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Preparation and properties of a washable flame-retardant coated fabric

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In this study, a flame-retardant-coating (FRC) agent has been prepared using hydrophobic organic silicone-phosphorus-nitrogen flame retardant and acrylic emulsion. Polyester-cotton blend fabric (P/C) has been treated with FRC agent, and the finishing process, thermal decomposition, flame retardancy, washability, softness and other properties are studied. Results show that the treated fabrics are of good flame retardancy; LOI is up to 32%, thermal degradation rate reduces by 7.8 %/min and thermal damage reduces by 74%. Limiting oxygen index (LOI) is found to be 24.6% and 23.7% for 5 and 10 times washing. The fastness shows excellent washability.

Keywords: Flame retardant fabrics, Coated fabrics, Combustion performance, Polyester/cotton blend fabrics

1 Introduction

Polyester/cotton blended fabrics (P/C) are widely used in the apparel industry and decorative areas because of their complementary physical and chemical properties. P/C fabric not only has the advantages of synthetic fabric, such as high strength, good wearing resistance, high color fastness, good heat resistance and acid resistance, but also has excellent wearability of natural fabric, such as moisture absorption, breathability, and soft handle. However, P/C blended fabric shows higher flammability than any of the two components of the blend due to its "scaffolding effect" during combusting, hence it is difficult to extinguish fire once it starts burning, thus causing fire disaster by textile burning[1-3]. But flame retardant (FR) textile can slow down fire spread rate, reduce fire hazards and extend escape time, thereby protecting people's lives and property[4]. Hence, the need of study on flame retardant P/C fabric is not only of the great significance to the development of the apparel industry and decorative materials, but also of an urgent challenges[5].

In previous study, researchers developed a crosslinkable phosphorus FR with active group[6, 7], a series of phosphorus-nitrogen synergist FRs[8-9] and an excellent insoluble phosphorus-nitrogen-silicone synergist FRs (SIAP)[10]. In this study, we prepared a FR coating agent with SIAP, acrylic emulsion and thickener, and then investigated the thermal decomposition, flame retardancy, durability, softness and other properties of treated P/C with the FR coating agent.

2 Materials and Methods

2.1 Materials

A 65/35 polyester/cotton twill woven fabric weighing 90g/m^2 supplied by Sichuan Cotton Mill Ltd. An insoluble phosphorus-nitrogen-silicone synergist FRs (SIAP) was prepared using the procedure as reported in the literature[10]. The insoluble ammonium polyphosphate-II (AP) was supplied by Shifang Taifeng New Flame Retardant Ltd. The acrylic emulsion and the thickener were commercial products supplied by Chengdu Guixi Construction Chemical Company. The cyclohexane was supplied by Chengdu Kelong Chemistry Ltd.

2.2 Preparation of SIAP

In a three-necked flask (1000 mL), 500 g ammonium polyphosphate (AP) was uniformly dispersed in 600 mL cyclohexane solvent. And 75 g active organosiloxane was added into the flask under stirring. The mixture was uniformly mixed for 30 min under room temperature, and the solvent was removed at 90 ^{o}C. The mixture was allowed to react for 30 min at 140 ^{o}C and then cooled[10]. The product, i.e. the active organosiloxane modified ammonium polyphosphate (SIAP), was pulverized to fine particles of 25 - 30 μm; 528 g SIAP was obtained, and yield was 91.8%.

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2.3 Blade Coating Process

FR coating agent was prepared with 25% SIAP (w/w) and 75% acrylic emulsion (w/w), then controlled the viscosity (about 2500 mPa·s) with thickener and water, and the finally 42% content of SIAP was obtained in the dry coatings. The FR coating process of P/C blends is shown in Fig. 1. The thickness of coating on fabric was kept 0.3-1 mm by adjusting the gap width between the blade and the cloth or increasing the coating time, by pre-baking at 105 °C for 15 min, and by baking at 130 - 160 °C for 1 - 5 min. Parts of the fabric samples were tested directly without washing, and the remaining parts were first washed according to domestic laundering procedure ISO 10528:1995, and then tested. The add-on %, retention rate (R_{retent}, %) and loss rate (R_{loss}, %) of coating were calculated using the following equations:

$$\text{add-on}\% = \frac{w_t - w_o}{w_t} \times 100 \quad \ldots(1)$$

$$R_{retent}\% = \frac{w_n - w_o}{w_t - w_o} \times 100 \quad \ldots(2)$$

$$R_{loss}\% = \frac{w_{n-1} - w_n}{w_t - w_o} \times 100\% \quad \ldots(3)$$

where w_o and w_t are the weights of the P/C fabrics before and after blade coating with FR coating agent respectively; and w_n denotes the weights of the P/C fabrics after washing n times.

2.4 Flame Retardancy of Treated Fabrics

The LOI values of the samples were measured on an oxygen index flammability gauge (HC-2C, Nanjing Shangyuan Analytical Instruments, Nanjing, China) according to ASTM D 2863-97. The vertical burning test was conducted on a CZF-2 type instrument (Jiangning, China) according to ASTM D 6413-99. This testing method measures the vertical flame resistance of textiles in general, including after-flame time (t_{flame}), i.e. the length of time the material continues to burn after removal of the burner after a 12 s ignition time; afterglow time (t_{glow}), i.e. the length of time the material glows after the flame extinguishes; and char length (L_{char}), i.e. the distance from the edge of the fabric which is exposed to the flame to the end of the area affected by the flame. The horizontal burning test was conducted on a YG(B)815D-II type instrument (Wenzhou Darong Textile Equipment, China) according to FZ/T 01028-1993. The 45° slope burning test was conducted on a YG(B)815D-III type instrument (Wenzhou Darong Textile Equipment, China) according to GB/T 14644-1993. The both of the tests methods measure flame spread time and char length (L_{char}). The flame spread rate (v_{spread}) was calculated using the following equation:

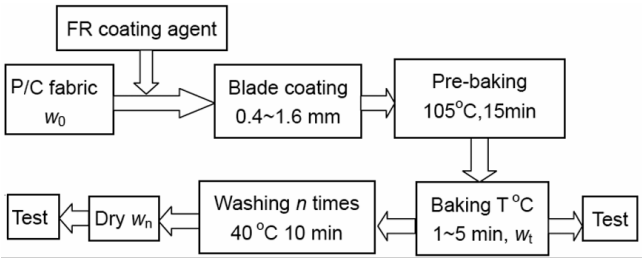

Fig. 1—Schematic diagram of blade coating process of P/C fabrics

$$v_{spread} = \frac{L_{char}}{t_{spread}} \quad \ldots(4)$$

where t_{spread} is the length of time the fabric continues to burn after removal of the burner after a 12 s ignition time; L_{char}, the distance from the edge of the first line in the fabric to the end of the area affected by the flame.

2.5 Thermal Analysis

TGA and derivative thermogravimetry (DTG) of FR, treated and untreated fabrics were conducted on a Synchronization Thermal Analysis STA 449C (Netzsch, German) measurement at a heating rate of 10 °C/min. Aluminum sample pans were used. The samples (5-7 mg) were heated in the analyzer at temperatures ranging from 40 °C to 580 °C under N_2 at a flow rate of 45 mL/min.

2.6 Relative Softness of Fabric

The relative softness of fabric was measured on a module with 45° slope. FR-P/C samples (20 mm × 150 mm) were placed on the plane of modules; the front edge of the sample was kept close to the top of 45° slope. The sample moved forward at 60 mm/min until its front edge bent to touch the slope, then measured the distance traveled (d) by sample. The relative softness was calculated using the following equation considering the average value of three repeated test:

$$\text{Soft}_{relative} = \frac{d_{FR}}{d_0} \quad \ldots(5)$$

2.7 Tensile Breaking Strength of Fabrics

The tensile breaking strength was performed on YG 026C electronic fabric strength tester (Nantong Sansi Textile Technology, China) according to GB/T 3923.1-1997 method, considering fabric samples width 50 mm, clamping length 200 mm, jog rate 100 mm/min and the test rate 100 mm/min.

2.8 Boiling Water Blot Test

Three black fabric samples (70 mm×70mm) were placed on a horizontal plane with the coating side down, and 2 mL boiling water (97 - 100 ^{o}C) was dropped vertically to the central place of the non-coated side, then they were dried for 12 h through natural ventilation. If no white blot appeared on the surface of the three samples, the test was passed. If a white blot appeared on the surface of any two samples, the test was not passed. If a white blot appeared on the surface of single sample, the test need to be repeated for three samples according to the foregoing method.

3 Results and Discussion

3.1 Effect of Add-on of Coating on Tensile Strength and Relative Softness

An effective method to improve the flame retardancy is to increase FR content on fabric (improve P%) [5]. Table 1 shows that the coating add-on is controlled from 17.5% to 70.7%, the content of FR SIAP on fabric reaches from 2.63% to 10.50%, and the content of phosphorus (P%) on fabric reaches 0.79-3.15%. However, with the increase in FR content, the tensile breaking strength decreases significantly from 17160 N•m^{-1} to 12410 N•m^{-1} (28% reduction), and the relative softness is increased 2.1 times. For 56.2% add-on, the retention of tensile breaking strength is 81% (general standards, decline rate of tensile breaking strength is ≤20%), and relative softness is increased 1.84 times, which can meet the standards. The coated fabrics can be used as seat fabrics, decorative fabrics and so on.

3.2 Effect of Baking on Tensile Strength

Figure 2(a) shows that the increase in baking temperature reduces the tensile breaking strength by 32% from 17160 N•m^{-1} to 11710 N•m^{-1}. The retention of tensile breaking strength is found to be 84% under 150 ^{o}C curing. As can be seen from Fig. 2(b), with the increase in baking time, the tensile breaking strength decreases by 27% from 17160 N•m^{-1} to 12320 N•m^{-1}. The retention of tensile breaking strength is found to be 85% under 150 ^{o}C curing for 3 min. So, the optimum baking is found to be 150 ^{o}C for 3 min.

3.3 Burning Performance

The data of vertical, horizontal and 45^{o} slope burning test of samples are shown in Table 2. It is observed that when the coating add-on is higher than 42% (P% >1.89%), the LOI is more than 27.9% and their all burning test can be up to self-extinguishing (i.e. B1 rank). The results show that SIAP is a good FR for P/C fabric.

As can be seen from Fig. 3(b), during the vertical burning test, amount of white smoke produces while igniting, and the fire is self-extinguished after igniting for 12s, carbon length is only 43 mm. The coated fabric is charred significantly [Fig. 3(c)], but the char of the non-coated side remains gray and black, and the original appearance of fabric is completely maintained [Fig. 3(d)], but it does not become ashes.

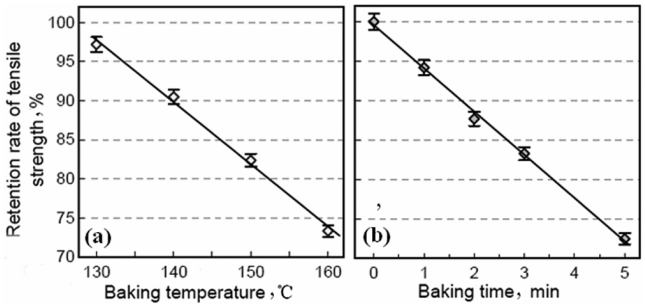

Fig. 2—Effect of baking temperature (a) and time (b) on tensile strength after washing once

Table 1—Effect of add-on of coating on tensile strength and softness considering *at* 140^{o}C for 3 min and washing once

Trial	Coating add-on %	SIAP%	P%	Tensile breaking strength, N.m^{-1}	Retention of tensile strength %	Soft$_{relative}$	Decline rate of softness %
0	-	-	-	17160±30	100	1.00	-
1	17.5	2.63	0.79	16940±10	98	1.18	18.3
2	28.1	4.20	1.26	16230±20	95	1.28	27.7
3	35.2	5.25	1.58	15480±20	90	1.43	33.0
4	42.4	6.30	1.89	14810±30	86	1.62	42.1
5	56.2	8.40	2.52	13880±20	81	1.84	54.0
6	70.7	10.50	3.15	12410±30	72	2.10	69.5

Table 2—Data of treated fabrics burning test

Trials	Add-on %	LOI %	Horizontal[a] mm/min		45° slope[a] mm/min	Vertical burning test[a]			
			v_{max}	v_{aver}	(v)	T_{flame}, s	T_{glow}, s	L_{char}, mm	Rank
0	-	17.2±0.1	9/9	7/7	340/340	Burn up	Burn up	Burn up	Failed
1	17.5	24.8±0.3	52/71	48/64	120/158	8/43	0/2	263	Failed
2	28.0	26.7±0.4	0/14	0/12	0/65	0/27	0/0	148	B2
3	35.0	27.3±0.3	0/8	0/5	0/28	0/15	0/0	112	B2
4	42.0	27.9±0.2	0/0	0/0	0/0	0/0	0/0	43	B1
5	56.0	29.6±0.1	0/0	0/0	0/0	0/0	0/0	36	B1
6	70.0	32.9±0.2	0/0	0/0	0/0	0/0	0/0	34	B1

[a]Flame touching coating side / flame touching non-coating side.

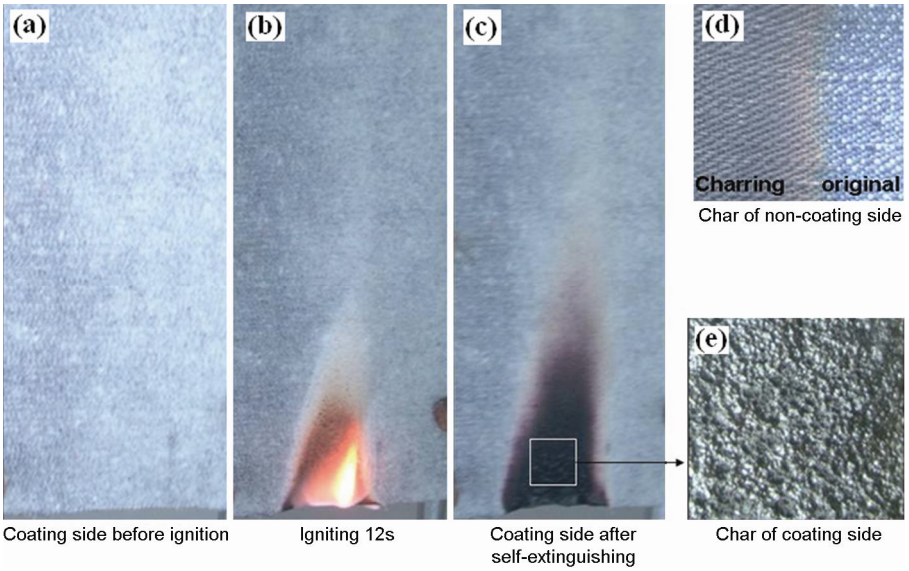

Fig. 3—Digital photos of vertical burning test

The surface of char layer of coated side is uneven but smooth [Fig. 3(e)], which contributes to inhibit the exchange of combustible gas and oxygen to prevent continuous burning.

3.4 Thermal Degradation Performance

TGA is the most effective technique to evaluate the thermal stability of various polymers[6,11] and a favored method for evaluating flame retardancy of organic materials[7]. The data of TGA of SIAP, P/C and FR-P/C fabrics are represented in Table 3. There are main decomposition stages in three TGA curves. The onset decomposition temperature (T_{on}) and the temperatures of maximum weight loss rate (T_{1max} and T_{2max}) of SIAP are found as 217°, 253°, and 360 °C respectively. The maximum weight loss rates (v_{1max} and v_{2max}) of SIAP are 0.4 %/min, and 1.3 %/min respectively. This indicates that the T_{on} and v_{max} of SIAP are all lower than those of P/C fabric. The residue weight ($W_{residue}$) at 580 °C is found very high (80%), which shows that SIAP can play a good role in barrier protection due to difficulty in decompose at high temperature. It is known that phosphorous-containing FRs can reduce cellulose and polyester inflammability, primarily by dehydration, phosphorylation, and phosphate-ester decomposition mechanisms, further forming a crosslinked network within the cellulose and PET. This can inhibit the release of volatile combustible fragments and enhance char formation[12]. Generally, the FR is expected to decompose before or near the decomposition temperature of the substrate to interfere with the burning process[13]. As the thermal decomposition temperatures of SIAP (T_{on}, T_{1max}, and T_{2max}) are lower (127, 106, and 70 °C) than those of P/C, FR treated fabrics are decomposed before the decomposition of untreated P/C blended fibre, which helps to inhibit the burning of the P/C fabrics[12].

As shown in Table 3 and Fig. 4(a), T_{on}, T_{1max} and T_{2max} of the FR-P/C fabric are lower (71, 16 and 39 °C) than those of original fabric. The residue weight ($W_{residue}$) of the untreated and treated P/C fabrics at 580 °C is increased from 23% to 32.4%. The total residue is, respectively, improved by 9.4% (increased 6.5%) in comparison with the theoretical calculated value (25.9%). As the prior decomposition of FR catalyzes the dehydration charring reaction and weakens intensity of pyrolysis of the FR-P/C fabric, its two T_{max} values are shifted towards the lower temperature, and the residue is higher than that of untreated one. This suggests that the FR coatings on the fibre may have reduced the flammability via SIAP dehydration into char[8].

Both the treated and untreated P/C fabrics show two significant stages of weight loss [Fig. 4(a)]. The first and second stages are the pyrolysis of cotton and polyester components respectively. The 1st pyrolysis stages of untreated and treated P/C fabrics are prolonged from 4 min to 10 min. The 2nd stages of them are prolonged from 8 min to 9 min. The end temperature (T_{end}) in 1st and 2nd pyrolysis stages of treated P/C fabrics are found lower, i.e. 11°C and 1°C than those of original fabrics respectively. The results show that SIAP is more FR effective for cellulose than for polyester [13]. The weight loss (W_{loss}) during 1st and 2nd pyrolysis stages of them are reduced about 10% and 6%, respectively; the v_{max} of 1st and 2nd stages of them are to reduced to 1.2 %/min and 7.8 %/min respectively. This suggests that the residue of 1st pyrolysis stages can help inhibiting the 2nd pyrolysis stages. The reduction of the decomposition temperature and the enhancement of the residue indicate that the treated fabrics have good flame retardancy[14,15].

As can be seen from Fig. 4(b) and Table 3, there are five endothermic peaks during decomposition of FR SIAP, the maximum peak (281-375 °C) is 3rd one, its absorbing heat is 1223 J/g, the total of decomposition endotherm is 1702.9 J/g. This indicates that a large amount of absorbing heat is very beneficial to drop the temperature of the combustible material, which greatly decreases the generation rate

Table 3—Data of TGA and DTG of SIAP, treated and untreated P/C fabrics

Sample	Add-on %	$W_{residue}$ at 580°C, %	1st stage				2nd stage			
			T_{1on}-T_{1end},°C	T_{1max},°C	v_{1max} %/min	W_{1loss},°C	T_{2on}-T_{2end},°C	T_{2max},°C	v_{2max} %/min	W_{2loss},°C
P/C	0	23.0	344-385	359	8.2	25.6	385-467	430	11.2	48.3
SIAP	-	80.1	217-296	253	0.4	3.0	296-498	360	1.3	13.7
FR-P/C	27.6	32.4	273-374	343	7.0	15.0	374-466	391	3.4	42.6

$W_{residue}$—residue weight; T_{on}—onset decomposition temperature; T_{end}—end *decomposition temperature;* T_{max}—temperature of maximum weight loss*;* v_{max} —maximum weight loss rate*;* and W_{loss} —weight loss at the different pyrolysis stages.

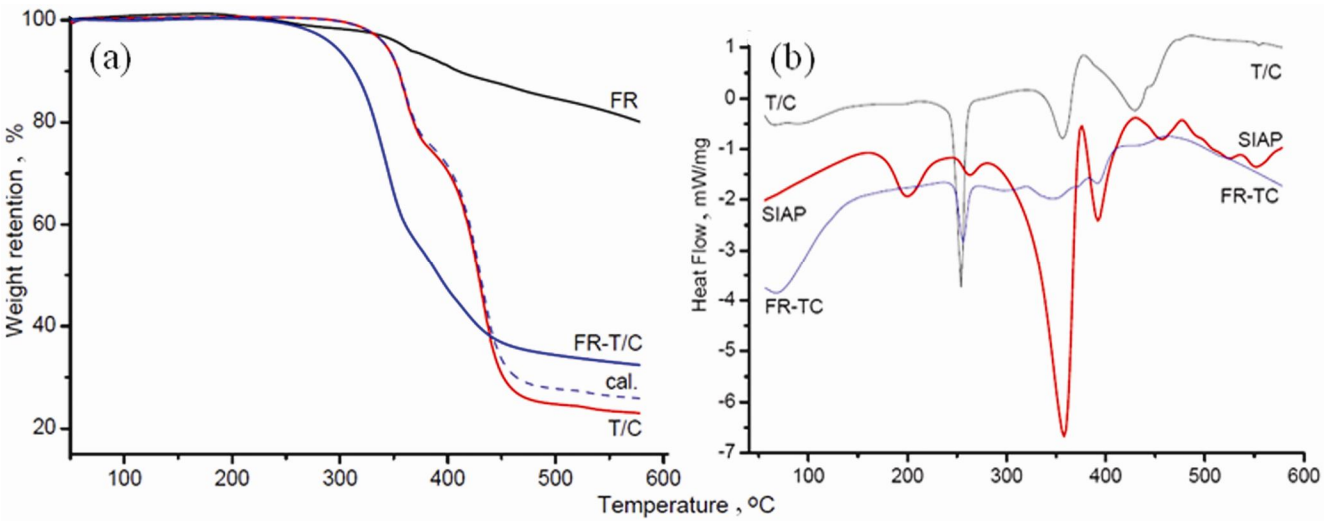

Fig. 4—TGA (a) and DSC (b) of SIAP, P/C and FR-P/C in N_2 at heating rate of 10 °C/min

of combustible fragments during polymer pyrolyzing, and shows excellent absorbing-heat flame retardant mechanism [16, 17].

From Fig. 4(b), it is clear that there are three endothermic peaks in DSC curve of untreated P/C, the first endothermic peak shows melting process of polyester component, and the 2nd and 3rd peaks show the thermal decomposition process of the cotton and polyester components respectively. However, five endothermic peaks are appeared in DSC curve of FR-P/C. The 1st peak is still melting peak of polyester component, but the endothermic peaks in the decomposition process become many and small due to complex pyrolysis process. Table 4 shows that the maximum endotherm is 66.7 J/g, and the total endotherm of FR-P/C decreases from 678 J/g to 175.5 J/g, lowered by 74%. The results indicate that the char layers greatly weaken the heat transfer to internal fibre due to the barrier effect during thermal decomposition of treated P/C fabric with SIAP, the degradation process of fibre becomes slower and slower. This again shows that SIAP is an effective flame retardant for P/C fabric[18,19].

3.5 Boiling Water Blot Test

Table 5 shows that all the samples have no blot appearing except for trial **1**. As FR SIAP has good hydrophobic properties, almost insoluble in boiling water[10], P/C fabrics show good insolubility in boiling water.

Table 4—Data of DSC of SIAP, treated and untreated P/C fabrics

Sample	Endothermic, J/g					Total endothermic J/g
	1st	2nd	3rd	4th	5th	
SIAP	-152.7	-26.3	-1223	-249.1	-51.8	-1702.9
P/C	-175.6	-168.1	-334.3	-	-	-678
FR-P/C	-62.6	-13.4	-66.7	-24.6	-8.2	-175.5

3.6 Wash Fastness of FR- P/C Fabrics

To further study the durability of flame retardant[8], the effect of washing times on retention rate and loss rate of coating weight is shown in Fig. 5. Figure 5(a) shows that the retention rate of coating reduces from about 70% after washing once to 45% after washing five times or more, but decreasing trend is found to be slower. The retention rate of coating after 5 washing is found to be more than 45%, and the add-on of coating is more than 17%. Figure 5(b) shows that the loss rate of coating reduces from 25% during first washing to 0.23% after washing five or more times, the largest loss rate is found after washing once, but the decreasing trend is slower, and the loss rate after washing up to four times is found less than 1.8%. It is suggested that FR coating shows good wash fastness[20,21].

Table 6 shows flame retardancy of FR fabrics after washing 1, 5 and 10 times. The add-on of coating is decreased from 30.88% to 18.21% and then 17.81% respectively. The retention rate of coating is decreased from 74.2% to 45.87% and then 44.69% respectively. The P% of fabrics is reduced from 2.93% to 0.81% and then 0.57% respectively. The LOI is up to 26% for Ist washing and then gradually reduces with washing; LOI is found to be 23.7% for

Table 5—Data of boiling water blot test for FR fabrics (washed once)

Trials	add-on %	Boiling water blot test			Results
		1st times	2nd times	3rd times	
1	17.5	Yes	Yes	Yes	Failure
2	28.0	No	No	No	Pass
3	35.0	No	No	No	Pass
4	42.0	No	No	No	Pass
5	56.0	No	No	No	Pass
6	70.0	No	No	No	Pass

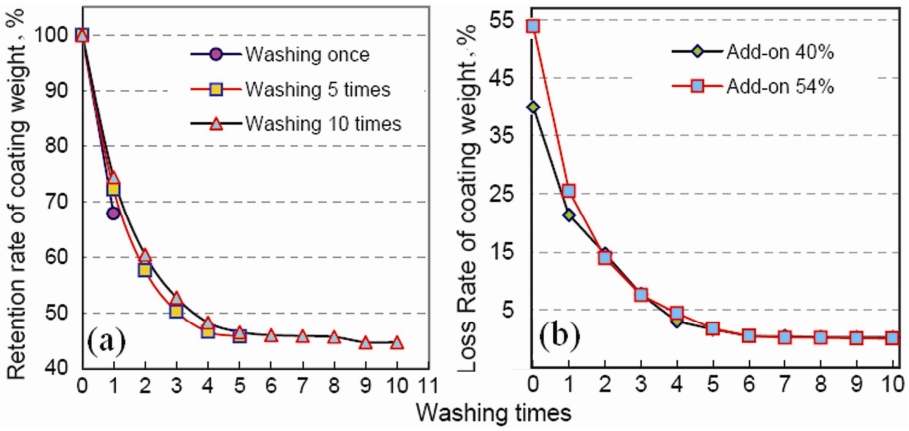

Fig. 5—Effect of retention rate (a) and loss rate (b) of coating weight on washing times

Table 6—Effect of washing times on flame retardancy of FR P/C fabrics

Washing times	Add-on %	P%	Retention rate of coating, %	LOI, %	V_{aver} [a] mm/min
0	39.96	4.87	-	27.1±0.1	0
1	30.88	2.93	74.20	26.2±0.2	15
5	18.21	0.81	45.87	24.6±0.2	53
10	17.81	0.57	44.69	23.7±0.3	61

[a]Horizontal burning test.

washing 10 times. The average burning rate (v_{aver}) is faster from 15 mm/min to 61 mm/min. The results indicate that FR-P/C fabric shows good wash fastness and durability of flame retardant due to insolubility of FR SIAP in water.

4 Conclusion

The polyester/cotton fabrics were treated with SIAP FR coating agent. The optimum blade coating conditions were SIAP 25%, baking at 150 ^{o}C for 3 min and add-on about 42%. It is observed that with the increase in add-on of FR coating, the flame retardancy evidently increases, tensile breaking strength decreases obviously, and softness of fabric increases. The LOI after 1st washing is up to 26%, and more than 23.7% after washing 10 times. The LOI is only lowered by 0.8% by washing 5-10 times. The flame retardant effect of SIAP for cellulose is better than that for polyester. During thermal decomposition of treated P/C fabric with SIAP, the char layers greatly weaken the heat transfer to internal fibre due to the barrier effect, and the degradation process of fibre becomes greatly slower than original fabric. So, SIAP is an effective flame retardant for P/C fabric.

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