

Flame Retardant Finishing of Cotton Fleece Fabric. II. Inorganic Phosphorus-Containing Compounds

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ABSTRACT: Cotton fleece is not able to meet the federal flammability standard for general apparels (CFR 1610) without flame retardant treatment. Consequently, cotton fleece is not available in the market in spite of high demands. In our previous research, we studied the application of a hydroxyl-functional organophosphorus oligomer as a flame retardant finishing agent for cotton fleece. In this research, we investigated the use of aluminum hydroxyphosphate (AHP) formed *in situ* on cotton by the reaction of aluminum sulfate and sodium phosphates to reduce the flammability of cotton fleece. We found that the AHP formed on cotton is effective in reducing the cotton fleece's flammability from "Class 3" to "Class 1." Elemental analysis of aluminum and phosphorus in the AHP shows that the mole ratio of

Al/P changes as the pH value of the sodium phosphates solution changes. The pH of the sodium phosphate solutions also affect the quantity of AHP formed on the cotton fleece. The treated cotton fleece retains "Class 1" flammability after one home laundering or the combination of dry-cleaning and hand washing procedures. The treatment increases the whiteness of the cotton fleece whereas it reduces its bursting strength. The cotton fleece thus treated is also investigated using differential scanning calorimetry and scanning electron microscopy. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1582–1590, 2008

Key words: aluminum hydroxyphosphate; cotton fleece; flammability; flame retardant finishing; textile flammability

INTRODUCTION

Raised surface and lightweight apparel fabrics including fleece fabrics are regulated by the federal government in the U.S. under "General Wearing Apparel Standard" (16 CFR 1610).¹ Compared with other fabrics, raised surface fabrics have lower density and contain more air in their fuzzy surfaces, therefore have higher flammability. Fleece, a knitted fabric with a napped surface, is particularly more flammable than other raised surface fabrics. Generally, 100% cotton fleece fabrics are not able to meet the 16 CFR 1610 standard without chemical treatment.^{2–4}

There are three ways to reduce the flammability of cotton fleece, i.e., blending cotton fiber with a synthetic fiber, such as polyester, treating cotton fleece with a flame retardant, and changing the construction of fleece fabric. However, blending cotton with a synthetic fiber is not always a guarantee for success. Many 90/10 and 80/20 cotton/polyester fleece fabrics still fail the 16 CFR 1610 standard. Blending cotton with polyester also changes the properties of 100% cotton fleece. Changing the construction alters the desirable characteristics of cotton fleeces. Thus, treating cotton fleece with a flame retardant using a

traditional finishing procedure is probably the most practical method to reduce the flammability of cotton fleece fabrics.

The durable flame retardant chemicals most commonly used in the industry including tetrakis(hydroxymethyl)phosphonium chloride known as "Probane" and *N*-methylol dimethylphosphonopropionamide under the commercial name of "Pyrovatex CP"^{5–7} are not practical or suitable for uses on cotton fleece. Polycarboxylic acids have been investigated as flame retardants for cotton/polyester fleece.⁸ In our previous research, we successfully applied a hydroxyl-functional organophosphorus compound in combination with dimethyloldihydroxyethyleneurea to treat cotton fleece.⁹ However, all those technologies have not been commercialized.

Alumina trihydrate and magnesium hydroxide are commonly used as flame retardants for plastics including elastomers, thermoset, and thermoplastic polymers.^{10,11} Both of them could not be applied to cotton textiles as durable flame retardants except as back coatings because they are not water-soluble and are not able to form covalent bonding with cellulose. The back coating method is not applicable to cotton fleece.

In the absence of phosphate anions, an aluminum ion (Al^{3+}) precipitates in an aqueous solution to form amorphous aluminum hydroxide at pH 4.5 to 8.0.^{12,13} In the presence of phosphate anions, Al^{3+} forms aluminum hydroxyphosphate (AHP) as a precipi-

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TABLE I
The Concentrations of $\text{Al}_2(\text{SO}_4)_3$ and NaH_2PO_4 Solutions Used for the Treatment of Cotton Fleece

$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$		NaH_2PO_4	
Mole Concentration (M)	W/V (g/L)	Mole Concentration (M)	W/V (g/L)
0.150	100	0.320	38.4
0.225	150	0.480	57.6
0.300	200	0.640	76.8
0.375	250	0.800	96.0

The X of $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ is calculated as 18.

tate.^{13,14} In this research, the AHP was formed *in situ* on cotton fleece when the fleece was first impregnated in an $\text{Al}_2(\text{SO}_4)_3$ solution, dried, and then treated in a 2nd solution containing NaH_2PO_4 at different pHs. We studied the effectiveness of the AHP thus formed *in situ* on the cotton fleece in reducing the flammability of cotton fleece and its durability to home laundering (HL), hand washing (HW), and dry-cleaning (DC) procedures. We also evaluated the physical properties of the treated cotton fleece.

EXPERIMENTAL

Materials

The cotton fleece fabric (233 g/m^2) was produced by Cotton Inc., Cary, NC. $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ ($x = 14-18$) and "Tergitol," a nonionic wetting agent, were supplied by Sigma-Aldrich, Milwaukee, WI. $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ were supplied by Fisher Scientific, Fair Lawn, NJ. NaOH was supplied by Mallinckrodt Baker, Phillipsburg, NJ.

Fabric treatment, home laundering, dry-clean, and hand-wash procedures

The cotton fleece fabric was treated using a two-step procedure. In the first step, the fleece was impregnated in an $\text{Al}_2(\text{SO}_4)_3$ solution, which also contained 0.02% wetting agent, Tergitol, for 5 min. The fabric sample was padded through a two-roll laboratory padder with two dips and two nips. The wet pick-up was $140 \pm$

TABLE II
The pH of the 40 mL 0.600M NaH_2PO_4 Solution before and after Addition of 0.300M $\text{Al}_2(\text{SO}_4)_3$ Solution of Different Volumes

$\text{Al}_2(\text{SO}_4)_3$ Added (mL)	pH	
	Before Addition	After Addition
1.9	8.5	7.8
2.2	7.5	7.2
2.8	6.5	6.2
3.4	5.5	4.9

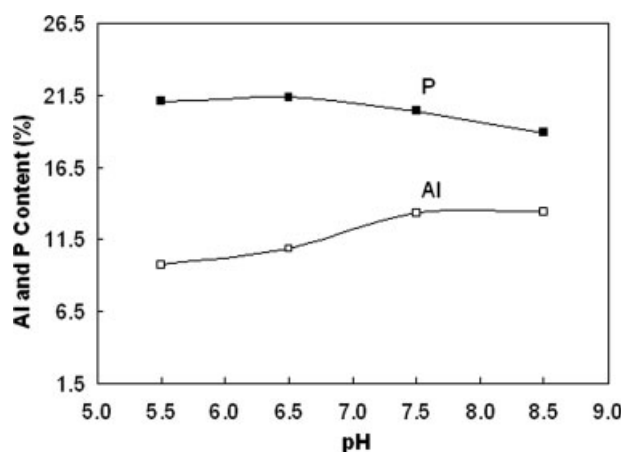


Figure 1 The aluminum and phosphorus content of the AHP precipitated at different pH.

2%. The sample was then dried at 100°C for 7 min in a laboratory oven manufactured by Werner Mathis, Oberhasli, Switzerland. In the second step, the fabric sample was again impregnated in a solution consisting of the mixture of NaH_2PO_4 and NaOH with different pH for 5 min, then padded as described above, and finally dried at 100°C for 7 min. The HL procedure was performed according to "AATCC Method 124" using a standard reference detergent ("AATCC Detergent 1993"). The DC procedure was carried out by a commercial dry-cleaner. The HW was performed following the 16CFR1610 procedure except that we used a standard reference detergent ("AATCC Detergent 1993") instead of a neutral detergent. The fleece was naturally dried following the HW procedure.

Fabric 45° flammability test

The flammability of the cotton fleece was measured according to ASTM Method D 1230-94 ("Standard

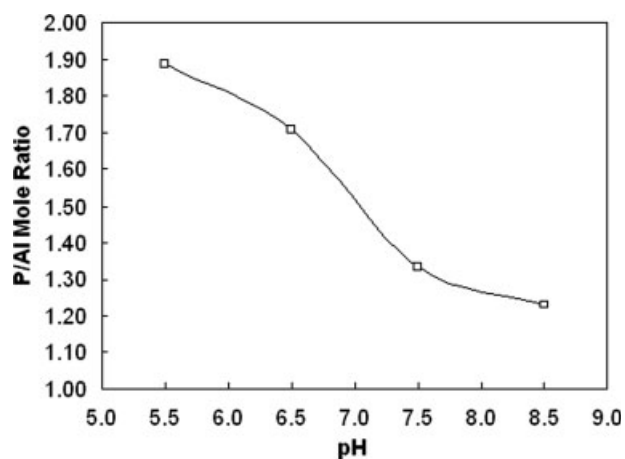
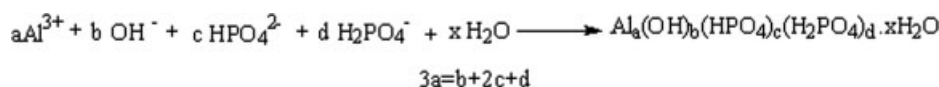


Figure 2 The aluminum/phosphorus mole ratio of the AHP precipitated at different pH.



Scheme 1 Formation of AHP.

Test Method for Flammability of Apparel Textiles" re-approved in 2001). According to ASTM D 1230, a fabric specimen mounted in a specimen holder was first brushed, dried at 105°C in an oven for 30 min, cooled down in a desiccator for 50 min, and then moved to a special 45° flammability tester (Model TC-45 manufactured by Govmark, Bellmore, NY). The specimen was then exposed to a standard butane flame for 1 s to cause ignition, the burning time and burning characteristics were recorded. The arithmetic mean burning time of 5 specimens and the burning characteristics were used as the basis to determine the flammability classifications. The flammability classifications for the fabrics with a raised surface are divided into the following three categories: (1) "Class 1" (normal flammability): fabric having burning time more than 7 s or having surface flash (SF) without base burn (BB) regardless of burning time; (2) "Class 2" (intermediate flammability): fabric having burning time 4–7 s with BB; (3) "Class 3" (high flammability with rapid and intense burning): fabric having burning time less than 4 s and BB. A fabric can be classified as "Class 1" only when the fabric before and after a refurbish procedure consisting of a DC procedure followed by HW procedure using a neutral detergent are determined to be "Class I."

Quantitative analysis of aluminum and phosphorus of AHP

To determine the composition of the AHP precipitated on cotton fleece, we analyzed the aluminum (Al) and phosphorus (P) contents of the AHP precipitated by mixing a NaH_2PO_4 solution with a $\text{Al}_2(\text{SO}_4)_3$ solution. The 0.300M (200 g/L, see the concentration conversions in Table I) $\text{Al}_2(\text{SO}_4)_3$ solutions (different volumes) were added to five 0.600M NaH_2PO_4 solutions (40 mL each) to achieve the final pHs ranging from 4.8 to 8.5. The pH of the mixtures thus prepared is presented in Table II. The pHs after mixing the solutions presented in Table II were the same as the pHs of the solutions used in the second treatment step after impregnation of the fleece when the pH effect was studied. The precipitates were separated and dried to constant weight, and 0.10 g precipitate of each sample was weighed and completely dissolved in a 10% HCl solution. The homogeneous solution thus prepared was transferred to a 50 mL volumetric flask, and then diluted with distilled water to the mark. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively

coupled plasma atomic emission spectrometer (ICP-AES) to determine the P and Al concentrations.

Thermal analysis

Differential scanning calorimetry (DSC) analysis was performed using a Mettler Toledo DSC 821 calorimeter at the heating rate of 10°C/min in nitrogen. The sample size was 4–8 mg.

Scanning electron microscopy

Cotton fleece fabric was studied using Zeiss1450 EP environmental scanning electron microscope (ESEM). The ESEM was operated at 20 kV to observe the cotton fiber of the fleece.

Fabric bursting strength and whiteness index

The bursting strength of the cotton fleece was measured according to ASTM Method D 3786-01 ("Standard Test Method for Hydraulic Bursting Strength of Textile Fabrics-Diaphragm Bursting Strength Tester Method") using a "Truburst" tester made by James H. Heal and Company, Halifax, UK. The fabric CIE whiteness index was measured according to AATCC Method 110 ("Whiteness of Textiles") using a "Macbeth Color-Eye" 7000A spectrophotometer made by Hunter Associates Laboratory, Reston, VA.

RESULTS AND DISCUSSION

Formation of AHP

A variety of analytical techniques have been used in the past to study the structures of AHP. Researchers find that the structures of AHPs are difficult to determine because they are amorphous and possibly heterogeneous. The situation becomes even more complicated when several different structures coexist in one AHP sample.^{13,14}

TABLE III
The Percent Mole Compositions of Phosphate Solutions at Different pHs

Solution pH	H_3PO_4 (%)	H_2PO_4^- (%)	HPO_4^{2-} (%)	PO_4^{3-} (%)
5.0	0.44	99.36	0.20	0
5.5	0.04	98.00	1.96	0
6.5	0	83.33	16.67	0
7.5	0	33.35	66.65	0
8.5	0	4.60	95.40	0

TABLE IV
The pH of the Solutions Used for the 2nd Step Treatment before and after the Impregnation of the Cotton Fleece and the 45° Flammability of Treated Cotton Fleece

pH of the NaH ₂ PO ₄ Solutions		45° Flammability			
Before Treatment	After Treatment	No. of Specimen SF	Ave. Burning Time (s)	No. of Specimen BB	Class
Control	–	5	1.1	5	III
5.5	4.9	5	1.1	0	I
6.5	6.2	5	1.1	0	I
7.5	7.2	5	1.1	0	I
8.5	7.8	5	1.1	0	I

SF: surface flash only; BB: base burn.

To investigate the composition of the AHP formed on the cotton fleece, we studied the AHP precipitated in an aqueous solution by adding a Al₂(SO₄)₃ solution to a NaH₂PO₄ solution as described in Table II. The contents of Al and P and the P/Al mole ratio of the AHP precipitated from the solutions with different pHs are shown in Figures 1 and 2, respectively. One observes that both the Al and P contents of AHP depend on the pH of the solution at which it is precipitated. The Al content increases whereas P content decreases as the pH increases from 6.5 to 8.5 (Fig. 1). Consequently, the P/Al mole ratio decreases from 1.71 to 1.23, respectively, (Fig. 2). The data presented here indicate that the composition of the AHP formed by the reaction of Al³⁺ and the phosphate anions in an aqueous solution is pH-dependent and that the AHP formed at pH 8.5 has the lowest P/Al mole ratio.

The reaction to form AHP in an aqueous solution is shown in Scheme I. Phosphoric acid (H₃PO₄) ionizes to form three different anions (H₂PO₄⁻, HPO₄²⁻, and PO₄³⁻) in an aqueous solution. The percent mole composition of those anionic species at different pH values are presented in Table III. Since the solution pH affects the concentrations of those anionic species in the solution, it affects the composition of the AHP precipitated from the solution. As the solution pH is increased from 5.0 to 8.5, the percent mole concentration of H₂PO₄⁻ decreases from 99.36 to 4.60, whereas that of HPO₄²⁻ increases from 0.20 to 95.40. This explains why P/Al ratio decreases as the pH increased as shown in Figure 2.

The effectiveness of AHP as a flame retardant for the cotton fleece

Cotton fleece fabric is treated with a 0.300M Al₂(SO₄)₃ solution, dried, then treated with a 0.600M NaH₂PO₄ solution with pH ranging from 5.5 to 8.5, and finally dried. The 45° flammability of the cotton fleece thus treated is shown in Table IV. After the 2nd step treatment, the pH of the NaH₂PO₄ solution decreases because of the acidic nature of Al₂(SO₄)₃ on

the fleece. The flammability data include the number of specimens having SF only, the average burning time and the number of specimens having BB. The flammability ranking of the fleece is based on those data as discussed previously. The untreated cotton fleece fails the test ("Class III" flammability). All the treated fleece fabrics pass the test with "Class I" flammability ranking. Therefore, the data demonstrate that the AHP formed on the cotton fleece by the two-step procedure is indeed effective in reducing the flammability of cotton fleece.

Shown in Figure 3 is the weight increase of the cotton fleece first treated with a 0.300M Al₂(SO₄)₃ solution then treated in the 2nd step with a 0.600M NaH₂PO₄ solution as a function of the pH of the NaH₂PO₄ solutions. The weight increase of the cotton fleece thus treated increases sharply as the pH increases from 5.5 to 7.5 (Fig. 3). We observe that a significant amount of AHP precipitated in the solution when pH is below 6.5, indicating some of the Al₂(SO₄)₃ dissolves in the solution and consequently reacts with NaH₂PO₄ to form AHP. When pH is increased above 7.5, little AHP precipitate is seen in the solution after impregnation of the fleece. There-

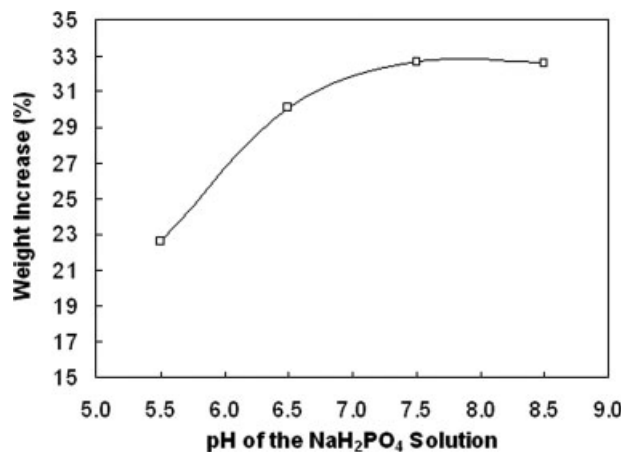


Figure 3 The weight increase of the cotton fleece first treated with 0.300M Al₂(SO₄)₃ then with 0.600M NaH₂PO₄ of different pH.

TABLE V
The pHs of the NaH₂PO₄ Solution before and after Impregnation and 45° Flammability of the Cotton Fleece Treated Using Different Concentrations of NaH₂PO₄

Al ₂ (SO ₄) ₃ (M)	NaH ₂ PO ₄ (M)	pH of the NaH ₂ PO ₄ Solution		Weight Increase (%)	45° Flammability			Class
		Before Treatment	After Treatment		No. of Specimen SF	Ave. Burning Time (s)	No. of Specimen BB	
Control		—	—	—	5	1.1	5	III
0.375	0.400	8.5	6.8	26.1	5	1.1	0	I
0.375	0.600	8.5	7.1	35.9	5	1.1	0	I
0.375	0.800	8.5	7.2	43.8	5	1.1	0	I

fore, the data show that the quantity of AHP formed on the cotton fleece is pH-dependent. In all the experiments discussed in the rest of this paper, we adjusted the pH of NaH₂PO₄ solutions to 8.5 in the 2nd step experiment.

We studied the effect of NaH₂PO₄ concentration in the 2nd step treatment on the weight increase and the flammability of the treated fleece (Table V). The concentration of Al₂(SO₄)₃ in the first treatment solution is 0.375M. The pH of all the NaH₂PO₄ solutions decreases after the 2nd treatment. The weight increase of the treated fleece becomes higher as the NaH₂PO₄ concentration increases, indicating that more AHP is formed on cotton fleece at higher NaH₂PO₄ concentrations (Table V). The data show that all the treated fleece samples pass the flammability test and achieve the flammability of "Class I". We also observe that Na₂SO₄, which is formed by the reaction during the 2nd step treatment, becomes saturated and starts to precipitate on the fabric surface when the NaH₂PO₄ concentration is increased above 0.800M. Therefore, we used the Al₂(SO₄)₃/NaH₂PO₄ mole ratio of 0.47 in all the experiments discussed in the rest of this paper.

The cotton fleece was treated using Al₂(SO₄)₃/NaH₂PO₄ with a constant mole ratio of 0.47 but different concentrations. The 45° flammability of the treated cotton fleece is shown in Table VI. The data show that the fleece treated using Al₂(SO₄)₃/

NaH₂PO₄ at the lowest concentration still passes the flammability test and achieves "Class I" flammability ranking. All the data presented here clearly demonstrate the effectiveness of the AHP formed *in situ* on the cotton fleece in reducing the flammability of the fleece.

The durability of AHP to different refurbishing procedures

The cotton fleece is treated with Al₂(SO₄)₃/NaH₂PO₄ (mole ratio 0.47) at different concentrations, and the treated fleece was subjected to one HL cycle. The weight increase of the cotton fleece before and after the laundering procedure is shown in Figure 4. Before HL, the percent weight increase of the treated cotton fleece increases from 15.9 to 43.4% as the concentration of Al₂(SO₄)₃ is increased from 0.150 to 0.375M, respectively. After 1 HL, the percent weight increase of the cotton fleece decreases significantly due to the removal of the AHP from the cotton fleece during the laundering procedure. When the fleece is treated with 0.150M Al₂(SO₄)₃, the percent weight increase is 3.6% after 1 HL, representing 23% retention of the AHP formed on the fleece after the 2nd treatment. When the Al₂(SO₄)₃ concentration is increased to 0.375M, the percent weight increase of the fleece becomes 13.0%, representing 30% retention of the AHP. The data indicate that significant amount

TABLE VI
The 45° Flammability of the Cotton Fleece Treated at Different Concentrations of Al₂(SO₄)₃/NaH₂PO₄ before Laundering

Al ₂ (SO ₄) ₃ (M)	NaH ₂ PO ₄ (M) ^a	45° Flammability			Class
		No. of Specimen SF	Ave. Burning Time (s)	No. of Specimen BB	
Control		5	1.1	5	III
0.150	0.320	5	1.1	0	I
0.225	0.480	5	1.1	0	I
0.300	0.640	5	1.1	0	I
0.375	0.800	5	1.1	0	I

^a The pH of the NaH₂PO₄ solutions used in 2nd step treatment was adjusted with NaOH solution to 8.5, and it became 7.3 after the treatment.

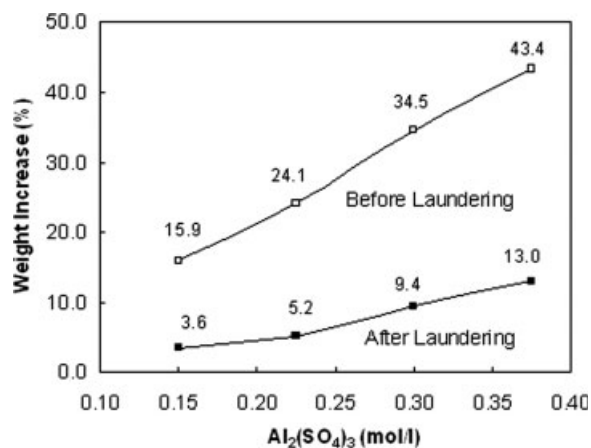


Figure 4 The weight increase of the cotton fleece treated with $Al_2(SO_4)_3/NaH_2PO_4$ before and after one HL cycle.

of AHP remains on the fleece after one HL cycle whereas the laundering procedure removes more than 2/3 of the AHP from the fleece. Therefore, the AHP formed *in situ* on the cotton fleece is considered to be a semidurable flame retardant.

We also applied DSC to study the thermal degradation of the untreated cotton fleece and the cotton fleece treated with 0.375M $Al_2(SO_4)_3$ and 0.800M NaH_2PO_4 after one HL cycle (Fig. 5). The untreated cotton fleece shows a strong endothermic peak at 355°C due to the depolymerization of cellulose with the formation of levoglucosan and its decomposition products.^{15,16} For the cotton fleece treated with $Al_2(SO_4)_3/NaH_2PO_4$ and subjected to one laundering cycle, the endothermic peak shifts to 360°C and the peak is much weaker than that of untreated cotton fleece. Thus, the data indicate that the AHP on cotton fleece retards cellulose depolymerization process.

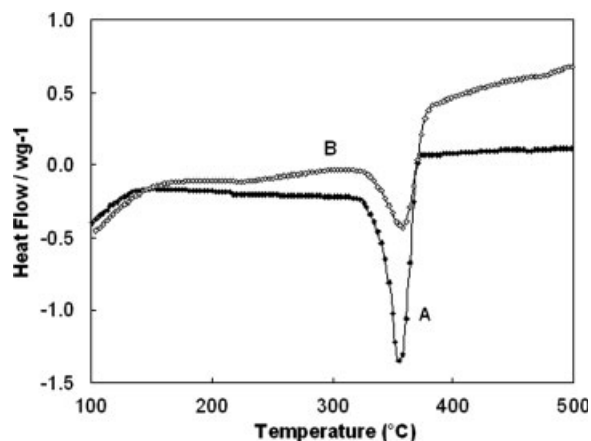


Figure 5 The DSC curve of (A) the cotton fleece without treatment and (B) the cotton fleece treated with 0.375M $Al_2(SO_4)_3$ and 0.800M NaH_2PO_4 and subjected to one HL procedure.

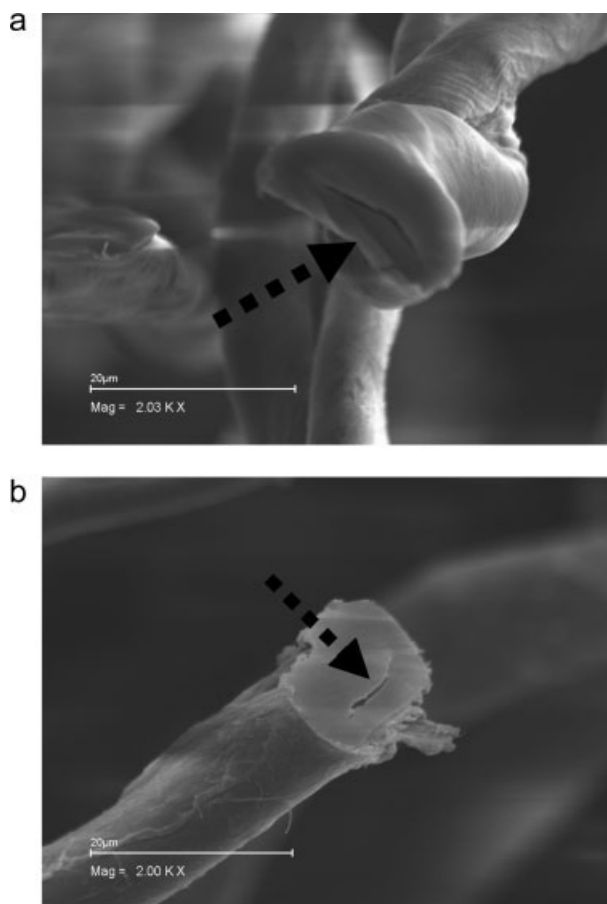


Figure 6 The SEM images of (a) a cotton fiber taken from the untreated fleece and (b) a cotton fiber taken from the fleece treated with 0.375M $Al_2(SO_4)_3$ and 0.800M NaH_2PO_4 and subjected to one HL cycle.

This may explain why AHP reduces the flammability of the cotton fleece.

Presented in Figure 6(a,b) are the SEM images of the untreated cotton fleece fiber and the cotton fleece fiber treated with 0.375M $Al_2(SO_4)_3$ and 0.800M NaH_2PO_4 and subjected to one HL cycle, respectively. Figure 6(A) show the bean-shaped cross section of the untreated cotton fiber with a collapsed lumen (marked). The image of the cross section of

TABLE VII
The 45° Flammability of the Cotton Fleece Treated With Different Concentrations of $Al_2(SO_4)_3/NaH_2PO_4$ and Subjected to One HL

$Al_2(SO_4)_3$ (M)	NaH_2PO_4 (M)	45° Flammability				Class
		No. of Specimen SF	Ave. Burning Time (s)	No. of Specimen BB		
Control		5	1.1	5	III	
0.150	0.320	5	1.1	5	III	
0.225	0.480	5	1.1	5	III	
0.300	0.640	5	1.1	0	I	
0.375	0.800	5	1.1	0	I	

TABLE VIII
The Weight Increase of the Cotton Fleece Treated With 0.375M $\text{Al}_2(\text{SO}_4)_3$ and NaH_2PO_4 of Different Concentrations and Subjected to HL, DC, and DC/HW

NaH ₂ PO ₄ Concentration (M)	Weight Increase before Refurbishing (%)	Weight Increase after Refurbishing (%)		
		1 HL Cycle	DC	DC/HW
0.400	26.5	9.5	24.1	11.4
0.600	35.5	12.3	27.3	12.6
0.800	43.4	13.0	36.4	13.6

^a The pH of the NaH_2PO_4 solution was adjusted with NaOH to 8.5.

the treated cotton fiber shown in Figure 6(B), however, is different. The fiber appears to be swollen and has a round-shaped cross section. The lumen (marked) almost disappears in Figure 6(B) due to the presence of AHP inside. Therefore, the SEM images shown in Figure 6 confirm that the AHP formed inside the lumen and it is retained after the laundering procedure. The data presented in Figure 4 show that that particular treated fleece still have 13.0% weight increase after 1 HL cycle.

The 45° flammability of the cotton fleece treated with $\text{Al}_2(\text{SO}_4)_3/\text{NaH}_2\text{PO}_4$ at different concentration after 1 HL cycle is presented in Table VII. The untreated cotton fleece fails in the 45° flammability test before and after laundering. All the four treated fleece samples pass the 45° flammability test before HL as shown in Table VI. However, the two fleece samples treated with 0.150 and 0.225M $\text{Al}_2(\text{SO}_4)_3$ with weight increase of 3.6 and 5.2%, respectively, after one HL cycle fail the 45° flammability test. Only when the concentration of $\text{Al}_2(\text{SO}_4)_3$ is increased to 0.300 and 0.375M with weight increase of 9.4% and 13.0%, respectively, the cotton fleece samples thus treated pass the 45° flammability test after 1 HL (Table VII). It is evident that removal of the AHP by the laundering procedure increases the flammability of the fleece and makes it necessary to use higher $\text{Al}_2(\text{SO}_4)_3/\text{NaH}_2\text{PO}_4$ concentrations to maintain "Class I" flammability ranking.

TABLE IX
The Percent Retention of the AHP on the Cotton Fleece Treated With 0.375M $\text{Al}_2(\text{SO}_4)_3$ and NaH_2PO_4 of Different Concentrations and Subjected to HL, DC, and DC/HW

NaH ₂ PO ₄ Concentration (M)	Weight Increase before Refurbishing (%)	AHP Retention after Refurbishing (%)		
		1 HL Cycle	DC	DC/HW
0.400	26.5	36	90	43
0.600	35.5	35	77	35
0.800	43.4	30	80	31

TABLE X
The 45° Flammability of the Cotton Fleece Treated With 0.375M $\text{Al}_2(\text{SO}_4)_3$ and NaH_2PO_4 of Different Concentrations and Subjected to HL, DC, and DC/HW

NaH ₂ PO ₄ Concentration (M)	45° Flammability Ranking		
	1 HL Cycle	DC	DC/HW
Control	III	III	III
0.400	I	I	I
0.600	I	I	I
0.800	I	I	I

We also measured the weight increase of the cotton fleece treated with 0.375M $\text{Al}_2(\text{SO}_4)_3$ and NaH_2PO_4 of different concentrations and subjected to different refurbish procedures (Tables VIII and IX). The weight increase of the fleece after the 2nd treatment increases from 26.5 to 43.4% as the NaH_2PO_4 concentration is increased from 0.400 to 0.800M, respectively, (Table VIII). After one HL cycle, the weight increase decreases to 9.5–13.0%, representing 30–36% retention of the AHP formed on the fleece (Tables VIII and IX). When the treated fleece is subjected to DC, the weight increase becomes 24.1–36.4%, representing 77–90% retention of the AHP. The weight increase of the fleece subjected to a DC procedure is much higher than that subjected to a HL procedure. Therefore, a DC procedure is a much milder process and it removes far less AHP than a HL procedure. The weight-increase after the combination of DC and HW procedures is in the range of 11.4–13.6% representing 31–43% retention, which is similar to that after the laundering procedure. One also observes that the weight increase of the treated cotton fleece increases as the NaH_2PO_4 concentration increases after the refurbishing procedures.

The 45° flammability of cotton fleece treated with 0.375M $\text{Al}_2(\text{SO}_4)_3$ and NaH_2PO_4 of different concentrations after HL, DC, and DC/HW is shown in Table X. All the treated cotton fleece samples pass the 45° flammability test to achieve "Class I" after the three different refurbishing procedures, but we also observe more severe SF due to the partial removal of

TABLE XI
The Weight Increase of Cotton Fleece Treated With Different Concentration of $\text{Al}_2(\text{SO}_4)_3/\text{NaH}_2\text{PO}_4$ and Subjected to one HL, DC, and DC/HW

$\text{Al}_2(\text{SO}_4)_3$ (mol/L)	NaH_2PO_4 (mol/L)	Weight Increase before Refurbishing (%)	Weight Increase after Refurbishing (%)		
			1HL Cycle	DC	DC/HW
0.150	0.320	15.9	3.6	11.8	5.6
0.225	0.480	24.1	5.2	23.6	8.2
0.300	0.640	34.5	9.4	29.4	11.2
0.375	0.800	43.4	13.0	35.4	13.8

TABLE XII
The Percent Retention of the AHP on the Cotton Fleece Treated With Different Concentrations of $\text{Al}_2(\text{SO}_4)_3/\text{NaH}_2\text{PO}_4$ and Subjected to HL, DC, and DC/HW

$\text{Al}_2(\text{SO}_4)_3$ (mol/L)	NaH_2PO_4 (mol/L)	Weight Increase before Refurbishing (%)	AHP Retention after Refurbishing (%)		
			1 HL Cycle	DC	DC/ HW
0.150	0.320	15.9	23	74	35
0.225	0.480	24.1	22	98	34
0.300	0.640	34.5	27	85	32
0.375	0.800	43.4	30	82	32

AHP from the fleece after the refurbishing procedure.

The durability of cotton fleece treated with different concentrations of $\text{Al}_2(\text{SO}_4)_3/\text{NaH}_2\text{PO}_4$ is evaluated and the weight increase of the treated fleece after different refurbish process is presented in Tables XI and XII. The weight increase of treated cotton fleece increases with the concentration of $\text{Al}_2(\text{SO}_4)_3/\text{NaH}_2\text{PO}_4$ from 15.9 to 43.4% when the concentration of $\text{Al}_2(\text{SO}_4)_3$ is 0.150 and 0.375 mol/L, respectively, (Table XI). The weight increase decreases to 3.6–13.0% after 1 HL, representing 22–30% of the AHP retention (Tables XI and XII). DC procedure removes a part of the AHP from the treated fleece. After DC, the AHP retention is 74–98% (Table XII). DC/HW process further removes AHP from the treated cotton fleece. The weight increase of treated cotton fleece decreases to 5.6–13.8% after DC/HW, representing 32–35% of the AHP retention.

The 45° flammability of cotton fleece treated with different concentrations of $\text{Al}_2(\text{SO}_4)_3/\text{NaH}_2\text{PO}_4$ after different refurbish procedure is presented in Table XIII. After DC and DC/HW, all the treated fabrics still have Class I flammability and pass the 45° flammability test. To pass the 45° flammability test after 1 HL, the weight increase of cotton fleece should be higher than 9.0%. But here when the weight increase of the treated cotton fleece after DC/HW is only 5.6%, it still passes the 45° flamma-

TABLE XIII
The 45° Flammability of the Cotton Fleece Treated With Different Concentrations of $\text{Al}_2(\text{SO}_4)_3/\text{NaH}_2\text{PO}_4$ and Subjected to HL, DC, and DC/HW

$\text{Al}_2(\text{SO}_4)_3$ (mol/L)	NaH_2PO_4 (mol/L)	45° Flammability Ranking		
		1 HL Cycle	DC	DC/HW
Control		III	III	III
0.150	0.320	III	I	I
0.225	0.480	III	I	I
0.300	0.640	I	I	I
0.375	0.800	I	I	I

TABLE XIV
Bursting Strength Retention and CIE Whiteness Index of Cotton Fleece Treated With Different Concentrations of $\text{Al}_2(\text{SO}_4)_3/\text{NaH}_2\text{PO}_4$ before Wash

$\text{Al}_2(\text{SO}_4)_3$ (M)	NaH_2PO_4 (M)	Bursting Strength (Kg/cm ²)	Bursting Strength Retention (%)	CIE Whiteness Index
0.150	0.320	1.37	55	138
0.225	0.480	1.35	54	137
0.300	0.640	1.39	55	130
0.375	0.800	1.34	53	135
0.000	0.000	2.51	–	130

bility test. This is because cotton fleece becomes less fluffy after DC/HW, which decreases the flammability of cotton fleece. On the contrary, cotton fleece becomes fluffier after 1 HL cycle, which requires higher weight increase of AHP to pass the 45° flammability test.

The physical properties of the treated cotton fleece

The bursting strength retention and CIE whiteness index of the cotton fleece treated with different concentrations of $\text{Al}_2(\text{SO}_4)_3/\text{NaH}_2\text{PO}_4$ and that with NaH_2PO_4 are shown in Tables XIV and XV, respectively. The treated fabric retains 53–58% of the original bursting strength. The fabric strength loss as a result of the treatment can be attributed to two factors. First, the AHP imbedded inside and between the yarns may reduce the flexibility of yarns, and thus, reduces the bursting strength. Secondly, cotton fleece is subjected to Lewis acid degradation when it is impregnated in $\text{Al}_2(\text{SO}_4)_3$ solution and dried. $\text{Al}_2(\text{SO}_4)_3$ has high acidity and is a strong Lewis acid. Both acid and Lewis acid cause cellulose depolymerization, thus reduces the fabric strength.¹⁷ One also observes that the CIE whiteness index of the treated cotton fleece increases after the treatment. This is obviously caused by the additional light scattering of the AHP particles on the fabric surface.

TABLE XV
Bursting Strength Retention and CIE Whiteness Index of Cotton Fleece Treated With 0.375 mol/L $\text{Al}_2(\text{SO}_4)_3$ at Different Concentrations of NaH_2PO_4 before Wash

NaH_2PO_4 (M)	Bursting Strength (psi)	Bursting Strength Retention (%)	CIE Whiteness Index
0.400	1.41	56	139
0.600	1.45	58	139
0.800	1.34	53	137

CONCLUSIONS

- (1). The composition of the AHP formed by the reaction of Al^{3+} and the phosphate anions in an aqueous solution is pH-dependent and the AHP formed at pH 8.5 has the lowest P/Al mole ratio. The quantity of AHP formed on the cotton fleece treated with $\text{Al}_2(\text{SO}_4)_3$ and NaH_2PO_4 is also pH-dependent.
- (2). The AHP formed *in situ* on the cotton fleece by the two-step procedure is effective in reducing the flammability of cotton fleece. AHP on cotton fleece retards cellulose depolymerization process at elevated temperatures.
- (3). The AHP formed *in situ* on the cotton fleece is a semidurable flame retardant. The lumen of a cotton fiber is filled with AHP solid upon the 2nd step treatment of the cotton fleece. A significant portion of AHP remains on the fleece after the treated fleece is subjected to one HL procedure or the combination of DC and HW procedure. Consequently, the treated cotton fleece fabric passes the 45° flammability test both before and after one HL procedure or the combination of DC and HW procedure. A HL procedure using a detergent removes significantly more AHP from the treated fleece than a DC procedure.
- (4). The treatment of the cotton fleece increases the whiteness and decreases the bursting strength of the treated cotton fleece by 42–47%.

References

1. US Consumer Product Safety Commission, <http://www.cpsc.gov/BUSINFO/frnotices/fr02/flammability.html>
2. Rearick, W. A.; Martin, W. B.; Wallace, M. L. In Proceedings of the Conference on Recent Advances in Flame Retardancy of Polymeric Materials, Vol. XIII; BCC Communications: Stamford, Connecticut 2002, p 251.
3. Rearick, W. A.; Wallace, M. L.; Martin, W. B. AATCC Rev 2002, 2, 12.
4. Rearick, W. A.; Wakelyn, P. In Proceedings of the Conference on Recent Advances in Flame Retardancy of Polymeric Materials, Vol. XI; BCC Communications: Stamford, Connecticut, 2000, p 221.
5. Horrocks, A. R. In Textile Finishing, Heywood, D., Ed.; The Society of Dyers and Colourist, Bradford, West Yorkshire, UK, 2003; Chapter 6.
6. Weil, E. D. In Kirk-Other Encyclopedia of Chemical Technology, 4th ed.; Grayson, M., Ed; Wiley: New York, 1995; Vol. 10, p 976.
7. Weil, E. D. In Handbook of Organophosphorus Chemistry; Engel, R., Ed.; New York: Marcel Dekker, 1992; p 683.
8. Blanchard, E. J.; Graves, E. E. AATCC Rev 2005, 5, 26.
9. Yang, C. Q.; Qiu, X. Fire Mater 2007, 31, 67.
10. Beyer, G. Fire Mater 2001, 25, 193.
11. Horn, W. E., Jr.; Stinson, J. M. In Fire Safety Developments: Emerging Needs, Product Developments, Non-Halogen FR's, Standards and Regulations; Fire Retardant Chemicals Association: Lancaster, PA, 2000; p 101.
12. Cotton, F. A.; Wilkinson, G.; Gaus, P. L. In Basic Inorganic Chemistry, 3rd Ed.; Wiley: New York, 1995; p 361.
13. Klein, J.; Ushio, M.; Burrell, L. S.; Wenslow, B.; Hem, S. L. J Pharma Sci 2000, 89, 311.
14. Shirodkar, S.; Hutchinson, R. L.; Perry, D. L.; White, J. L.; Hem, S. L. Pharma Res 1990, 7, 1282.
15. Jandura, P.; Riedl, B.; Kokta, B. V. Polym Degrad Stab 2000, 70, 387.
16. Soares, S.; Camino, G.; Levchik, S. Polym Degrad Stab 1995, 49, 275.
17. Yang, C.; Wei, W. Textile Res J 2000, 70, 910.