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Development of an environmentally friendly halogen-free phosphorus–nitrogen bond flame retardant for cotton fabrics

Thach-Mien D. Nguyen, SeChin Chang*, Brian Condon, Minori Uchimiya and Chanel Fortier

A novel flame retardant diethyl 4-methylpiperazin-1-ylphosphoramidate (CN-3) containing phosphorous and nitrogen was prepared. Its chemical structure was confirmed by nuclear magnetic resonance (^1H -, ^{13}C -, and ^{31}P -NMR), Fourier transform infrared spectroscopy, and elemental analysis. Print cloth and twill fabrics were treated with CN-3 to achieve different levels of add-on (7–22 wt% add-ons for print cloth and 3–18 wt% add-ons for twill). Thermogravimetric analysis, vertical flame test, and limiting oxygen index (LOI) were performed on the treated cotton fabrics and showed promising results. When the treated print cloth and twill fabric samples were tested using the vertical flame test (ASTM D6413-08), we observed that the ignited fabrics self-extinguished and left behind a streak of char. Treated higher add-ons fabrics were neither consumed by flame nor produced glowing ambers upon self-extinguishing. LOI (ASTM 2863-09) was used to determine the effectiveness of the flame retardant on the treated fabrics. LOI values increased from 18 vol% oxygen in nitrogen for untreated print cloth and twill fabrics to maximum of 28 and 31 wt% for the highest add-ons of print cloth and twill, respectively. The results from cotton fabrics treated with CN-3 demonstrated a higher LOI value as well as a higher char yield because of the effectiveness of phosphorus and nitrogen as a flame retardant for cotton fabrics. Furthermore, FT-IR and SEM were used to characterize the chemical structure on the treated fabrics as well as the surface morphology of char areas of treated and untreated fabrics. Published 2012. This article is a US Government work and is in the public domain in the USA.

Keywords: cotton; flame retardant; phosphoramidate; flammability test; thermal degradation

INTRODUCTION

In reviewing the history of flame retardants (FRs), most treatments, chemical formulations, and additives were derived from chemistry developed in the 1950s to 1980s.^[1] Since this time, increasing concerns over the toxicological and environmental consequences of using these chemicals on textile surfaces and in close contact with the skin have brought into attention the development and applications of new chemistry by both research scientists and industry. In the past 20 years, many workers have launched into research that enhances FR performance at an inexpensive cost and improves efficiency. This was performed by replacing areas of concern with other existing formulations or by using known chemistry in novel ways.

During their development, nitrogen and nitrogen–phosphorous compounds have been known to evolve low toxic gases or vapors as well as low evolution of smoke during combustion and are better in the aspects of recyclability.^[2] Nitrogen–phosphorus compounds of this category are nitrogen containing phosphorous compounds such as melamine or ammonium phosphate.^[3,4] A combination of phosphorous and nitrogen, such as phosphoric acid and urea on cotton, was found to be synergistic.^[5] The reason for the synergistic effect is that phosphorous offers the tendency of char formation, and nitrogen forms a protective char during fire.^[6–10] Basic interaction of nitrogen and phosphorous in cellulose flame retardancy has been evaluated and shows N–P synergism.^[11,12]

Among nitrogen–phosphorous compounds, phosphoramidates are very promising^[13–18] FRs. They are cheap to manufacture, have

low volatility, provide good thermal stability, and enhance char formation during the burning process. They provide better flame retardancy on cellulose than phosphates themselves.^[14,19,20] Reaction between phosphoramidates or phosphoramides and the substrates, such as cotton and wood, have been investigated by some workers.^[13,20,21]

This article describes the preparation and thermal behavior of a new phosphoramidate FR for cotton print cloth and twill fabrics. Diethyl 4-methylpiperazin-1-ylphosphoramidate, **1**, has been synthesized from 1-amino-4-methyl piperazine. The structure of **1** was characterized by nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), and elemental analysis by inductively coupled plasma (ICP). Its thermal properties and flame retardancy were investigated by thermogravimetric analysis (TGA), limiting oxygen index (LOI), and vertical flammability testing. The content of nitrogen and phosphorous was examined; meanwhile, microstructures of treated and untreated cotton print cloth and twill fabric were studied.

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EXPERIMENTAL

Materials

Chemicals were purchased from Aldrich and used as received. Tetrahydrofuran (THF) solvent was purchased from Aldrich and was dried using a Solvent Purification System from Innovative Technology. The reaction was conducted under nitrogen atmospheric conditions and monitored using silica gel 60F₂₅₄ thin layer chromatography purchased from EMD. Print cloth fabric, 107 g/m² (Testfabrics, Inc., Style 400M), was bleached, desized, and mercerized. Twill fabric, 258 g/m² (Testfabrics, Inc., Style 423), was bleached and mercerized.

Synthesis and characterization of diethyl 4-methylpiperazin-1-ylphosphoramidate (CN-3)

To a solution of 1-amino-4-methyl piperazine (3.0 gm, 26 mmol) in dry THF, we added triethylamine (3.64 ml, 26 mmol) in dry THF, and the mixture was cooled to 0 °C. A solution of diethyl chlorophosphate in dry THF was slowly added by addition funnel to the above mixture while stirring under nitrogen. After the addition, the reaction was allowed to warm up to room temperature and monitored by TLC using 10% MeOH/EtOAc as an eluent and iodine as staining reagent. When the reaction was over, a white solid was filtered off. The removal of the solvent gave a yellowish oil as product in 82% yield with no purification needed. ¹H-NMR (400 MHz, CDCl₃) δ-ppm: 1.34 (t, 6H, -CH₃), 2.30 (s, 3H, -CH₃), 2.54 (s, 4H, -CH₂-), 2.83 (s, 4H, -CH₂-), 4.10 (m, 4H, -CH₂-), and 4.70 (d, 1H, ²J_{H-P} = 32 Hz, NH). ¹³C-NMR (400 MHz, CDCl₃) δ-ppm: 16.3 (d, J_{C-P} = 28 Hz), 45.5 (s), 54.4 (s), 57.6 (d, J_{C-P} = 24 Hz), and 62.8 (d, J_{C-P} = 24 Hz). ³¹P-NMR (400 MHz, CDCl₃) δ-ppm: 6.00–6.25 (m), IR (cm⁻¹) 959, 1026, 1143, 1159, 1231, 1459, 2794, 2937, 2977, and 3169. Anal. Calcd for C₉H₂₂N₃O₃P: C = 43.02%, H = 8.83%, N = 16.72%, P = 12.33%. Found C = 42.18%, H = 9.23%, N = 16.90%, P = 12.12%.

Measurements

NMR spectra were recorded on a Varian 400-MHz instrument using CDCl₃ as solvent. ¹H- and ¹³C-NMR are given in δ relative to TMS. ³¹P is given in δ relative to external 85% aqueous H₃PO₄. Elemental analyses were carried out on a 2400 series II CHNS/O Analyser, PerkinElmer and ICP Leeman Labs Prodigy/Prism at 253 and 561 nm. FT-IR spectra were recorded in a Bruker Vertex 70 spectrometer equipped with a MIRacle ATR accessory (Pike Technologies) fitted with a diamond/ZnSe crystal plate. Samples were placed atop the crystal plate without any special preparation. A scan of the clean crystal plate was used as the background. All reported spectra were collected with a spectral resolution of 4 cm⁻¹ and are shown as the co-addition of 64 scans. Spectra are presented without modifications. Fabric degradations were observed for treated and untreated fabrics. Vertical flame tests were performed on strips of fabric (30 × 7.6 cm) according to ASTM D-6413-08.^[22] LOI tests were conducted using strips of fabric (13 × 6 cm) according to ASTM D2863-09.^[23] Thermogravimetric analyses were performed using a TA Instruments Q500 under nitrogen and air conditions. Analyses were monitored between 20 and 600 °C at a heating rate of 10 °C/min and a flow rate of 60 ml/min. The onset of degradation^[24] and char contents at 600 °C were obtained from TGA thermograms. SEM experiment was performed on Philips XL 30 ESEM with a magnification of 1500×. Samples were coated with gold for analysis purposes.

Analyses were carried out on different regions of print cloth and twill fabrics: treated/unburned, treated/edge, and treated/burned.

Fabric treatment

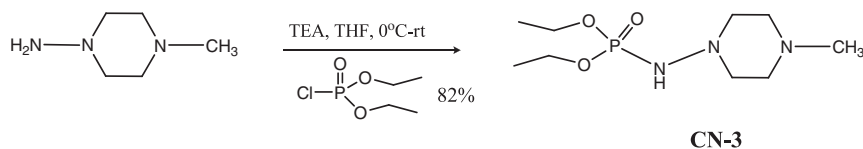
Cotton fabrics were treated with 30% aqueous isopropanol formulations containing various percentages of diethyl 4-methylpiperazin-1-ylphosphoramidate (CN-3). Fabric samples were immersed in the treatment solution overnight for thorough wetting, then padded (10 psi), dried (100 °C, for 5 min), and cured in air (160 °C, for 5 min).

RESULTS AND DISCUSSION

Syntheses and structural characterization of CN-3

Diethyl 4-methylpiperazin-1-ylphosphoramidate (CN-3) was synthesized in one simple step in high yield of 82% (Scheme 1). Starting materials were available at low cost. There was no purification required and thus made the synthesis very accessible. No previous report on the synthesis of CN-3 has been found. CN-3 readily dissolved in most solvents such as MeOH, THF, CH₃CN, EtOAc, CHCl₃, CH₂Cl₂, and acetone. Figure 1 presents the ¹H-NMR, ¹³C-NMR, and ³¹P-NMR of CN-3. ¹H, ¹³C, ¹⁵N, and ³¹P all have the same spin quantum number *I* = 1/2, which gives rise to coupling interactions that split ¹H-³¹P, ¹³C-³¹P, and ¹⁵N-³¹P resonances by the 2*nI* + 1 rule. This explains the doublet patterns in all proton, carbon, and phosphorous spectra. In ¹H-NMR, the doublet at 4.70 ppm with *J* = 32 Hz corresponds to the two-bond P-H coupling constant of NH proton.^[25] The multiplet at 4.10 ppm is attributed to the -CH₂- of the phosphate group because these protons not only couple with -CH₃ proton but also couple with phosphorous. Two singlets at 2.83 and 2.54 ppm are protons of the piperazine ring. One singlet at 2.30 ppm corresponds to -CH₃ of the piperazine ring. A triplet at 1.34 ppm is due to the -CH₃ of the phosphate group. The ¹³C presents two doublet resonances at 15.9 ppm (*J* = 27.2 Hz) and 62.8 ppm (24.4 Hz) belonging to carbons of the phosphate group (based on the ¹³C-NMR of phosphate reagent). One doublet at 57.3 ppm (*J* = 21.2 Hz) is carbon from NH-N-C. The resonance of phosphorous is in a form of two multiplets resulting from the heteronuclear coupling between ³¹P and ¹⁵N nuclei and then ³¹P and ¹H and ³¹P and ¹³C.^[26]

In Fig. 2, the FTIR data of CN-3 (top) show the absorption of NH at 3169 cm⁻¹, which is very much the same position as in normal amines. The NH stretching and deformation vibrations are barely affected by the presence of the phosphorous atom.^[27] The absorption band of saturated carbon (sp³) is observed at 2977 to 2936 cm⁻¹.^[28] The stretch at 2794 and 1378 cm⁻¹ corresponds to the vibration of tertiary nitrogen of NCH₃, and the deformation vibration of the methyl group attached to nitrogen, respectively.^[29] The absorption band of the secondary amine is seen at 1459 cm⁻¹. P=O stretches show at 1231, 1159m and 1142 cm⁻¹. The first absorption represents P=O frequency with two O-Alkyl groups and NHR group attached.^[30] The next two absorptions can be contributed to the stretching bands of hydrogen bonding between P=O and neighboring NH.^[27] The P-O-ethyl vibrations fall in the normal range, 1026–959 cm⁻¹, as extremely strong absorption.^[27,31,32] In addition, the absorption at 790 cm⁻¹ corresponds to the P-N single-bond vibration arising from the perturbation of -N-(C)₂ attached to the nitrogen atom of NH.^[33]



Scheme 1. Synthesis of diethyl 4-methylpiperazin-1-ylphosphoramidate (CN-3).

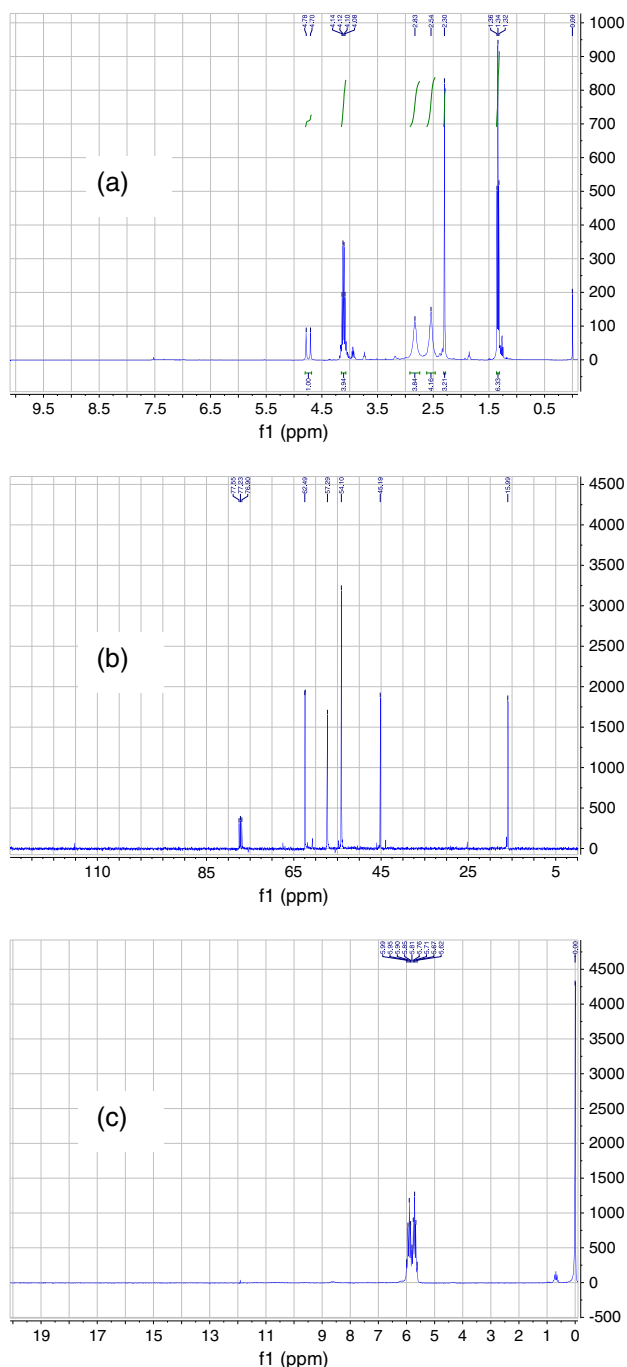


Figure 1. ^1H -, ^{13}C -, and ^{31}P -NMR spectra of diethyl 4-methylpiperazin-1-ylphosphoramidate (CN-3): (a) ^1H -NMR, (b) ^{13}C -NMR, and (c) ^{31}P -NMR (close-up). This figure is available in colour online at wileyonlinelibrary.com/journal/pat

Fabric treatment

Cotton twill and print cloth fabrics were treated with solutions of CN-3 (w/v in 30% aqueous isopropanol) at room temperature. The add-on values are summarized in Table 1. At this point, no attempt was made to test the durability of the FR with multiple laundering tests.^[34] After application, drying, and curing, the treated samples appeared white. Samples of 22% print cloth and 18% twill were washed by stirring in 40 °C water for 10 min and then dried and cured. The original add-ons in both were reduced to 83% to 84% after the first wash and remained the same after the third wash.

FTIRs of CN-3 and control and treated print cloth and twill fabrics are presented in Fig. 2. The treated fabrics show the absorption of P=O with (O-alkyl)₂ and NHR attached at 1231 cm⁻¹ and P-N with perturbation effect at 790 cm⁻¹. These stretches are observed originally in CN-3.

The content of nitrogen and phosphorous was determined analytically for each add-on sample with three observations for nitrogen and six observations for phosphorous. The results were summarized in Table 2 and presented graphically in Fig. 3. It is apparent that the content of phosphorous and nitrogen increases with the increase of add-on value, and nitrogen content is always higher than phosphorous content in each sample. Nitrogen has been recognized to play a role in fire retardancy and adding nitrogen often reduces the need for phosphorous.^[35] The graphical P-N synergistic effect for a variety of phosphorus-nitrogen systems on cotton twill showed that P + N should be 3.5% to 6% for flame retardancy.^[12,36] Table 2 shows that this combination was achieved at 8, 13, and 18 wt% add-on in treated twill and at 16 and 22 wt% add-on in treated print cloth.

Thermal properties of treated fabric

The thermal degradation data were obtained in a nitrogen atmosphere. Values of char content (% at 600 °C) for compound CN-3, untreated and treated twill, and print cloth fabric samples at different add-ons are listed in Table 3.

Untreated print cloth fabric degraded at 323 °C and showed a char residue of 3% of the original weight at 600 °C. When print cloth treated with CN-3 at 7–22 wt% add-on were degraded, they showed onsets of degradation between 132 and 263 °C and provided char yields between 18% and 23%. The comparison of print cloth samples and compound CN-3 degradation by TGA is depicted in Fig. 4a. Untreated twill fabric showed an onset temperature at 327 °C and char residue of 2% of the original weight at 600 °C. Treated twill with CN-3 at 3–18 wt% add-ons were degraded between 138 and 266 °C and provided char yield between 19% and 22%. Degradation of twill samples and compound CN-3 is presented graphically in Fig. 4b. It is apparent that the rapid degradation of CN-3 occurs earlier at 153 °C and later at 429 °C, and char yield was 4% at 600 °C compared with untreated and treated fabric samples. The char percentage appears to be higher in high add-on (22 wt% print cloth and

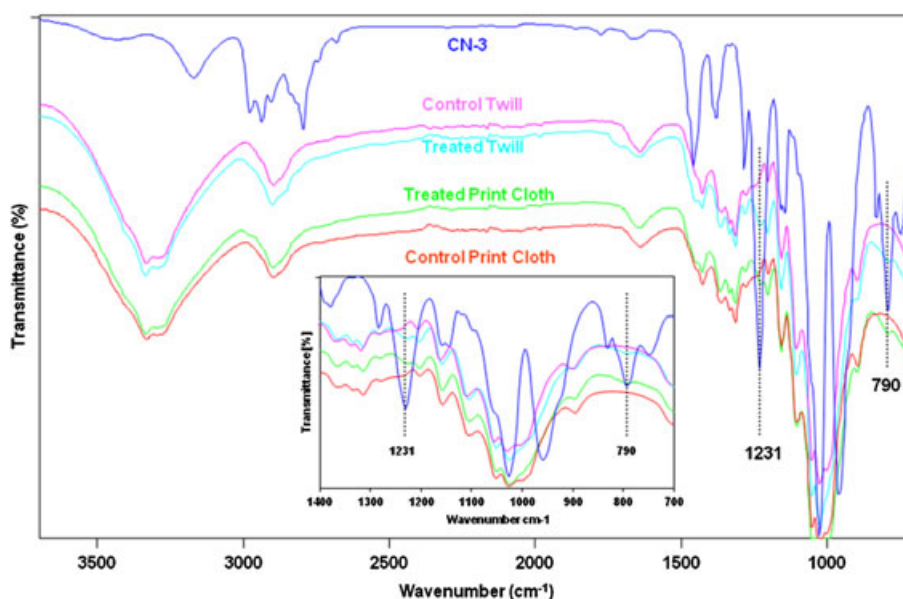


Figure 2. FTIR of diethyl 4-methylpiperazin-1-ylphosphoramidate (CN-3), control and treated (18 wt%) twill, and control and treated (22 wt%) print cloth. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

Table 1. Add-ons (wt%) after cure of treated twill and print cloth fabrics with CN-3

Samples numbers	Twill add-on (wt%)	Print cloth add-on (wt%)
1	3	7
2	8	10
3	13	16
4	18	22

Table 2. Content of nitrogen (average of three trials) and phosphorous (average of six trials) in treated twill and print cloth fabrics

Add-on (wt%)	Twill			Print cloth			
	%N	%P	%N + %P	%N	%P	%N + %P	
3	1.25	0.90	2.15	7	1.44	1.16	2.60
8	2.00	1.50	3.50	10	1.55	1.22	2.77
13	2.04	1.74	3.78	16	2.03	1.73	3.76
18	3.25	2.70	5.95	22	2.27	2.10	4.37

18 wt% twill) samples than in low ones (7 wt% print cloth and 3 wt% twill) and untreated samples. Between treated samples of the same or different fabric types, the changes in char residue are not significant.

As shown in Table 3, the low add-on samples of print cloth (7 and 10 wt%) and twill (3 and 8 wt%) have onset of degradation close to the onset of degradation of untreated ones (323 °C for untreated print cloth and 327 °C for untreated twill). When CN-3 presents in a sufficient amount (16 and 22 wt% for print cloth and 13 and 18 wt% for twill) to act as an FR, the treated fabrics appear to have two onsets of degradation. Their first onset

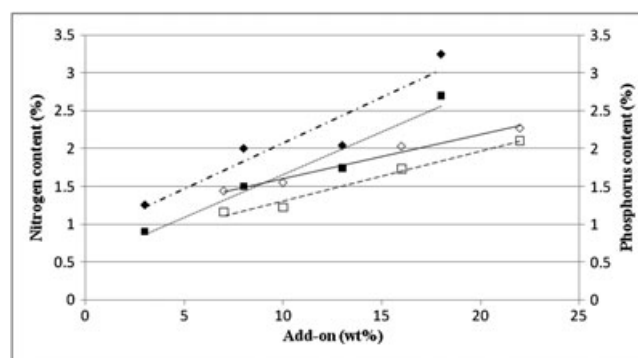


Figure 3. Content of phosphorous and nitrogen in treated fabrics: %N in twill (♦), %P in twill (■), %N in print cloth (◇), and %P in print cloth (□).

Table 3. Degradation and char content determination of CN-3 and different add-ons (wt%) of treated print cloth and twill fabrics by TGA at 600 °C in nitrogen atmosphere (two observations for each sample)

Samples	Onset of degradation (°C)	Char at 600 °C (%)	
CN-3	153, 429	4	
Print cloth (add-on, wt%)	0	323	3
	7	263	18
	10	258	19
	16	151, 251	20
	22	132, 238	23
Twill (add-on, wt%)	0	327	2
	3	266	19
	8	259	21
	13	148, 253	22
	18	138, 252	22

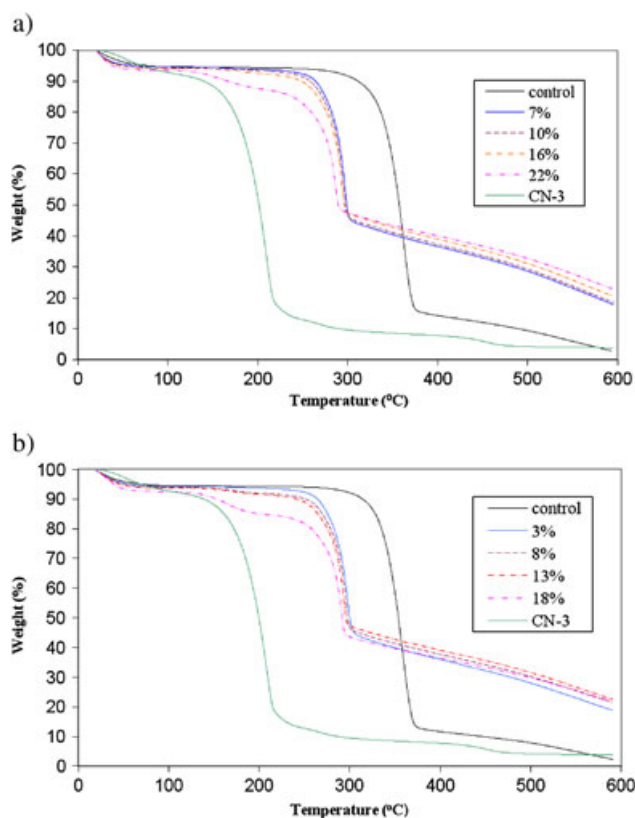


Figure 4. Degradation thermograms of compound CN-3, control, and treated fabrics at various wt% add-ons for (a) print cloth and (b) twill. This figure is available in colour online at wileyonlinelibrary.com/journal/pat

temperature is close to the first onset of degradation of CN-3, and their second onset of degradation is close to the onset of degradation of the lower add-ons and untreated samples. Generally, the FR is expected to decompose before or near the decomposition temperature of the substrate to interfere with the burning process.^[37] Because the first thermal decomposition temperature of CN-3 (153 °C) is lower than those of untreated twill and print cloth fabrics, CN-3 decomposes before the untreated fabrics and suppresses the burning process of the fabrics. This might be the explanation of two onsets of degradation in high add-on samples and how close they are to the onsets of degradation of CN-3 as well as the low add-on samples. It is known that FRs increase the rate of decomposition and lower the decomposition temperature.^[38] In the case of phosphorous-containing FRs, FRs can reduce cellulose inflammability, primarily by dehydration, phosphorylation, and phosphate-ester decomposition mechanism. This can inhibit the release of volatile combustible fragments, enhance char formation, and therefore lower the onset of degradation.^[37] The inverse relationship of the applied amount of FRs and the decomposition temperature is also observed in the treatment of fabrics with CN-3 and is presented in Fig. 5.

Flame retardant performance

To evaluate the FR properties of CN-3, we investigated two important parameters: vertical flammability and LOI. Vertical flammability test results in Table 4 and Fig. 6 show the effectiveness of CN-3 as an FR when applied on twill and print cloth fabrics at add-on levels of 13, 18, and 22 wt%, respectively. Twill fabric shows flame retardancy at lower add-on compared with print

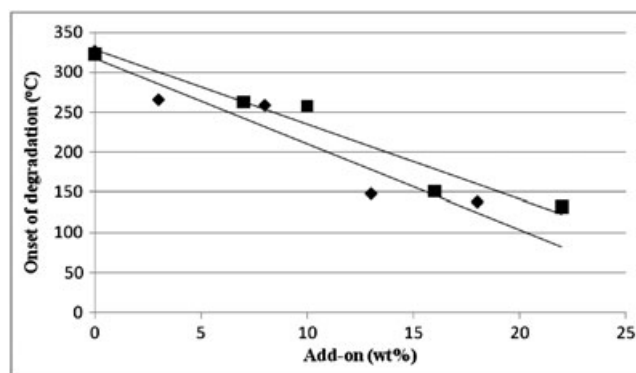


Figure 5. Onset of degradation versus add-on value in twill (♦) and print cloth (■). For higher add-ons, first onset temperature was selected.

cloth. There are many factors that influence the add-on on fabrics. They include the type of fiber (cotton, Lycra, embroidery, etc.), the type of fabric (woven, knitted, nonwoven), the structure of fabric (plain, weave, twill, satin, etc.), the construction of fabric (weight of fabric per unit area), and the treatment conditions (in dipping, drying, curing, etc.). Print cloth and twill samples in this experiment were cotton, and they were treated in the same way. The possible cause for different add-on can be the construction of fabric. As mentioned in the Materials section, the weight per unit in print cloth was much lighter than that in twill. As the result, there is more space for air or oxygen to occupy in print cloth. Therefore, print cloth needs to pick up more CN-3 to become FR.

There was no after-flame or after-glow for all three samples. Char lengths were 2.0–2.5 cm for 18 wt% and 2.5–4.0 cm for 13 wt% of twill and 4.0–5.0 cm for 22 wt% add-on of print cloth. Samples with 3 and 8 wt% add-ons of twill had after-flame burning of less than 20 sec with the char length more than 30 cm and no after-glow. The 10 and 16 wt% add-on samples of print cloth also had the char length more than 30 cm and no after-glow but less than 10 sec of after-flame burning time. The 7 wt% add-on sample of print cloth did not have both after-flame and after-glow and the char length was also more than 30 cm.

The flame retardancy of CN-3 is further supported by average LOI results. As shown in Table 4, the amounts of oxygen required to burn to the 5-cm line were 31 vol% for 18 wt% add-on and 29 vol% for 13 wt% add-on of twill and 28 vol% for 22 wt% add-on of print cloth. The required time to burn to the 5-cm line ranged from 41 ± 5 to 44 ± 6 sec for twill samples and 20 ± 3 sec for print cloth sample. Because air is composed of approximately 21 vol% oxygen by volume, any material with an LOI of less than 21 will burn easier in air. Materials that rank in the 21 to 27.9 vol% range are known as slow burning. Above this range, materials are considered to be self-extinguishing.^[39] For 3 and 8 wt% add-on of twill and 7 and 10 wt% add-on of print cloth, LOI test showed that the 5-cm line burned within 50 ± 5 to 63 ± 2 sec and 24 ± 2 to 27 ± 2 sec when 24 to 27 vol% and 23 to 25 vol% oxygen were supplied, respectively. On the basis of vertical flammability and LOI results, it can be concluded that CN-3 acts as a good FR when applied on cotton twill and print cloth fabrics at the level of 13 to 18 and 22 wt% add-ons, respectively.

From the results of thermal degradation and LOI testing, it is obvious that the percentage of char at 600 °C and the minimum concentration of oxygen that will support combustion of the treated fabrics increase with the increase of add-on value. This positive relationship is presented in Fig. 7.

Table 4. Vertical flammability test (ASTM D-6413-08)^[1] and LOI test (ASTM D-2863-09)^[2] of treated twill and print cloth fabrics at different wt% add-on

Add-on (wt%)	After-flame time (sec)	After-glow time (sec)	Char length (cm)	Average LOI (%) [σ] ^a and time (sec) [σ] to burn to the 5-cm line
Twill	3	14–19	0	>30
	8	17–18	0	>30
	13	0	0	2.3–4.0
	18	0	0	2.0–2.5
Print cloth	7	0	0	>30
	10	2–4	0	>30
	16	3–7	0	>30
	22	0	0	4.0–5.0

^a[σ] = standard deviation.

Microstructure studies of different regions of twill and print cloth fabrics

The microstructures of treated/burned, treated/edge, and control/burned areas of twill and print cloth fabrics are presented in Fig. 8. All burned samples were collected at the area where flame contacted with the fabrics and turned the fabrics from white to black. Treated/edge sample was obtained in the region between the burned and the unburned area and appeared to be brown. All samples were obtained after vertical flammability testing.

It can be seen that compound CN-3 acts the same on both types of fabric. The surface of treated/edge (Fig. 8A) shows material that appears to be frothy and swollen. The occurrence of the blisters (nodules) can be due to the entrapment of decomposition gases in the coating of CN-3 on the surface. In the treated/burned area, these nodules become bigger because the high heat causes the

expansion of gases (Fig. 8B). The internal pressure of these blisters continues to form and causes the explosion to release the built-up gases as seen in Fig. 8C, the low-magnification image of Fig. 8B. As seen in Figs 8B and 8C, the structure of cotton is not destroyed when the fabric is being burned.

The untreated fabrics are completely burned up in the air when flame is applied (Fig. 8D). The outer surface of its residue is more threadlike because during ignition, the cotton component is the initial and only source of fuel, which is first decomposed and caught fire and subsequently burned intensely. There are no additional chemicals or substances to cohere these threads together as seen in other case.^[40]

Possible mechanism of CN-3 on cotton fabrics

CN-3 belongs to the phosphoramidate class. Much of the chemical interest in this class of compounds is due to the presence of the P–N bond and its susceptibility to cleavage in aqueous acidic solution.^[41–43] Hydrolysis in alkaline solution leads principally to P–O bond cleavage.^[44] Phosphoramidates can thermally decompose. In this case, they can be transformed to acidic intermediate via several possible reaction pathways, depending on the group attached to the nitrogen.^[45] P–O bond cleavage in transesterification or P–N bond cleavage in hydrolysis is proposed depending on the environment and the substituent on the nitrogen. In the case of CN-3, transesterification is expected to happen because the cellulose is mercerized and physically absorbed

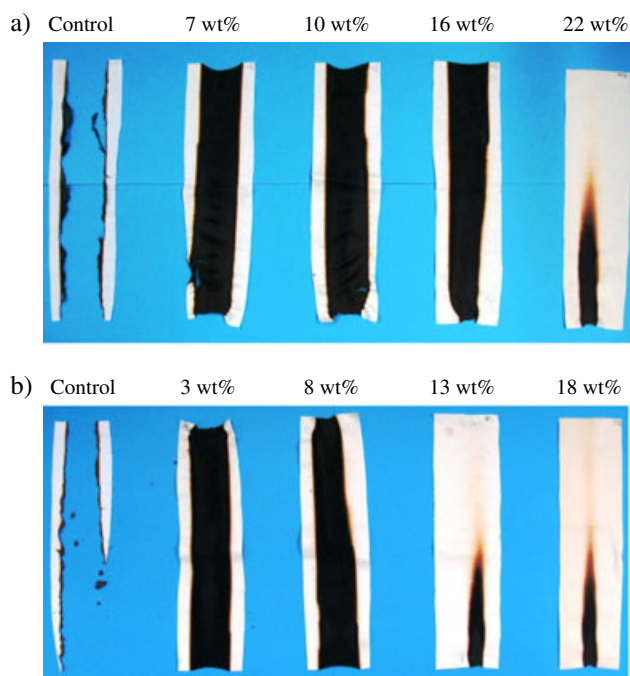


Figure 6. Vertical flammability test results of (a) control and treated print cloth fabric and (b) control and treated twill fabric (two trials for each add-on value). This figure is available in colour online at wileyonlinelibrary.com/journal/pat

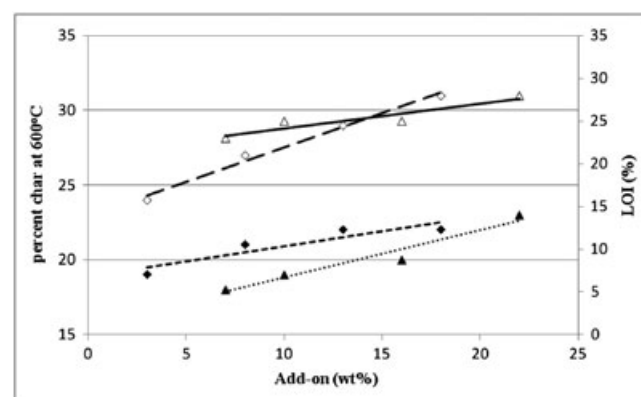
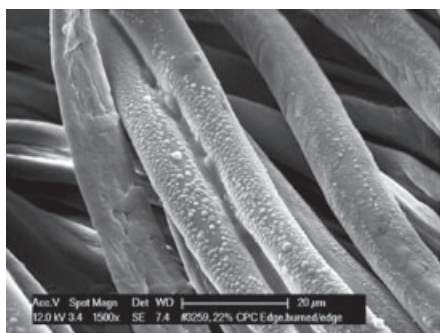


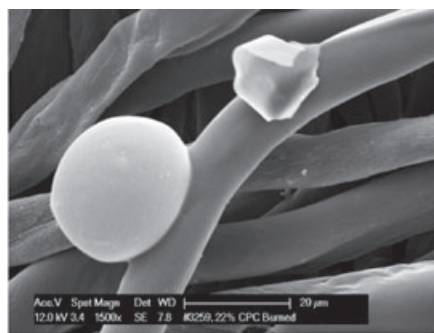
Figure 7. Percentage of char at 600 °C and LOI value versus add-on value in treated print cloth and twill fabrics. ♦ and ◇, ▲ and Δ are the percentage of char and the LOI value of treated twill and print cloth, respectively.

1) Print cloth

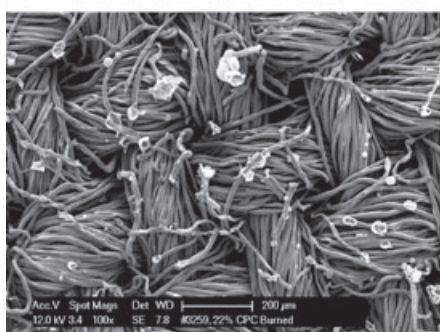
A



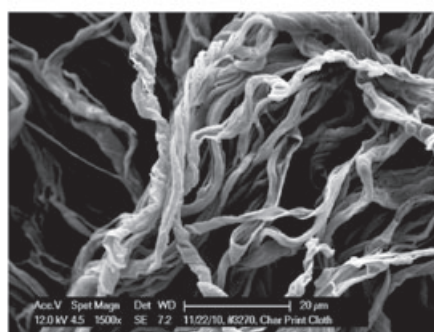
B



C

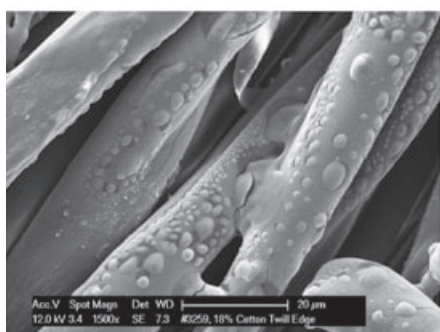


D

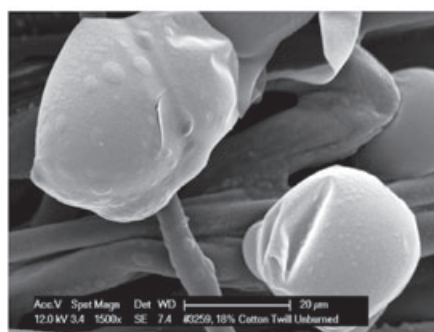


2) Twill fabric

A



B



C



D

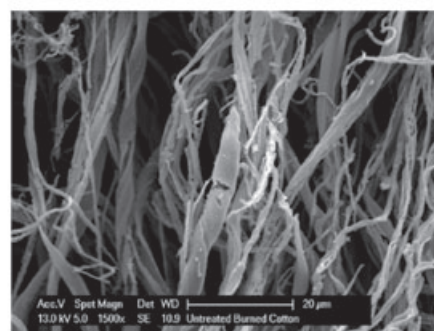
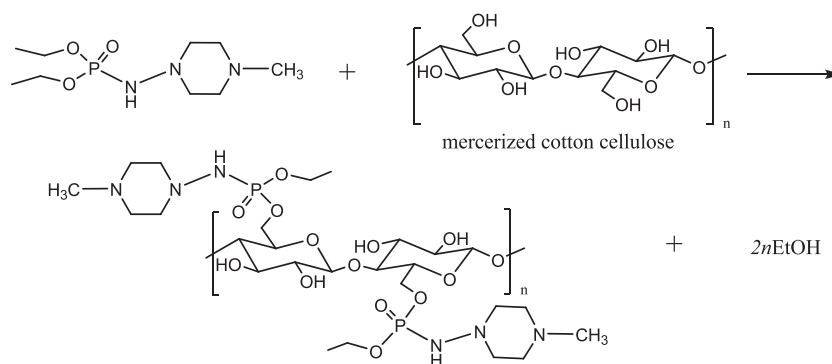


Figure 8. SEM micrographs of different regions of fabric: (1) print cloth (2) twill fabric with.

water in cotton can make the environment slightly basic to catalyze the exchange process between O-Cell and O-CH₂CH₃ at

high temperature. Moreover, FTIR data of treated twill and print cloth show the absorptions at 1231 and 790 cm⁻¹, which



Scheme 2. Thermal decomposition of cotton cellulose treated with diethyl 4-methylpiperazin-1-ylphosphoramidate (CN-3).

represent P=O frequency with O-Alkyl and NHR groups attached and P-N with perturbation effect, respectively. Scheme 2 postulates the reaction between the CN-3 and the cotton cellulose.

CONCLUSIONS

A novel reactive FR, CN-3, for cotton twill and cotton print cloth fabrics was successfully synthesized and characterized by reacting 1-amino-4-methyl piperazine with diethyl chlorophosphate. The decomposition of CN-3 in nitrogen by TGA occurred at 153 °C, and char yield was 4% at 600 °C.

For FR fabric treatment, twill and print cloth fabrics were soaked in a 30% aqueous isopropanol formulation at room temperature, dried at 100 °C for 5 min, and cured at 160 °C for 5 min dwell time. After applications, treated fabrics were cured to afford add-on values of 7 to 22 wt% for print cloth and 3 to 18 wt% for twill fabric. TGA results showed that compound CN-3 and the treated print cloth and twill fabrics were degraded at much lower temperatures and produced higher char yields at 600 °C in nitrogen compared with that of untreated fabrics.

Treated fabrics exhibited FR properties in vertical flame and LOI testing. They passed the vertical flame test when add-on values were 22 wt% for print cloth and 13 and 18 wt% for twill. Their char lengths were less than 50% of the original fabric with no after-flame and after-glow times. Untreated fabric showed an LOI value of 12 vol% for print cloth and 18 vol% for twill, whereas treated print cloth and twill appeared to have 28 vol% and 29 and 31 vol% of LOI value, respectively. SEM micrographs indicated that treated fabrics could form a protective layer, which prevented the fabric from being burned completely. Further investigation to improve the durability is underway.

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