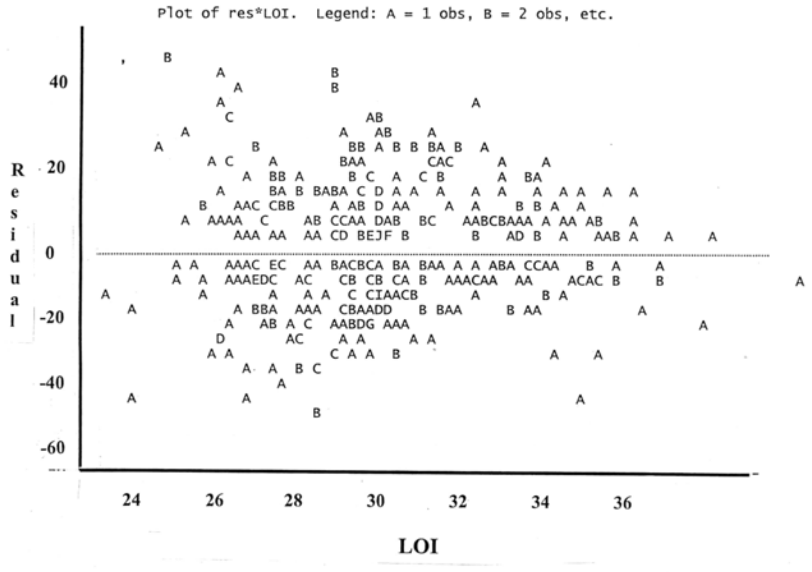

Figure 7.2. Plot of the residual vs. the independent variable of LOI

$\cdots\varepsilon_n$ have a identical distribution; and (3) ε_1, ε_2, $\cdots\varepsilon_n$ have a normal distribution, with mean 0 and variance σ^2 [11].

Table 7.8. Normality test for linear correlation between char length and LOI on flame retardant cotton.

Test	Statistics	p-value
Shapiro-Wilk	W 0.9766	< 0.0001
Kolmogorov-Smirnov	D 0.0494	< 0.0100
Cramer-von Mises	W-Sq 0.3496	< 0.0050
Anderson-Darling	A-Sq 2.3499	< 0.0050

In order to test whether this regression model can meet these assumptions, we first plotted the residuals against the predicted value of char length, and the independent variable LOI in Figure 7.1 and 7.2 respectively. The data presented here show a specific pattern, indicating the variance is not a constant. And also Shapiro-walk W test is also used to check the normality of the residuals. One observes that W is 0.9766, and p value is less than 0.0001 (Table 7.8). The p value is far less than significance level 0.05, meaning the residuals does not come from normal distribution, therefore, certain transformation is necessary [12].

Table 7.9. The non-linear model, R-square, and root square mean square error after different transformations for flame retardant cotton.

Non-linear Models	R-square	Root MSE
$CL = 311.35- 20.94\ (LOI)^{1/3}$	0.7169	14.4102
$CL =528.39 -77.96\ (LOI)^{1/2}$	0.7202	14.3124
$CL =844.12 -218.44 * Log\ (LOI)$	0.7412	13.8000
$CL = [46.66-10.79\ Log\ (LOI)]^{1/2}$	0.7769	0.6170
$CL = Exp\ [11.95 - 2.17\ Log\ (LOI)]$	0.7909	0.1189

We tried several transformations on independent variable of LOI: log transformation, square root transformation, cubic root transformation, and both log transformation on char length and LOI, the models, R square, and root square of mean square error are shown in Table 7.9. The data presented here shows that all those transformations can significantly improve the R-square. The R-square is increased from approximately 0.40 to above 0.70. Among all these transformations, both log transformations on char length and LOI shows the highest R-square of 0.7909 and the smallest root mean square error of 0.1198. The model we developed is as follows:

$$CL = \mathrm{Exp}\,[10.95 - 2.17 \log(LOI)] \qquad (3)$$

approximately 80% of the total variability of char length is associated with the variability of LOI within this non-linear model.

The plot of residuals against the predict variable of char length is shown in Figure 7.3. The data presented here show that all the residuals fall within a horizontal band centered on 0, displaying no systematic tendencies. It shows that all the residuals are random; therefore this non-linear regression model is appropriate.

Table 7.10. Normality test for non-linear correlation between char length and LOI on flame retardant cotton.

Test	Statistics	p-value
Shapiro-Wilk	W 0.9834	Pr<W 0.3058
Kolmogorov-Smirnov	D 0.0849	Pr<D >0.1652
Cramer-von Mises	W-Sq 0.0402	Pr< W-Sq >0.1333
Anderson-Darling	A-Sq 0.8245	Pr< A-Sq >0.1338

Shapiro-walk W test for the normality of the residuals is presented in Table 7.10. One observes that W is 0.9834, and p value is 0.3058. Both W and p values are large, meaning the residuals come from normal distribution. From the diagnostics of the regression model, we got

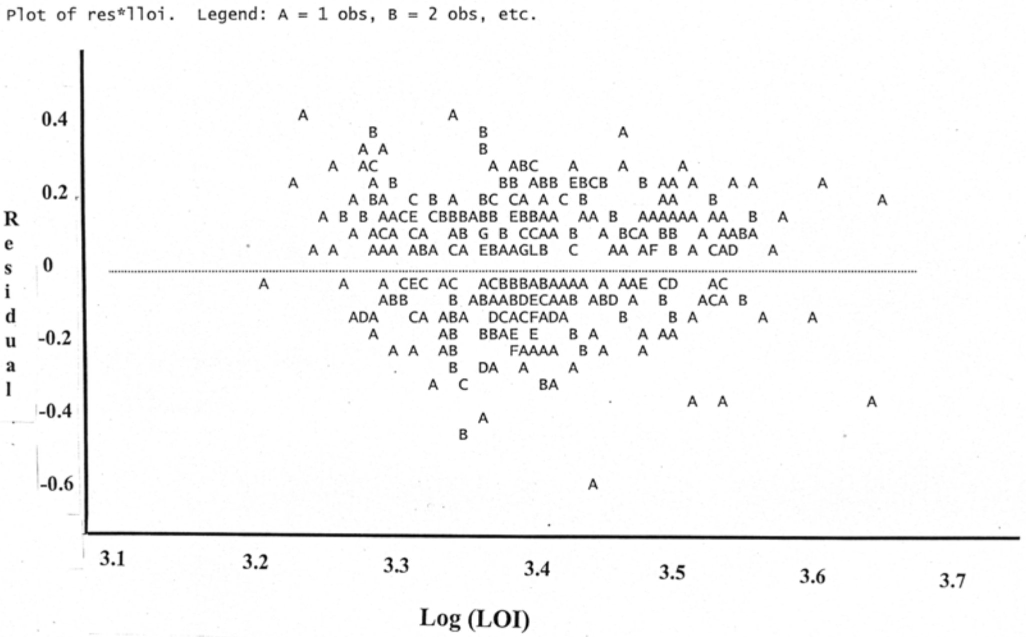

Figure 7.3. Plot of the residual vs. independent variable of log (LOI)

the conclusion that the non-linear regression function between char length and LOI is appropriate and meaningful.

The statistical analysis results of both different bonding systems and fabric weight on the correlation between char length and LOI are in Table 7.11. For different bonding systems, the data show that the p-value is 0.2779, which is higher than the significance level ($\alpha = 0.05$), meaning that the different flame retardant finishing systems: HFPO/BTCA, HFPO/DMDHEU, HFPO/TMM, and HFPO/(DMDHEU-TMM) has insignificant effect on the char length at a fixed LOI level, thus indicating that the different bonding systems for the flame retardant agent has no significant effect on the correlation between char length and LOI. For 100% cotton twill and plain fabric, the p-value is 0.0030, less than significance level, thus we can reject the null

Table 7.11. The statistical analysis of the effects of different flame retardant finishing systems and fabric weight on the correlation between char length and LOI on flame retardant cotton.

Contrast	DF	Contrast SS	Mean square	F value	Pr >F
Flame Retardant Systems	1	432.2631	432.2631	1.20	0.2739
Fabric Weight	1	3205.2502	3205.2502	8.89	0.0030

hypothesis, and conclude that the fabric factor has a significant influence on the char length at a fixed LOI level, and also fabric factor has a significant influence on this non-linear correlation between char length and LOI.

CONCLUSION

When the combination of a hydroxy-functional organophosphorus oligomer (HFPO) and a bonding agent are used as a durable flame retardant finishing system for cotton, a non-linear least square estimated regression function exists between the char length and limiting oxygen index. Analysis of regression shows that this is an appropriate and meaningful regression model. The use of different bonding systems for the flame retardant agent has no significant effect on the correlation between char length and LOI. The use of fabrics with different weight has a significant influence on this non-linear correlation model between char length and LOI.

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CHAPTER 8

CONCLUSIONS

New feasible durable flame retardant finishing systems based on a hydroxyl-functional organophosphorus oligomer and a bonding agent has been developed. DMDHEU and TMM both function as the bonding agent for the hydroxy-functional organophosphorus flame retardant agent. DMDHEU is more effective for crosslinking cotton than TMM, thus causing higher fabric wrinkle resistance and higher fabric strength loss. DMDHEU is also more reactive for bonding HFPO to cotton than TMM, and the HFPO bound to cotton by DMDHEU is more durable to home laundering than that by TMM. The cotton fabric treated with HFPO/TMM has significantly higher initial flame resistance than that treated with HFPO/DMDHEU. When the concentrations of the flame retarding organophosphorus compound and the crosslinker reach certain levels, the cotton fabric treated with HFPO/TMM maintain a higher level of flame retarding properties than that treated with HFPO/DMDHEU even after 12 home laundering cycles in spite of the fact that the phosphorus retention after laundering on the fabric treated with HFPO/DMDHEU is significantly higher than that treated with HFPO/TMM.

The statistical analysis of the performance of the cotton fabric treated with HFPO/(DMDHEU+TMM) using a two-factorial experimental design method reveals the following:

The DMDHEU/(DMDHEU+TMM) ratio in a HFPO/(DMDHEU+TMM) formula has a profound effect on the bonding of HFPO to cotton, the laundering durability of the HFPO bound to cotton and the strength retention of the treated fabric. An increase in the DMDHEU content in the mixture of the two binders increases the amount of HFPO bound to cotton, increases the laundering durability of HFPO on cotton, and reduces the fabric tensile strength retention.

An increase in HFPO concentration in a formula decreases the amount of HFPO bound to cotton, whereas it reduces the percent retention of HFPO after laundering and the laundering durability of the treated fabric. An increase in HFPO concentration also decreases fabric strength loss.

Since the flame retarding performance and the strength of the cotton fabric treated with the HFPO/(DMDHEU+TMM) system are determined by the HFPO concentration, the total concentrations of the total binders as well as the ratio of the two binders, the desirable performance of the treated cotton fabric can be achieved by adjusting the concentrations of the three components in a formula.

MDPA by itself can be bound to the cotton cellulose via its N-methylol group. The presence of TMM can improve the amount of MDPA bound to cotton (approximately a 25% increase in phosphorus at 8% TMM level). The percent retention of MDPA bound to cotton cellulose is independent of the MDPA concentration in the system. The bonding agent, such as TMM or DMDHEU, is necessary for the HFPO finishing system. The type and concentration of binder significantly affect the amount of HFPO bound to cotton. The amount of the flame retardant agent bound to cotton is significantly higher for the HFPO system than that for the MDPA system when the equal moles of the phosphorus and N-methylol group are used. The better laundry durability of MDPA/TMM treated fabric is attributed to the higher content of N-methylol in the MDPA system. The H_3PO_4 is the optimum catalyst for MDPA system, and the NH_4Cl-based catalyst is the best catalyst for the HFPO system.

The MDPA/TMM treated fabric has a higher initial LOI than that of HFPO/TMM treated fabric due to the nitrogen content in the MDPA molecule, which enhances the flame resistance performance by means of phosphorus-nitrogen synergism. The flame resistance of cotton is identical for both the HFPO system and MDPA system when there is an equal amount of the phosphorus and nitrogen on the fabric. The fabric treated with MDPA/ TMM and HFPO/TMM had similar LOI values after 1, 10, and 25 laundering cycles. The better flame resistance of the MDPA/TMM treated cotton is attributed to the higher phosphorus content of MDPA/TMM treated fabric after 50 laundering cycles.

Both the HFPO/TMM and MDPA/TMM treated fabric remained at a low level of WRA. The tensile strength loss of the treated fabric did not increase as the TMM concentration was increased. The fabric stiffness significantly increased when a high TMM concentration is used. And MDPA/TMM treated fabric showed lower dimensional retention during the laundering cycles and higher formaldehyde release level.

Both TMM and DMDHEU finishes by themselves can marginally increase the flame resistance of cotton fabric, DMDHEU to a greater degree. TMM and DMDHEU are nitrogen providers to the organophosphorus-based flame retardant finishing system, therefore useful to enhance the flame resistance performance of cotton fabric by means of phosphorus-nitrogen synergism. TMM is found to be a more efficient synergistic agent than DMDHEU. The interaction between phosphorus and nitrogen alters the thermal decomposition path: the phosphorus-nitrogen interaction inhibits the thermal decomposition of cellulose by depolymerization, and contributes to the dehydration process, thus reducing levoglucosan formation and evaporation, increasing the amount of solid char, and substantially improving the flame resistance of treated cotton fabric. The nitrogen and phosphorus content have a different influence on the dehydration temperature. The extent of dehydration, not the dehydration temperature is discovered to have the significant effect on the flame resistance.

When the combination of a hydroxy-functional organophosphorus oligomer (HFPO) and a bonding agent are used as a flame retardant finishing system for cotton, a non-linear least square estimated regression function exists between the char length and limiting oxygen index. Analysis of regression shows that this is an appropriate and meaningful regression model. The use of different bonding systems for the flame retardant agent has no significant effect on the correlation between char length and LOI. The use of fabrics with different weight has a significant influence on this non-linear correlation between char length and LOI.

APPENDIX A

CORRELATION BETWEEN LIMITING OXYGEN INDEX AND PHOSPHORUS/NITROGEN CONTENT OF COTTON FABRICS TREATED WITH A HYDROXY-FUNCTIONAL ORGANOPHOSPHORUS FLAME RETARDING AGENT AND DMDHEU[1]

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[1] Wu, W and Yang, CQ. 2003. Journal of Applied Polymer Science. 90:1885-1890. Reprinted here by permission.

ABSTRACT

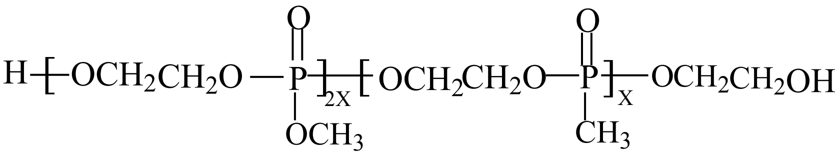
The combination of a hydroxy-functional organophosphorus flame retardant agent (HFPO) and dimethyloldihydroxyethyleneurea (DMDHEU) was used as a durable flame retardant finishing system for cotton fabrics. DMDHEU functions as a bonding agent between HFPO and cotton cellulose, thus making this flame retardant finishing system durable to home laundering. DMDHEU also provides nitrogen to this system, and therefore enhances its performance. Limiting oxygen index (LOI) is one of the most commonly used parameters to indicate the flammability of textiles and other polymeric materials. In this research, we investigated the correlation between LOI and phosphorus/nitrogen contents on the cotton fabric treated with that durable flame retardant finishing system. Phosphorus concentration on the fabric was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES), whereas the nitrogen content was determined indirectly by measuring the carbonyl band intensity in the infrared spectra of the treated fabric. We developed a statistical model to predict LOI of the cotton fabric treated with HFPO and DMDHEU based on the phosphorus concentration and the intensity of carbonyl band of DMDHEU on cotton.

INDEX WORDS: Cotton, DMDHEU, Flame retardant finishing, Organophosphorus chemicals, Limiting oxygen index, and Infrared spectroscopy.

INTRODUCTION

Durable flame retardant finishes for cotton commonly used by the industry include the tetrakis (hydroxymethyl) phosphonium chloride-based system and reactive organophosphorus chemicals [1-3]. However, several limitations are associated with those flame retardant finishing systems [4], thus making it urgent to develop effective durable flame retardant systems for cotton.

N-methylol reagents, such as dimethyloldihydroxyethyleneurea (DMDHEU), have long been used in the textile industry as crosslinking agents for cotton to produce wrinkle-resistant cotton fabric [5]. Hydroxy-functional organophosphorus compounds (HFPO), such as the one shown in Scheme A.1 [6], can be used as durable flame retardant finishing agent for cotton when DMDHEU is present as a crosslinking agent.



$$H\left[OCH_2CH_2O-\underset{OCH_3}{\overset{O}{\overset{\|}{P}}}\right]_{2x}\left[OCH_2CH_2O-\underset{CH_3}{\overset{O}{\overset{\|}{P}}}\right]_{x}OCH_2CH_2OH$$

Scheme A.1

The use of the oxygen index method for evaluating the flammability of plastics and textiles started in 1966 [7]. Since then oxygen index, often called limiting oxygen index (LOI), has been used extensively in academic community as well as in industries, and it continues to be widely used today in evaluation of flame retardant materials [8]. LOI is defined as the minimum percentage of oxygen which allows a sample to sustain combustion under specified conditions in a candle-like fashion [2]. A number of researchers have showed the correlation between LOI and results of other testing methods [9-15].

The LOI test is easy to run and usually reproducible, but it is also time consuming. Determining phosphorus content and carbonyl band intensity using ICP/AES and FT-IR spectroscopy is fast, efficient and requires much smaller sample size. In this research, we investigated the correlation between LOI and the phosphorus/nitrogen contents on the cotton fabric treated with the durable flame retarding system, and developed a statistical model to predict LOI based phosphorus/nitrogen content of the treated cotton fabric.

EXPERIMENTAL

Materials

The fabric used was a desized, scoured, and bleached 40×40 cotton printcloth weighing 108 g/m^2 (Testfabric Style 400). The hydroxy-functional organophosphorus oligomer (with commercial name Fyroltex HP) was supplied by Akzo Nobel Chemical Corporation, New York. DMDHEU ("Freerez 900") and the catalyst ($MgCl_2$ based catalyst with commercial name "Catalyst 531") were supplied by Noveon, Ohio, and OMNOVA Solution, South Carolina, respectively.

Fabric Treatment and Home Laundering Procedures

The cotton fabric was first immersed in a finish solution containing HFPO, DMDHEU, and the catalyst, then passed through a laboratory padder with two dips and two nips, dried at 90 °C for 3 min, and then cured in a Mathis curing oven at a specified temperature. All the concentrations presented here are based on weight of bath (w/w, %). The wet pick-up of the cotton fabric was approximately 115±2%. After curing, the treated cotton fabric was subjected to one home laundering washing/drying cycle without the use of a detergent (specified here as "water wash") to remove the chemicals not bound to the fabric. The home laundering process was done using a standard detergent ("AATCC Detergent 1993") according to AATCC Test Method 124-1996. The water temperature was approximately 46 °C.

LOI Measurement

LOI of the treated cotton fabric was measured according to ASTM Standard Method D2863-00.

Determination of Phosphorus Concentration on the Treated Cotton Fabric

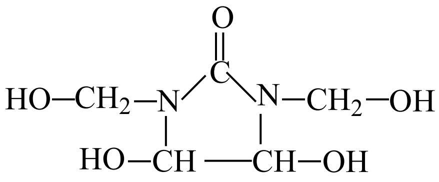
Approximately 2g of the treated cotton fabric taken from different parts of a larger fabric specimen were ground in a Wiley mill into a powder to improve sample uniformity. 2 ml of concentrated H_2SO_4 was added to 0.1 g of cotton powder. 10 ml of 30% H_2O_2 was added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250°C to digest the powder and to evaporate the water until dense SO_3 vapor is produced. The completely digested cotton sample as a clear solution was transferred to a 50-ml volumetric flask, and then diluted with distilled/deionized water. The sample thus prepared was analyzed using a Thermo-Farrell-Ash Model 965 ICP/AES instrument to determine the % concentration of phosphorus.

Infrared Spectroscopy Measurement

All the infrared spectroscopy data presented here are diffuse reflectance spectra and are presented in absorbance mode ($-\log R/R_0$). Resolution for all the infrared spectra is 4 cm^{-1}, and there were 120 scans for each spectrum. Potassium bromide powder was used as a reference material to produce a background diffuse reflectance spectrum. To measure the carbonyl band intensity, the treated and cured cotton fabric was first washed in water to remove the HFPO and DMDHEU not bound to cotton and the catalyst, then dried at 80°C for 5 min. To improve sample uniformity, a fabric sample was ground in a Wiley mill to form a powder before infrared spectroscopy analysis. The carbonyl band intensity in the infrared spectra was normalized against the 1318 cm^{-1} band associated with a C-H bending mode of cellulose.

RESULTS AND DISCUSSION

The cotton fabric was treated with 24% HFPO in combination of DMDHEU with concentration ranging from 1 to 12%, and then cured at 165°C for 2.5min. The infrared spectra of the cotton fabric thus treated are presented in Figure A.1, in which the band at 1723 cm^{-1} is due to the carbonyl stretching mode of DMDHEU (Scheme A.2). The intensity of carbonyl band increases as the DMEHEU concentration of the solution increases. The carbonyl band intensity is plotted against the DMDHEU concentration in the solution (Figure A.2). One observes a linear relationship between the carbonyl band intensity of the treated fabric and the DMDHEU concentration in the solution (Figure A.2). Since the carbonyl band intensity is proportional to the quantity of DMDHEU, the carbonyl band intensity can be used as an indirect measure of the nitrogen content on the fabric due to DMDHEU bound to the fabric.



Scheme A.2

DMDHEU has four hemi-acetal groups to react with the hydroxyl groups of cellulose as well as ones of HFPO. Among the four groups, the two hemi-acetal groups derived from formaldehyde are significantly more reactive than those derived from glyoxyl. DMDHEU

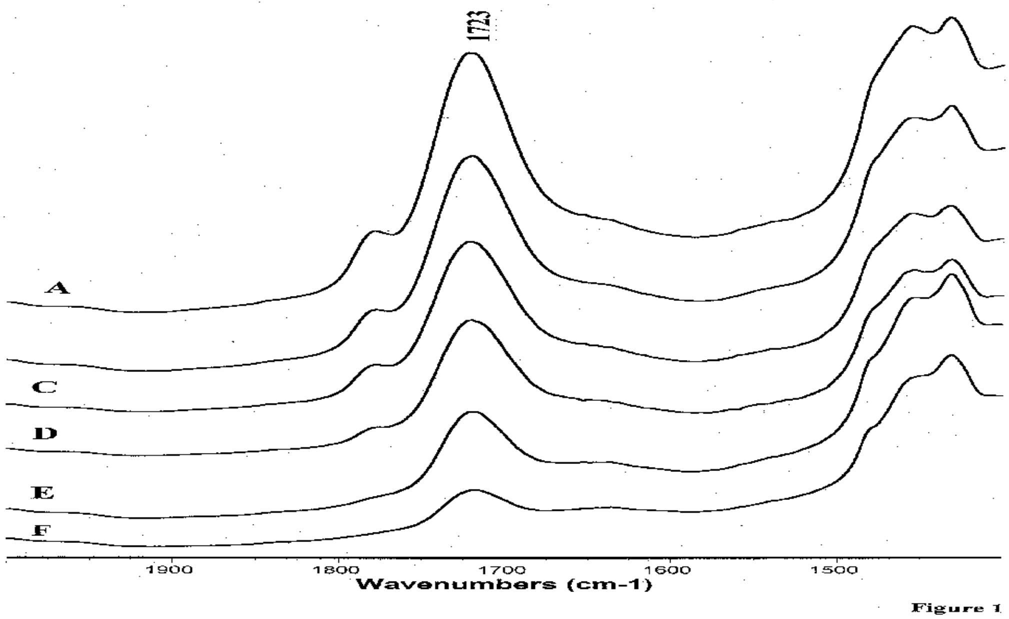


Figure A.1. Diffuse reflectance infrared spectra of the cotton fabric treated with 24% HFPO and DMDHEU of different concentrations (A-F): 12, 10, 8, 4, 2, and 1%.

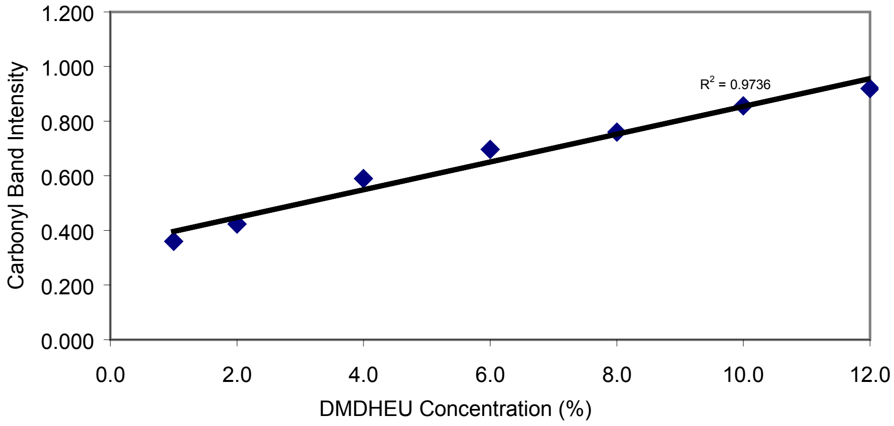
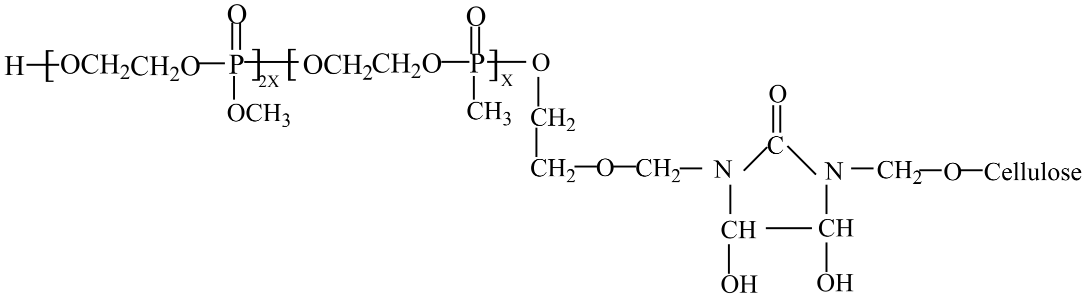


Figure A.2. The carbonyl band intensity of the fabric treated with 24% HFPO and different concentrations of DMDHEU, and cured at 165°C for 2.5 min as a functional of DMDHEU concentration.

functions as a binder between HFPO and cotton fabric (Scheme A.3), thus making this flame retardant finishing system a durable one. DMDHEU also provides nitrogen to this system, therefore enhances performance of this flame retardant system by means of phosphorus/nitrogen synergism.



Scheme A.3

The cotton fabric was treated with 24% HFPO and DMDHEU of different concentrations, cured at 165°C for 2.5 min. The LOI, carbonyl band intensity and phosphorus concentration of treated fabrics are shown in Table A.1. LOI and carbonyl band intensity increase as the concentration of DMDHEU increases. As the concentration of DMDHEU increases from 1% to 12%, one observes that the phosphorus content of the treated fabric remain practically unchanged, whereas the LOI value (before wash) increases from 29.5 to 31.6 (Table A.1). The data indicate that DMDHEU provides phosphorus/nitrogen synergism to the flame retardant finishing system, thus improving the flame resistance of the treated fabric.

The treated cotton fabric was also subjected to different number of HLTD cycles. At each DMDHEU concentration level, the higher the number of home laundering cycle is, the lower the phosphorus content and LOI value for the treated fabric become. LOI values of the cotton fabric treated with 24% HFPO and DMDHEU of different concentrations is plotted against the phosphorus content on the treated fabric (Figure A.3), in which a linear correlation exists

Table A.1. LOI, carbonyl band intensity and phosphorus content of the cotton fabric treated with 24% HFPO and DMDHEU of different concentrations, and cured at 165°C for 2.5 min.

DMDHEU (%, owb)	LOI (%)				Carbonyl Band intensity				Phosphorus (%)			
	Before wash	1 wash	5 washes	10 washes	Before wash	1 wash	5 washes	10 washes	Before wash	1 wash	5 washes	10 washes
1	29.2	25.4	23.3	21.2	0.306	0.270	0.249	0.233	3.42	1.58	1.01	0.65
2	29.5	27.6	26.3	23.5	0.428	0.423	0.393	0.345	3.72	2.22	1.82	1.03
4	31.0	29.1	28.8	28.0	0.631	0.628	0.626	0.546	3.92	2.84	2.55	2.35
6	31.3	29.0	28.9	28.2	0.699	0.697	0.690	0.680	3.97	3.22	2.89	2.59
8	30.6	29.2	28.9	28.3	0.871	0.843	0.839	0.821	4.02	3.25	2.92	2.65
10	31.6	29.8	29.6	29.4	0.872	0.856	0.866	0.841	4.08	3.28	3.02	2.90
12	31.6	29.8	29.6	29.5	0.934	0.920	0.917	0.908	4.10	3.34	3.02	3.00

between LOI and the phosphorus content of the treated fabric.

The cotton fabric was treated with 24% HFPO and 8% DMDHEU, and cured at different temperatures for 2.5 min. The treated and cured fabric was also subjected to different numbers of HLTD cycles. The LOI, carbonyl band intensity, and phosphorus content of the cotton fabric cured at different temperatures are presented in Table A.2. LOI is plotted against the phosphorus content of the treated fabric (Figure A.4). Once again, the data show a good linear relationship between LOI value and the phosphorus content of the fabric.

The cotton fabric was treated with HFPO/DMDHEU of different concentrations with a constant HFPO-to-DMDHEU ratio of 3:1 and cured at 165°C for 2.5min. The treated cotton fabric was then subjected to different number of HLTD cycles. The LOI, carbonyl band intensity, and phosphorus content of the fabric are presented in Table A.3. LOI, carbonyl band intensity and phosphorus content of the treated fabric increase as the concentration of HFPO/DMDHEU increases, and decrease as the number of laundering increases. At each

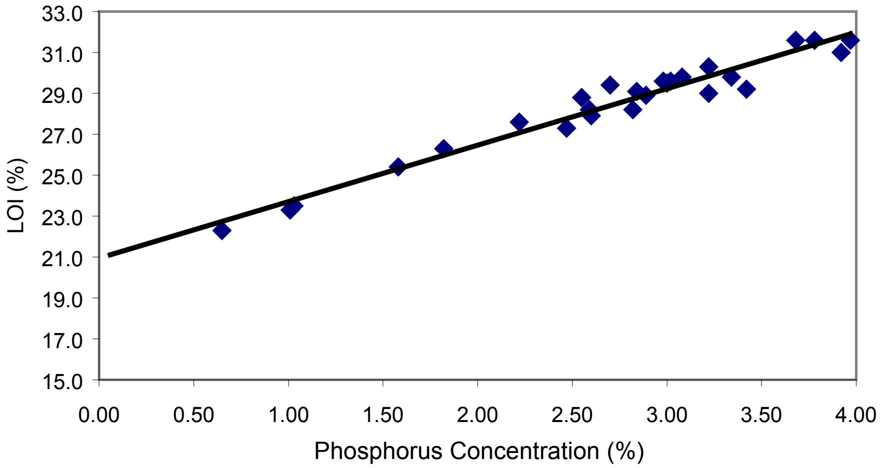


Figure A.3. LOI of the fabric treated with 24% HFPO and DMDHEU of different concentration, cured at 165°C for 2.5 min, and after different HLWD cycles, as a functional of phosphorus concentration on the fabric.

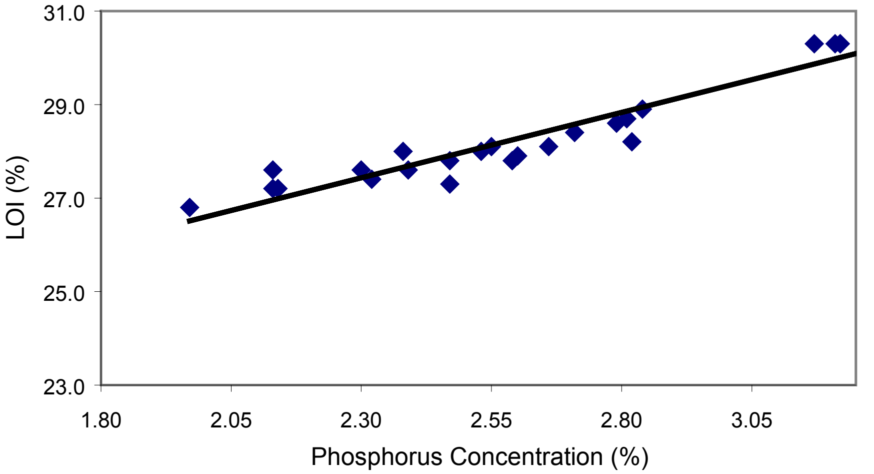


Figure A.4. LOI of the fabric treated with 24%HFPO/8%DMDHEU, cured at different temperatures for 2.5 min, and subjected to different number of home laundering cycles as a functional of phosphorus concentration on the fabric.

Table A.2. LOI, carbonyl band intensity and phosphorus concentration of the cotton fabric treated with 24% HFPO and 8% DMDHEU, and cured at different temperature for 2.5 min.

Temp. (^{o}C)	LOI (%)				Carbonyl Band intensity				Phosphorus (%)			
	Before wash	1 wash	5 washes	10 washes	Before wash	1 wash	5 washes	10 washes	Before wash	1 wash	5 washes	10 washes
130	30.3	28.4	28.0	27.6	0.830	0.737	0.790	0.732	3.29	2.71	2.38	2.13
140	30.3	28.6	28.0	27.6	0.803	0.791	0.802	0.801	3.22	2.79	2.53	2.30
150	30.3	28.7	28.1	27.6	0.827	0.784	0.813	0.800	3.28	2.81	2.66	2.39
160	30.3	28.9	28.1	27.4	0.870	0.810	0.824	0.805	3.34	2.84	2.55	2.32
165	30.3	28.2	27.9	27.3	0.871	0.843	0.839	0.821	3.22	2.82	2.60	2.47
170	30.3	27.3	27.8	27.2	0.837	0.800	0.848	0.794	3.21	2.74	2.59	2.14
180	30.3	27.8	27.2	26.8	0.913	0.862	0.845	0.825	3.17	2.47	2.13	1.97

Table A.3. LOI, carbonyl band intensity and phosphorus concentration of the cotton fabric treated with HFPO/DMDHEU (3:1) of different concentrations, cured at 165^{o}C for 2.5 min.

HFPO Conc. (%)	LOI (%)				Carbonyl Band intensity				Phosphorus (%)			
	Before wash	Before wash	1 wash	5 washes	Before wash	1 wash	5 washes	10 washes	Before wash	1 wash	5 washes	10 washes
4	22.2	20.3	19.7	19.4	0.389	0.372	0.443	0.399	0.82	0.50	0.39	0.33
8	24.5	22.5	22.0	21.9	0.562	0.504	0.542	0.504	1.44	1.04	0.88	0.76
12	26.8	24.9	24.7	24.2	0.655	0.638	0.616	0.596	2.09	1.57	1.39	1.27
16	28.5	26.9	26.7	26.5	0.742	0.709	0.684	0.676	2.62	2.13	1.85	1.92
18	29.6	27.7	27.7	27.6	0.781	0.730	0.713	0.691	2.83	2.33	2.16	2.08
20	30.0	28.8	28.5	27.9	0.787	0.748	0.753	0.729	3.01	2.44	2.33	2.13
24	30.3	28.2	27.9	27.3	0.871	0.843	0.839	0.821	3.22	2.82	2.60	2.47

HFPO/DMDHEU concentration level, a larger number of laundering cycle's results in lower phosphorus content and lower LOI value of fabrics. As the concentration of HFPO increased from 4% to 24%, the LOI after 10 HLTD increased from 19.4 to 27.3. LOI is plotted against the phosphorus content of the treated fabric (Figure A.5).

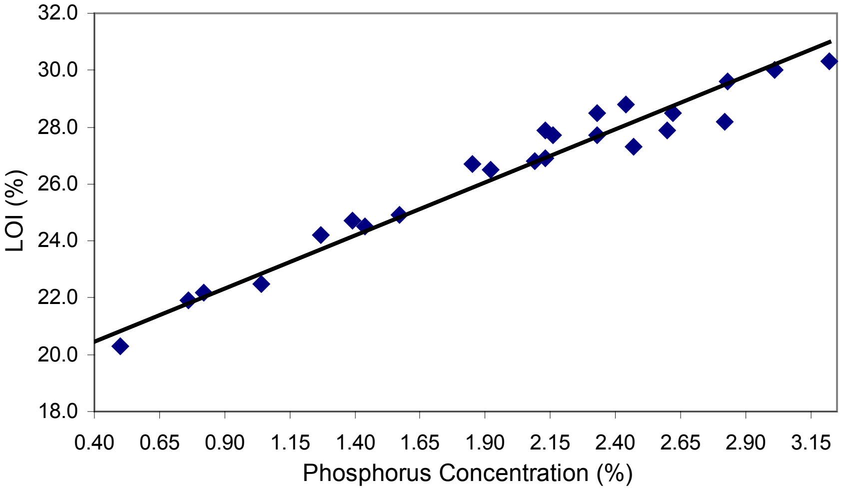


Figure A.5. LOI of the fabric treated with different HFPO/DMDHEU (3:1) concentrations, cured at 165^{o}C for 2.5 min, and subjected to different number of home laundering cycles as a functional of phosphorus concentration on the fabric.

Table A.4. Parameter estimates for cotton fabric treated with HFPO/DMDHEU.

Variable	DF	Parameter Estimate	Standard Error	t value	Pr > ׀ t ׀
Intercept	1	18.54531	0.24796	74.78	< 0.0001
X_1	1	2.87061	0.12124	23.68	< 0.0001
X_2	1	2.82948	0.50820	5.57	< 0.0001

All LOI values, phosphorus content, and carbonyl band intensities of the treated fabric were used as the basis to develop a statistical model. We used the SAS program to develop a least square estimated regression function between LOI value and the phosphorus content/carbonyl band intensity, shown in Equation 1 and Table A.4, where Y refers to the LOI value, X_1% refers to the phosphorus content, and X_2% refers to the carbonyl band intensity of the fabric.

$$Y(\%)=18.54+2.87X_1\% +2.83\ X_2\% \qquad (1)$$

Equation 1 gives an R^2 of 0.9567 (Table A.5), thus indicating that more than 95% of the total variability of LOI is associated with the variability of the independent variables (phosphorus content and carbonyl band intensity) within the framework of the equation. To achieve an appropriate linear regression model $Y=\beta_0+\beta_1X_1+\cdots\beta_nX_n+\varepsilon_i$, it is necessary to make the following assumptions on the residuals ε_i: (1) ε_1, ε_2, $\cdots\varepsilon_n$ are independent; (2) ε_1, ε_2, $\cdots\varepsilon_n$ have an identical distribution; and (3) ε_1, ε_2, $\cdots\varepsilon_n$ have a normal distribution, with mean 0 and variance σ^2 [16].

Table A.5. Analysis of variance for cotton fabrics treated with HFPO/DMDHEU.

Source	DF	Sum of Square	Mean Square	F value	Pr > F
Model	2	818.64285	409.32142	873.51	< 0.0001
Error	79	37.01911	0.46860		
Corrected Total	81	855.66195			
R-Square=0.9567; adjusted R-Square=0.9556					

The diagnostic plots of residuals, such as the one presented in Figure A.6, show that all the residuals fall within a horizontal band centered around 0, displaying no systematic tendencies, meaning that all the residuals are random, and the linear regression is appropriate.

From the Shapiro-Wilk W normality test [18], W is 0.977543, and p value is 0.2324 (Table A.6). Both W and p values are large, meaning the residuals come from normal distribution. Test of the overall hypothesis shows that F value is 873.51, and P value is <0·0001, meaning that we can accept the alternative hypothesis Ha, and demonstrates that at least one ofβ's not equal to zero (Table A.5). The statistical analysis shows that LOI value does depend on

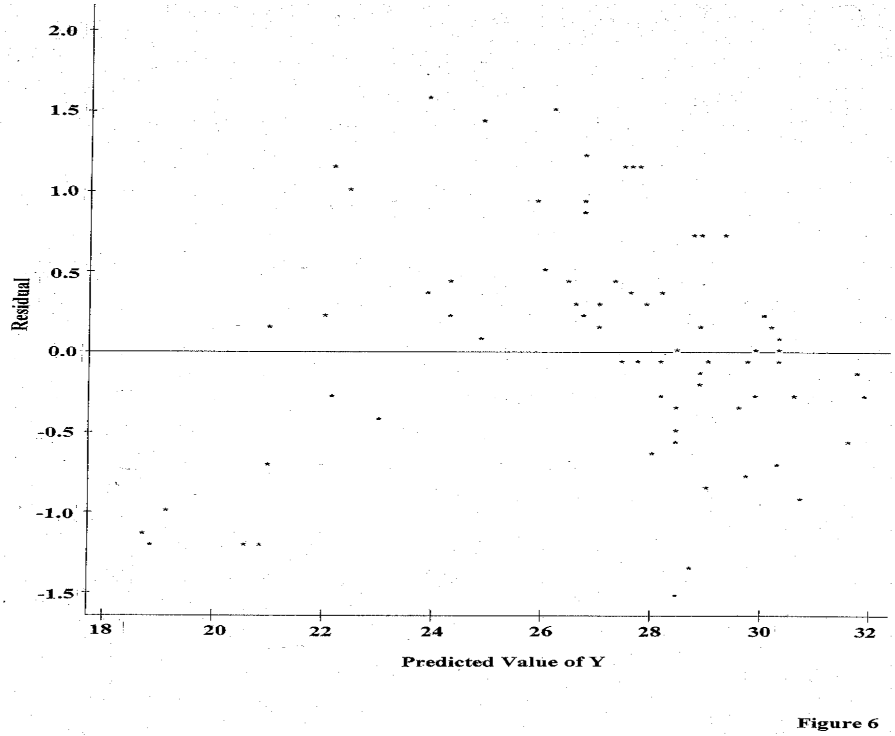


Figure A.6 Plot of the residual versus predicted value of Y (LOI).

Table A.6. Normality tests for cotton fabrics treated with FR/DMDHEU.

Test	Statistic	p- value
Shapiro-Wilk	W 0.980081	Pr < W 0.2324
Kolmogorov-Smirnov	D 0.07045	Pr < D >0.1500
Cramer-von Mises	W-Sq 0.068122	Pr < W-Sq >0.2500
Anderson-Darling	A-Sq 0.463778	Pr < A-Sq > 0.2500

all predictor variables: phosphorus content and carbonyl band intensity. The phosphorus content and carbonyl band intensity are the two significant factors for determining the flammability of the fabric. From the diagnostics of the regression model, we conclude that the linear least square estimated regression function between LOI and phosphorus content and carbonyl band intensity is appropriate, meaningful and useful.

CONCLUSION

When the combination of a hydroxyl-functional organophosphorus flame retardant agent and DMDHEU are used as a durable flame retardant finishing system for cotton, a linear least square estimated regression function exists between the limiting oxygen index and phosphorus content / carbonyl band intensity. The carbonyl band intensity is used as an indirect measure of the nitrogen content on fabrics due to DMDHEU bound to cotton. Analysis of regression shows that this is an appropriate and meaningful regression model. The model can be used to predict LOI of treated fabrics based on the phosphorus concentration and nitrogen concentration indirectly measured using the intensity of carbonyl band of DMDHEU in the infrared spectra of the treated fabrics.

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APPENDIX B

CORRELATION BETWEEN LIMITING OXYGEN INDEX AND PHOSPHORUS CONTENT OF THE COTTON FABRIC TREATED WITH A HYDROXY-FUNCTIONAL ORGANOPHOSPHORUS FLAME RETARDING FINISH AND MELAMINE-FORMALDEHYDE[1]

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[1] Wu, W, Zhen, X. and Yang, CQ. 2003. Journal of Fire Sciences. 90:1885-1890. Reprinted here by permission.

ABSTRACT

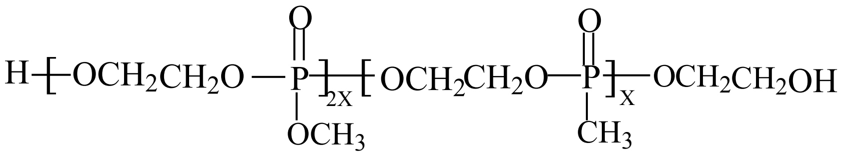
The combination of a hydroxy-functional organophosphorus flame retardant agent (HFPO) and trimethylolmelamine (TMM) was used as a durable flame retardant finishing system for cotton fabrics. TMM functions as a binder between HFPO and cotton cellulose, thus making this flame retardant finishing system durable to home laundering. TMM also provides nitrogen to this system, therefore enhances its flame resistance by means of phosphorus-nitrogen (P-N) synergism. Limiting oxygen index (LOI) is one of the most commonly used parameters to indicate the flammability of textiles as well as other materials. In this research, we investigated the correlation between LOI and the phosphorus content on the cotton fabric treated with the durable flame retarding system described above. Phosphorus concentration on the fabric was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). We developed a statistical model to predict the LOI of the treated cotton fabric based on the phosphorus concentration and the concentrations of the TMM in the finish solutions.

INDEX WORDS: Cotton, Flame retardant finishing, Limiting oxygen index, Organophosphorus chemicals, Trimethylolmelamine, Statistical regression.

INTRODUCTION

Cotton is a combustible textile fiber. Cotton burns or smolders in the presence of oxygen and heat (360-420°C) [1]. Resistance to burning is one of the most desirable properties for cotton, which can be imparted to cotton fabrics by chemical finishing techniques.

The most commonly used durable flame retardant finishes for cotton today are phosphorus-based compounds [2]. Recently, we developed a durable flame retardant finishing system for cotton based on the combination of HFPO as shown in scheme B.1, and TMM. Even though HFPO has been used as a flame retardant agent for polymeric materials and TMM is widely used together with N-methylol dimethylphosphonopropionamide [2], the use of the combination of HFPO and TMM resin as a bonding agent for HFPO has not been reported in details in the literature.



$$H\!-\!\left[OCH_2CH_2O-\overset{\overset{O}{\|}}{\underset{\underset{OCH_3}{|}}{P}}\right]_{2x}\!\left[OCH_2CH_2O-\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{P}}\right]_{x}\!-OCH_2CH_2OH$$

Scheme B.1

TMM also provides nitrogen to this flame retarding system, thus enhancing its performance by means of P-N synergism. Synergism has two different definitions. Strictly speaking, synergism refers to the use of two (or more) flame-retarding chemicals whose effect is greater than that based on the prediction of the combined effects of all the individual components [3]. The enhancing effects of a non-flame retarding additive to a flame retardant agent are also called synergism [3]. Some of P-N synergism can be explained by the fact that suitable nitrogen compounds increase the yield of the initial phosphorylation of cellulose [3]. Furthermore, the reactions of phosphorus-nitrogen bonds can increase flame retardancy by forming a cross-linked network within the cellulose that inhibits the release of volatile combustible fragments and promotes char formation [4]. In addition, phosphorus-nitrogen cross-linking fixes the phosphorus in the matrix and prevents the loss of phosphorus by volatilization during combustion [3].

LOI is defined as the minimum percentage of oxygen, which allows a sample to sustain combustion under specified conditions in a candle-like fashion [3]. Since its introduction in 1966, LOI has been used extensively for evaluating the flammability of materials [5-6]. The correlations between LOI and other flammability tests, such as tunnel test and cone calorimeter, have been reported in the literatures [7-13].

For the HFPO/TMM system, the amount of the organophosphorus compound bound to cotton is obviously the predominant factor in determining the flammability of the treated cotton fabric. The amount of the organophosphorus compound bound to cotton can be determined by quantitative analysis of the phosphorus content on the treated cotton fabric using ICP-AES. Since TMM provides P-N synergism, the flammability of the treated cotton fabric also depends on the amount of TMM bound to cotton, which in turn is affected by the TMM concentrations in a finish solution. In this research, we investigated the correlation between (a) LOI and (b) phosphorus contents on the treated cotton fabric and the TMM concentrations in finish solutions, and developed a statistical model to predict LOI based on phosphorus content of the treated cotton fabric and the TMM concentrations in finish solutions.

EXPERIMENTAL

Materials

The fabric was a desized, scoured, and bleached 40×40 cotton print cloth weighing 108 g/m^2 (Testfabrics Style 400). The hydroxy-functional organophosphorus oligomer with the trade name of Fyroltex HP and phosphorus acid (H_3PO_3) were supplied by Akzo Nobel Functional Chemicals, Dobbs Ferry, New York. TMM resin with the trade name of Ecco Rez M 300 was supplied by Eastern Color & Chemical Company, Rhode Island.

Fabric Treatment and Home Laundering Procedures

H_3PO_3 or NaOH was added the finish solution containing HFPO and TMM to adjust the pH to a specified value. The pH of solution containing 16% HFPO and 6% TMM is 4.9. The solution with pH of 2.0, 3.0, and 4.0 was adjusted by adding H_3PO_3, and the solution with pH of 5.0, 6.0, and 7.0 was adjusted by NaOH. The fabric was first immersed in the finish solution, and then passed through a laboratory padder with two dips and two nips, dried at 90°C for 3 min, and finally cured in a Mathis curing oven at a specified temperature. All the concentrations presented here are based on weight of bath (w/w, %). The wet pick-up of the cotton fabric was approximately 110±2%. After curing, the treated cotton fabric was subjected to one washing/drying cycle without use of a detergent (specified here as “water wash”) to remove the chemicals not bound to the fabric. The home laundering cycle process was done according to AATCC Test Method 124-1996 with AATCC “Detergent 1993”. The water temperature was approximately 46°C.

LOI Measurement

LOI of the cotton fabric was measured according to ASTM Standard Method D2863-00.

Determination of Phosphorus Concentration on the Treated Cotton Fabric

Approximately 2g of treated cotton fabric were ground in a Wiley mill into a powder to improve sample uniformity. 2 ml of concentrated H_2SO_4 was added to 0.1 g of cotton powder. 10 ml of 30% H_2O_2 was added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250°C to digest the powder and to evaporate the water until dense SO_3 vapor is produced. The completely digested cotton sample as a clear solution was transferred to a 50-ml volumetric flask, and then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the % concentration of phosphorus. We determined the phosphorus concentration (%) of the powder from four different parts in a 10"x12" fabric specimen, which was treated with 16%HFPO and 6% TMM and cured at 165°C for 2.5 min. The results were 2.23%, 2.19%, 2.20% and 2.22% with average of 2.20%. The data show that HFPO is uniformly distributed on the treated cotton fabric. To further improve the sample uniformity, we use three small pieces of fabric taken from three different areas in a 10"x12" fabric sample, totally weighing approximately 2g. The fabric was ground into a powder and thoroughly mixed. The cotton powder thus prepared was used to determine the phosphorus content by ICP-AES. Every time when we measured the phosphorus content using ICP-AES, we used a standard solution with a known phosphorus concentration of (12.00%). For a period of four months, we obtained the following results: 12.01%, 11.99%, 12.01%, 12.02%, 12.00%, thus showing that the phosphorus content measurement is highly reproducible.

RESULTS AND DISCUSSION

The cotton fabric was treated with 16% HFPO and TMM of different concentrations, and then cured at 165°C for 2.5 min. The LOI values and the phosphorus contents (P%) of the fabric thus treated are shown in Table B.1. The LOI of the cotton fabric treated with 6% TMM is identical to that of control (LOI 17.8%), thus indicating TMM by itself is not a flame retarding chemical. When the concentration of TMM increases from 6% to 14%, the P% of the treated fabric (before wash) remains practically unchanged, because all the finish solutions contain a constant HFPO concentration of 16% (Table B.1). The LOI value increases from 30.8 to 33.6 as the TMM concentration increases from 6 to 14% (Table B.1). The data presented here clearly indicate that TMM provides P-N synergism to the system by enhancing the flame resistance of HFPO, therefore the effect of TMM fits the second definition P-N synergism discussed previously [3].

Table B.1. LOI and phosphorus content of the cotton fabric treated with 16% HFPO and TMM at different concentrations, and cured at 165°C for 2.5 min

HFPO (%) (owb)	TMM (%) (owb)	Before wash		Water wash		1 HLTD		5 HLTD	
		LOI (%)	P (%)	LOI (%)	P (%)	LOI (%)	P (%)	LOI (%)	P (%)
0	6	17.8	0.00	-	-	-	-	-	-
16	0	26.2	2.03	-	-	-	-	-	-
16	6	30.8	2.07	29.8	1.49	28.8	1.33	27.3	1.12
16	8	31.3	1.96	31.0	1.51	30.5	1.47	29.7	1.36
16	12	33.3	2.02	32.0	1.73	32.0	1.70	30.4	1.46
16	14	33.6	2.10	33.4	1.83	32.5	1.78	31.4	1.58
Control		17.8	0.00	-	-	-	-	-	-

The treated cotton fabric was also subjected to different numbers of home laundering cycles. The data presented in Table B.1 indicate that TMM concentration in a finish solution also has a significant impact on the LOI value of treated fabric after laundering. This is because that TMM bonds HFPO to cotton, and consequently it affects the amount of HFPO bound to the fabric after laundering. Only 64% of original phosphorus is bound to cotton after one home

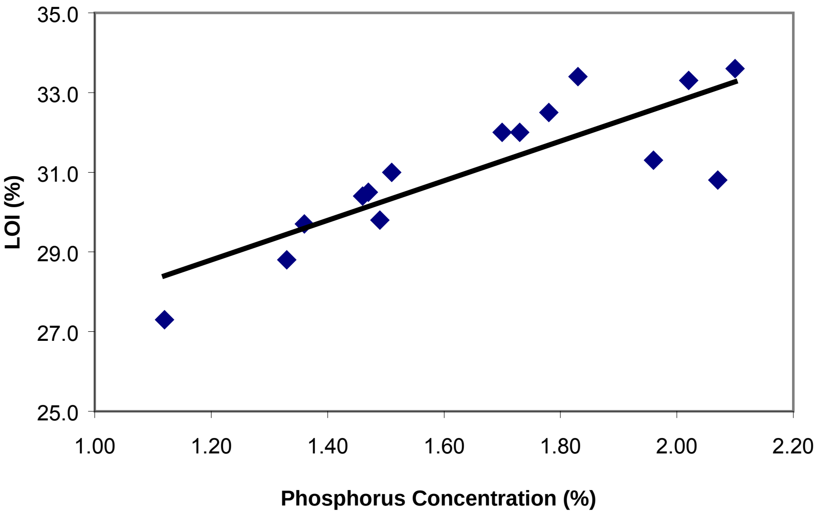


Figure B.1. LOI of the cotton fabric treated with 16% HFPO and TMM of different concentrations, cured at 165°C for 2.5 min, and after different numbers home laundering cycles as a function of phosphorus concentration on the fabric.

Table B.2. LOI and phosphorus content of the cotton fabric treated with 16%HFPO and 6% TMM at different pH values, and cured at 165°C for 2.5 min

HFPO (%, owb)	pH	Before wash		Water wash		1 HLTD		5 HLTD	
		LOI (%)	P (%)	LOI (%)	P (%)	LOI (%)	P (%)	LOI (%)	P (%)
0	2.0	31.1	2.11	28.4	1.41	27.8	1.28	26.1	1.07
16	3.0	30.8	2.10	29.1	1.59	29.0	1.45	28.0	1.26
16	4.0	31.2	2.24	29.8	1.78	29.7	1.69	29.1	1.48
16	5.0	30.7	2.12	29.3	1.72	29.1	1.64	28.9	1.46
16	6.0	30.7	2.13	29.1	1.68	28.9	1.55	28.7	1.40
16	7.0	29.8	2.02	28.6	1.54	28.5	1.42	28.3	1.35

laundering cycle when 6% TMM was used in the finish solution, whereas the phosphorus bound to cotton increases to 84% when the TMM concentration is increased to 14%. At each TMM concentration level, the higher the number of home laundering cycles is, the lower the phosphorus content and LOI value becomes. The LOI values of the cotton fabric treated with 16% HFPO and TMM of different concentrations is plotted against P% on the treated fabric in Figure B.1. A linear relationship exists between LOI and P% for the treated fabric as shown in Figure B.1.

The cotton fabric was treated with 16% HFPO and 6% TMM with different pH, and then cured at 165°C for 2.5 min. The cotton fabric thus treated was also subjected to different

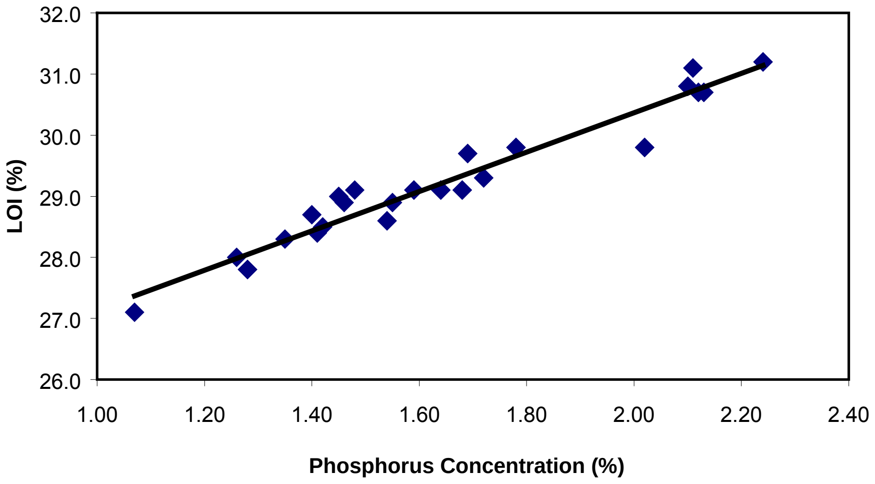


Figure B.2. LOI of the cotton fabric treated with 16% HFPO and 6% TMM with different pH values, cured at 165°C for 2.5 min, and after different numbers home laundering cycles as a function of phosphorus concentration on the fabric.

numbers of home laundering cycles. The LOI and P% of the fabric are presented in Table B.2. The data indicate that the optimum pH is around 4. The fabric treated with HFPO/TMM at pH 4 shows the highest LOI and P% after different numbers of home laundering cycles. LOI is plotted against the phosphorus content of the treated fabric in Figure B.2. Once again, the data show a linear relationship between LOI and P% of the fabric.

Table B.3. LOI and phosphorus content of the cotton fabrics treated with 6% TMM and HFPO at different concentrations, and cured at 165°C for 2.5 min

HFPO (%, owb)	pH	Before wash		Water wash		1 HLTD		5 HLTD	
		LOI (%)	P (%)	LOI (%)	P (%)	LOI (%)	P (%)	LOI (%)	P (%)
12	4.0	29.3	1.75	27.9	1.36	27.6	1.15	26.2	0.95
16	4.0	30.8	2.07	29.8	1.49	28.8	1.33	27.3	1.12
20	4.0	32.0	2.67	30.0	1.64	29.2	1.43	27.9	1.31

The cotton fabric was treated with 6% TMM and HFPO with different concentrations and cured at 165°C for 2.5 min. All the finish solutions maintained a constant pH value of 4. The treated cotton fabric was then subjected to different numbers of home laundering cycles. The LOI and P% of the fabric is presented in Table B.3. Both LOI and P% of the treated fabric increase as the concentration of HFPO increases, and decrease as the number of laundering increases. As the concentration of HFPO increases from 12% to 20%, the LOI value of the treated fabric (before wash) increases from 29.3 to 32.0, and P% increases from 1.75% to 2.67% (Table B.3). This is because the amount of HFPO on cotton increases as the HFPO concentration in the finish solution increases. However, the percent phosphorus bound to cotton after one home laundering cycle decreases from 66% to 54% as the HFPO concentration

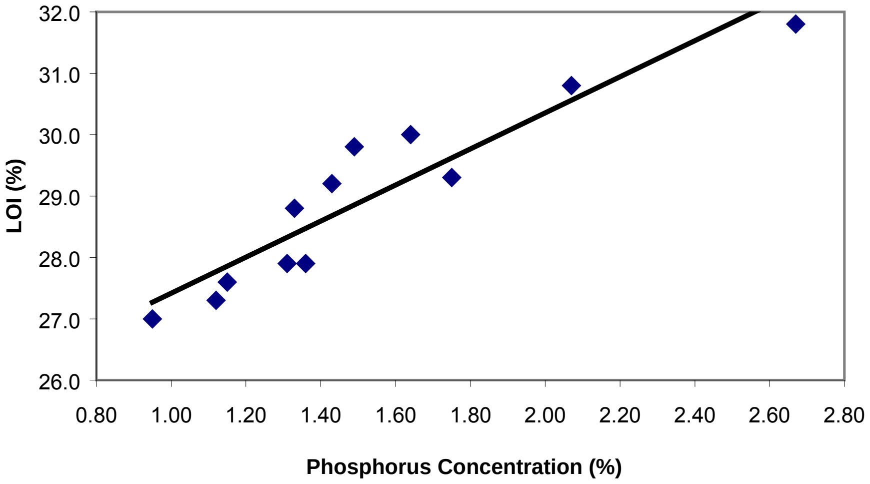


Figure B.3. LOI of the cotton fabric treated with 6% TMM and HFPO of different concentrations, cured at 165^{o}C for 2.5 min, and after different numbers home laundering cycles, as a function of phosphorus concentration on the fabric.

increases from 12 to 20%. Because TMM functions as a binder for HFPO, the increase in HFPO concentration reduced TMM/HFPO ratio, thus reducing the relative amount of HFPO bound to cotton. The data demonstrate the influence of TMM-to-HFPO ratio in a finish solution on the laundering durability of the flame retardant system is significant. At each HFPO concentration level, an increase in laundering cycles reduces P% and LOI of the fabric. The LOI is plotted against P% of the cotton fabric thus treated in Figure B.3.

The P% values of treated fabric and TMM concentrations in finish solutions were used as the basis for the statistical analysis. With the assistance of SAS program, we developed a least square estimated regression function between (a) LOI value and (b) P% on the fabric and TMM concentration in finish solution. From the SAS output, the parameter estimates are shown

Table B.4. Parameter estimates for the cotton fabric treated with HFPO/TMM.

Variable	DF	Parameter estimate	Standard error	t value	Pr > ǀ t ǀ
Intercept	1	17.5633	0.7248	24.23	< 0.0001
X_1	1	5.4572	0.4384	12.45	< 0.0001
X_2	1	0.5127	0.0665	7.71	< 0.0001

in Table B.4. The statistical model is expressed in Equation 1, where Y refers to LOI value, X_1% refers to P%, and X_2% refers to the TMM concentration in finish solution, $X_1 > 0$ and $X_2 \geq 0$.

$$Y (\%)=17.56+5.46X_1\% +0.51X_2\% \qquad (1)$$

Equation 1 gives an R^2 of 0.8701, thus indicating that approximately 90% of the total variability of LOI is associated with the variability of the independent variables (P% and TMM concentration) within the framework of the equation. We also added a term of $X_1\%X_2\%$ to the regression model, and obtained the following statistical model:

$$Y (\%) =17.77+4.57X_1\% +0.39X_2\% +0.21X_1\%\bullet X_2\% \qquad (2)$$

For Equation 2, the t-value of the coefficient of the term $X_1\%\bullet X_2\%$ is 0.76, and the p-value equals to 0.4510, larger than significance level 0.05, thus meaning that we can accept the null hypothesis H_0 (the coefficient of term $X_1\bullet X_2$ equals zero). Therefore, we should remove the term $X_1\%\bullet X_2\%$ from the statistical model. R^2 (0.8854) is not significantly improved for Equation 2. Therefore, we selected Equation 1 as the statistical model to predict LOI.

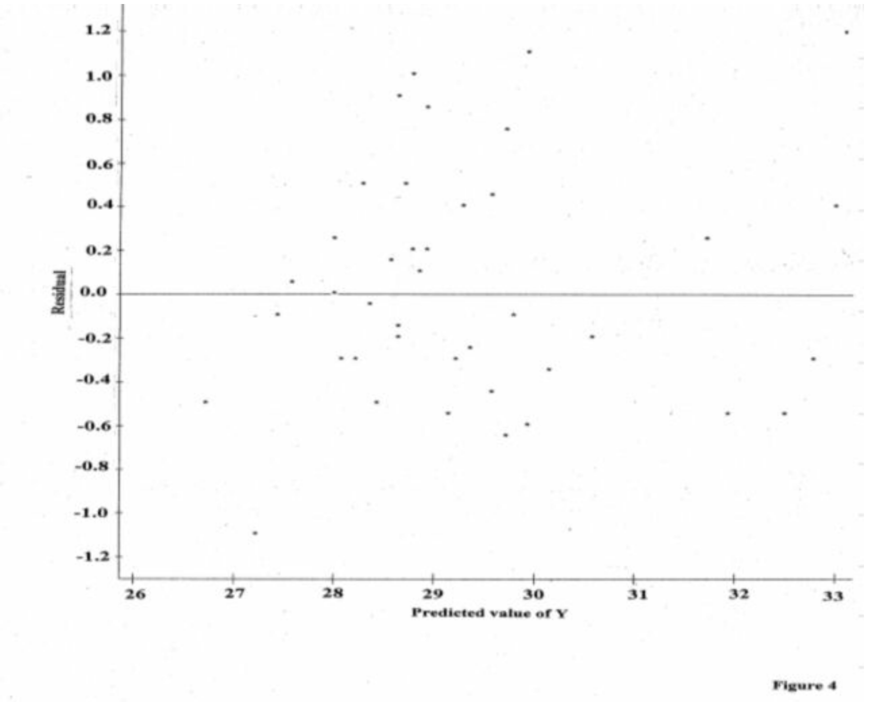


Figure B.4. Plot of the residual versus predicted value of Y (LOI).

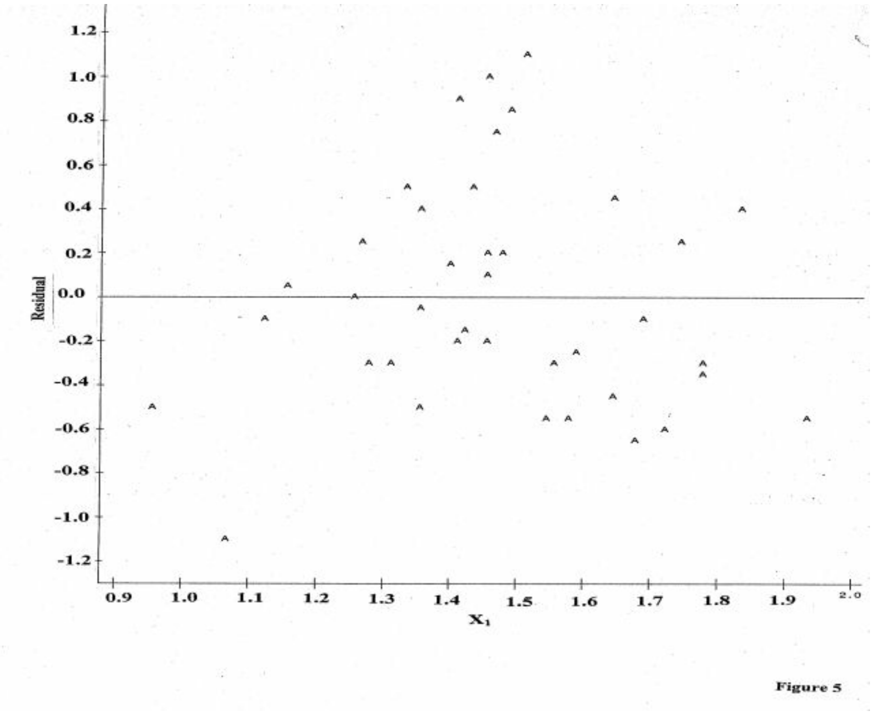


Figure B.5. Plot of the residual versus the independent variable of X_1 (phosphorus content).

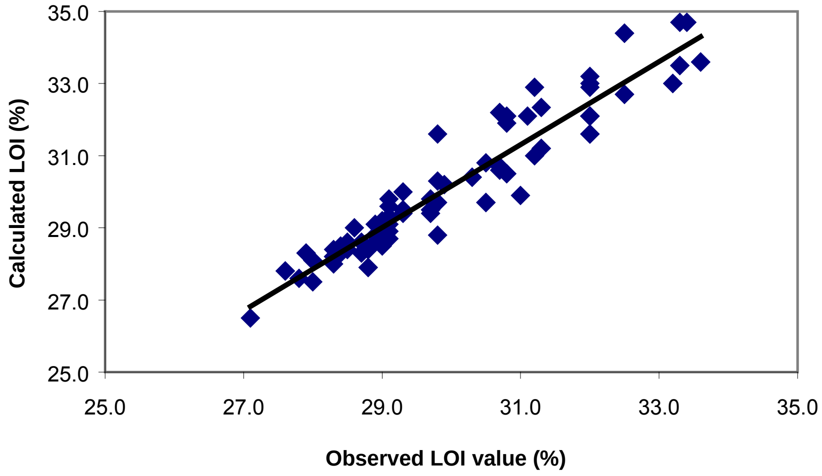


Figure B.6. LOI values calculated using the regression model versus LOI values observed.

To achieve an appropriate linear regression model $Y=\beta_0+\beta_1X_1+\cdots\beta_nX_n+\varepsilon_i$, the following assumptions on the residuals ε_i are necessary: (1) ε_1, ε_2, $\cdots\varepsilon_n$ are independent; (2) ε_1, ε_2, $\cdots\varepsilon_n$ have an identical distribution; and (3) ε_1, ε_2, $\cdots\varepsilon_n$ have a normal distribution, with mean 0 and variance σ^2 [14].

In order to test whether this regression model can meet these assumptions, we first plotted the residuals against the predicted value of Y (LOI) and the independent variable X_1 (P%) in Figures B.4, B.5, respectively. The data presented here show that all the residuals fall within a horizontal band centered on 0, displaying no systematic tendencies. It shows that all the residuals are random; therefore the linear regression model is appropriate.

Secondly, we used the Shapiro-Wilk W test [15] to check the normality of the residuals. One observes that W is 0.9693 and p value is 0.3578. Both W and p values are large, meaning that we cannot reject null hypothesis H_0, therefore the residuals come from normal distribution.

Finally, the overall hypothesis test shows that F value is 151.32, and P value <0.0001 (Table B.5), meaning that we can accept the alternative hypothesis Ha, and that at least one of β's is not equal to zero. The statistical analysis shows that LOI value does depend on all predictor variables (P% and TMM concentration). The P% and TMM concentration are the two critical factors for the flammability of the treated fabric. From the diagnostics of the regression model, we conclude that the linear least square estimated regression function between (a) LOI and (b) P% and TMM concentration is appropriate, meaningful and useful.

Table B.5. Analysis of variance for the cotton fabric treated with HFPO/TMM.

Source	DF	Sum of Square	Mean Square	F value	Pr > F
Model	2	199.0507	99.5254	127.31	< 0.0001
Error	38	29.7073	0.7818		
Corrected Total	40	228.7581			
R-Square=0.8701; adj. R-Square=0.8633					

The predicted value of LOI is plotted against the observed value of LOI on the treated fabric (Figure B.5). One observes a good linear relationship between the predicted LOI values using the statistical model (Equation 1) and the observed LOI values. It is further verified that the linear least square estimated regression function is a good one.

CONCLUSION

A linear least square estimated regression function exists between (a) LOI and (b) P% of the treated fabric and TMM concentration of the finish solution for the cotton fabric treated with the hydroxy-functional organophosphorus compound and TMM. Analysis of regression shows that it is an appropriate and meaningful regression model. The model can be used to predict LOI of a treated fabric sample based on the phosphorus concentrations on the fabric determined by atomic emission spectroscopy and the TMM concentration in the finish solutions.

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