

# Application of A Hydrolyzable Cationic Agent, Poly(acryloxyethyl trimethylammonium chloride), in Salt-Free Reactive Dyeing for Good Dyeing Properties

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**ABSTRACT:** Poly(acryloxyethyl trimethylammonium chloride) (PAOTAC), in which cationic groups were connected with the polymer skeleton through ester bonds, was applied in the salt-free reactive dyeing of cotton with the aim of achieving good dyeing properties. Exhaust and exhaust-pad-steam dyeing procedures were used with the cotton cationized with PAOTAC in the absence of salt; for comparison, both dyeing procedures were also applied with the untreated cotton in the presence of salt. The dyeing results show that only the exhaust-pad-steam dyeing procedure was suitable for dyeing cationic cotton to achieve a high dye fixation. Color yields, colorimetric properties, fastness properties, dyeing levelness, and pen-

etration behaviors with different dyeing methods were evaluated. Compared with the dyeings with untreated cotton in conventional exhaust dyeing, dyeings with cationic cotton in the exhaust-pad-steam procedure showed equivalent or even better fastness with generally higher color yields and good dye penetration. Possible reasons for the improved salt-free dyeing properties were proposed, and the hydrolysis of ester bonds within PAOTAC under the dyeing conditions was proven by IR spectroscopy. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2741–2748, 2011

**Key words:** dyes/pigments; fibers; FT-IR; polyamines

## INTRODUCTION

Cotton is one of the most widely used textiles because of its excellent properties of hygroscopicity, air permeability, and biocompatibility.<sup>1</sup> Reactive dyes are a very popular and important class of dyes for dyeing cotton fibers because of their brilliancy, wide range of hues, excellent fastness properties, and so on. As cotton fibers show a slightly negative charge and reactive dyes are anionic in solution, electrolytes, such as sodium chloride or sodium sulfate, need to be added for dye exhaustion on cotton.<sup>2</sup> The release of effluent containing large quantities of salt causes pollution of rivers and streams and upsets the biological equilibrium.<sup>3</sup> Increasing the substantivity of reactive dyes to cotton can reduce or even eliminate salt addition. In this regard, the cationization of cotton with cationic agents to realize salt-free dyeing has attracted great interest of dye chemists all over the world.<sup>4–10</sup>

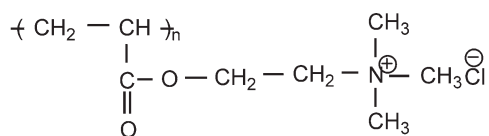
Cationic agents of cotton are mainly quaternary ammonium salts or polymeric amines or amide. Agents with low molecular weights have usually shown low substantivity, poor thermal stability, and high dosage.<sup>11</sup> The application of cationic polymers could have prevented the disadvantages mentioned previously; however, the reported polymers still showed some problems. For example, it was reported that the lightfastness of reactive dyes on cotton was affected by the chemical modification of cotton with polyamide-epichlorohydrin resin/ethylenediamine (PAE/EAD)<sup>12</sup> and *O*-acrylamidomethyl-*N*-[(2-hydroxy-3-trimethylammonium)propyl]chitosan chloride (NMA-HTCC).<sup>13</sup> The poor lightfastness was probably attributed to the presence of dyes mainly on the surface of the fibers, a phenomenon commonly called *ring dyeing*. Moreover, when PAE/EAD was applied, in the cases of H-acid-based reds, some bluing of the shade was noted; this indicated that the reaction with amino groups was responsible. Copolymers containing both quaternary ammonium groups and amino-functional nucleophiles, such as the copolymer of diallyldimethyl ammonium chloride and 3-aminoprop-1-ene, were designed for the physical modification of cotton to enable reactive dyeing at neutral pH.<sup>14</sup> Dye hydrolysis was greatly reduced by this method and washfastness was good, whereas, as reactive dyes were just fixed on the copolymers, it could be imagined that the lightfastness properties could not be very satisfactory.

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poly(acryloxyethyl trimethylammonium chloride) (i.e. PAOTAC)

**Figure 1** Structure of PAOTAC.

In addition, it was also reported that the improved color yield on cationic cotton was due to the adsorption of hydrolyzed dyes on account of electrostatic attraction rendered by cationic sites. Evidence for this was obtained by solvent extraction.<sup>11</sup> Our research also indicated that the reduced colorfastness of reactive dyes was associated with the hydrolyzed dyes staining on cotton.<sup>15</sup> As hydrolyzed dyes were difficult to wash off from cotton in a common soap-off procedure, the colorfastness properties of the dyes were affected.

On the basis of the previous studies, we considered that if the cationic groups of the cationic agents, together with the hydrolyzed dyes, could be removed from the fabrics and if the reactive dyes could penetrate well into the individual fibers and fix on cotton, it would be helpful in retaining the colorfastness and the brightness of the shade.

In this study, we designed a new polymeric cationic agent, poly(acryloxyethyl trimethylammonium chloride) (PAOTAC) (Fig. 1), for cotton to solve the problems mentioned previously. Within the molecules of PAOTAC, quaternary ammonium groups are connected with a carbon-chain backbone through

ester bonds. Under alkaline and high-temperature conditions, the ester bonds were not stable and broke. In this case, with the leaving of the cationic groups from the fibers in the soap-off procedure, the hydrolyzed dyes left away at the same time, and the removal of the staining color became much easier. In addition, to realize good dye penetration and high dye fixation on cotton, we used the exhaust-pad-steam dyeing procedure with the cationic cotton.

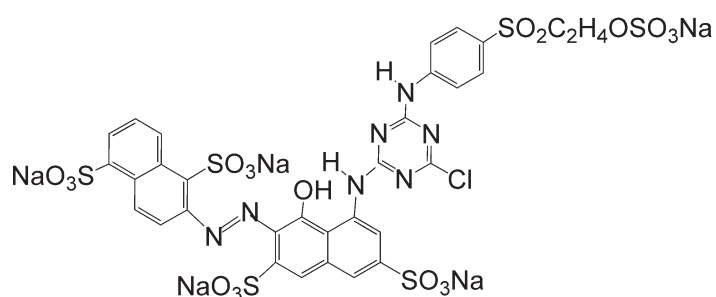
## EXPERIMENTAL

### Materials

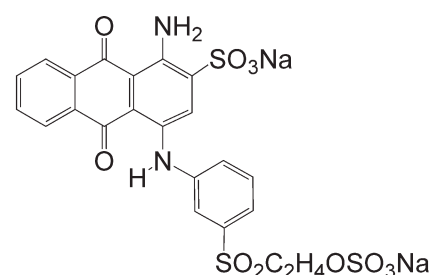
Bleached, scoured, fluorescent, brightener-free woven cotton (150 g/m<sup>2</sup>, Testfibers, Inc., Shanghai, China) was used. Acryloxyethyl trimethylammonium chloride (analytical reagent) was purchased from Guangchuangjin Co., Ltd. (Shanghai, China). The three reactive dyes (Shanghai Dyestuff Co., Shanghai, China) included C. I. Reactive Red 195 (RR 195), C. I. Reactive Yellow 145 (RY 145), and C. I. Reactive Blue 19 (RB 19), and their structures are given in Figure 2.

### Preparation of PAOTAC

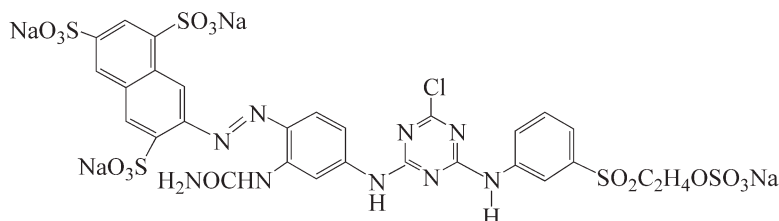
PAOTAC was synthesized as described previously by Takeda and Kawano.<sup>16</sup> The prepared PAOTAC was precipitated in ethanol and washed with acetone to remove any unreacted monomer or oligomers. Finally, the products were freeze-dried for 12 h in a FD-1A-80 vacuum freeze-drying machine (Bo Yi Kang



C.I. Reactive Red 195 (i.e. RR 195)



C.I. Reactive Blue 19 (i.e. RB 19)



C.I. Reactive Yellow 145 (i.e. RY 145)

**Figure 2** Structures of the reactive dyes used in this study.

Experimental Instruments Co. Ltd., Beijing, China). The weight-average molecular weight of PAOTAC was 8700 g/mol and was measured by a gel permeation chromatograph (Waters 1515 pump, Torrance, CA).<sup>17</sup>

#### Pretreatment of the cotton fibers with PAOTAC

Cotton (1.0 g) was dipped into 10 mL of a 2.0% (w/v) PAOTAC aqueous solution at 20°C for 2 min and then padded by a roller with a wet pickup of 80%. Subsequently, the pretreated cotton was baked at 100°C for 5 min in a baker.

#### Dyeing procedure

Exhaust dyeing and exhaust-pad-steam procedures were both used with the untreated and cationic cottons. Dyeing was carried out with a liquor ratio of 20 : 1. The RR 195 applied was 2% omf, the RY 145 was 1% omf, and the RB 19 was 3% omf.

#### Exhaust dyeing with cationic cotton (procedure 1)

The cotton pretreated with PAOTAC was dyed at 30°C for 30 min in a dye bath, and then, the temperature was increased up to the fixation temperature at 2°C/min. This was followed by the addition of 10 g/L sodium carbonate, and the temperature was kept at the fixation temperature for 60 min. The fixation temperature was that recommended by the dye manufacturer (i.e., 90°C for RR 195 and RY 145 and 60°C for RB 19).<sup>18</sup>

#### Exhaust-pad-steam procedure with cationic cotton (procedure 2)

The cotton pretreated with PAOTAC was dyed at room temperature for 30 min in a dye bath. Then, the fibers were taken out and dip-padded in 10 mL of a 10 g/L Na<sub>2</sub>CO<sub>3</sub> aqueous solution within 1 min with 80% wet pickup. The dyed cotton was then dried in air and steamed for dye fixation for 10 min.

#### Exhaust dyeing with untreated cotton (procedure 3)

Untreated cotton was dyed at 30°C for 30 min in a dye bath with the addition of 60 g/L anhydrous sodium sulfate, and then, the temperature was increased to the fixation temperature at a heating rate of 2°C/min. This was followed by the addition of 10 g/L sodium carbonate for dye fixation, and the temperature was kept at the fixation temperature for 60 min. The fixation temperature was that recommended for conventional dyeing (i.e., 90°C for RR 195 and RY 145 and 60°C for RB 19).<sup>18</sup>

#### Exhaust-pad-steam procedure with untreated cotton (procedure 4)

Untreated cotton was dyed at room temperature in a dye bath, and anhydrous sodium sulfate (60 g/L)

was added to the dye bath within 30 min. Then, the fibers were taken out and dip-padded in 10 mL of a 10 g/L Na<sub>2</sub>CO<sub>3</sub> aqueous solution for 1 min with 80% wet pickup. Then, the dyed cotton was dried in air and steamed for 10 min.

#### Washing process

All of the dyed cotton was rinsed successively in cold, hot, and cold water and soaped with Anionic Detergent LS (2 g/L, Shanghai Dyestuff) with a liquor ratio of 20 : 1 for 15 min. Then, the dyed samples were further extracted with an aqueous solution of 50% dimethylformamide (DMF) at boiling for 5 min and then rinsed with water. The bath was dropped, and the fibers were dried.

#### Hydrolysis of PAOTAC in solution

PAOTAC (0.2 g) and 10 mL of water were added to two flasks, and then, we increased temperature up to 100°C with stirring. Then, 0.03 g of Na<sub>2</sub>CO<sub>3</sub> ( $n_{\text{PAOTAC}}:n_{\text{Na}_2\text{CO}_3} = 1 : 0.25$  ( $n_{\text{PAOTAC}}$  and  $n_{\text{Na}_2\text{CO}_3}$  are the dosage of PAOTAC and Na<sub>2</sub>CO<sub>3</sub> in mole, respectively), partially hydrolyzed PAOTAC) was added to the first flask, and 0.06 g of Na<sub>2</sub>CO<sub>3</sub> ( $n_{\text{PAOTAC}}:n_{\text{Na}_2\text{CO}_3} = 1 : 0.5$ , completely hydrolyzed PAOTAC) was added to the second flask. After 10 min of reaction, the hydrolysis products were precipitated into ethanol and washed with acetone. Finally, the hydrolysis products were freeze-dried for 12 h to remove water in a vacuum freeze-drying machine (FD-1A-80).

#### Hydrolysis of PAOTAC on the cotton

##### Sample a

Cotton (1 g) was dipped into 10 mL of a 2.0% (w/v) PAOTAC aqueous solution at 20°C for 2 min and then padded by a roller with a wet pickup of 80%. Subsequently, the pretreated cotton was baked at 100°C for 5 min in a baker.

##### Sample b

Cotton (1 g) was first treated by the process for sample a and then dip-padded in 10 mL of a 2 g/L Na<sub>2</sub>CO<sub>3</sub> aqueous solution for 1 min with an 80% wet pickup. Then, it was dried in air and steamed for 10 min.

#### Characterization and measurement

##### Characterization

Fourier transform infrared (FTIR) spectra were achieved with a NEXUS EURO gas chromatograph/FTIR spectrometer (Nicolet, Madison, Wisconsin, USA).

Cross sections of the dyed pretreated cotton at a thickness of 1  $\mu\text{m}$  were prepared with an LKB-V ultramicrotome (Bomma, Stockholm, Sweden). Images of the cross sections were obtained at 800 $\times$  magnification with a BX<sub>51</sub> light microscope (Olympus, Tokyo, Japan).

#### Color measurement

The dye exhaustion percentage ( $E\%$ ) is the percentage between the adsorption amount on the fiber after the dyeing and the initial amount of dyes. It was determined with an HP 8453 ultraviolet-visible spectrophotometer (Agilent, San Francisco, California, USA) by sampling of the dyebath before and after dyeing, as in eq. (1):

$$E\% = (A_0 - A_1)/A_0 \times 100 \quad (1)$$

where  $A_0$  is the absorbance of the initial dyebath and  $A_1$  is the absorbance of the dyebath after the dyeing process.

The dye fixation percentage ( $F\%$ ) is the percentage between the reactive amount of dyes with the fiber and the initial amount of dyes. It was calculated using eq. (2):

$$F\% = (A_0 - A_1 - A_2)/A_0 \times 100 \quad (2)$$

where  $A_2$  was measured with an HP 8453 ultraviolet-visible spectrophotometer. We compared the absorbance of a standard soap bath with that of a soaping and extracting bath after soaping and extracting.

The dyed samples were measured with a UltraScanXE color measuring and matching meter (Hunter, Memphis, Tennessee, USA). The corresponding values of color strength ( $K/S$ , where  $K$  is the light absorption coefficient and  $S$  is the scattering coefficient) were calculated from the reflectance data at  $\lambda_{\text{max}}$  of the dyeing.

#### Fastness testing

Washfastness was tested according to ISO 105-E01-1995 with a S-1002 two-bath dyeing and testing apparatus (Roaches International, Ltd., Leek, United Kingdom).

Rubbing fastness was tested according to ISO 105-X12-1993 with a Y (B) 571-II crockmeter (Da Rong Textile Instruments Co. Ltd., Wenzhou, China).

Lightfastness was tested according to ISO 105-B06-1998 with a 150 s solarization and climate fastness instrument (Heraeus Co., Kleinostheim, DE).

## RESULTS AND DISCUSSION

### $E\%$ and $F\%$ values with different dyeing procedures

In the study of the salt-free dyeing of cotton cationized with PAOTAC, an exhaust dyeing method

**TABLE I**  
Comparison of  $E\%$  and  $F\%$  of the Three Reactive Dyes on the Untreated and Cationic Cotton

Dye	Procedure	$E\%$	$F\%$
RR 195	1	39.9	38.2
	2	95.1	88.4
	3	83.2	80.2
	4	77.4	75.5
RY 145	1	37.1	35.3
	2	93.3	87.1
	3	81.4	77.3
	4	72.8	69.2
RB 19	1	38.4	37.5
	2	91.0	86.4
	3	72.5	69.3
	4	65.5	63.4

1, nonsalt exhaust dyeing with cationic cotton; 2, nonsalt exhaust-pad-steam dyeing with cationic cotton; 3, conventional exhaust dyeing with untreated cotton in the presence of salt; 4, exhaust-pad-steam dyeing with untreated cotton in the presence of salt.

(procedure 1 in Table I) was first employed, whereas it was found that dye fixation could not be carried out smoothly. As shown in Table I,  $E\%$  and  $F\%$  in procedure 1 were very low for all three dyes. However, when the exhaust-pad-steam dyeing procedure (procedure 2) was used with cationic cotton, the  $F\%$  values of RR 195, RY 145, and RB 19 reached 88, 87, and 86%, respectively. It could be seen that these results were all higher than those obtained with untreated cotton in conventional exhaust dyeing with salt addition (procedure 3). For comparison, the exhaust-pad-steam dyeing procedure was also used with untreated cotton (procedure 4), and the  $F\%$  values of the three dyes were all lower than those obtained in procedure 3.

It was known that conventional exhaust dyeing (procedure 3) is a one-bath dyeing method; alkali was added directly to the dyebath to promote dye fixation on the cotton. With the processing of dye fixation, more dyes in the dyebath adsorbed on the cotton to further promote dye fixation, so when the dye exhaustion and fixation steps were separated, as in procedure 4, the dye fixation of reactive dyes was lower. However, the cases for the salt-free dyeing of PAOTAC cationized cotton were different. If alkali was added directly to the dyebath under high temperature, because of the hydrolysis of ester bonds within PAOTAC, quaternary ammonium groups, together with the adsorbed reactive dyes, left away from the surface of the cotton fibers. Thus,  $F\%$  of the reactive dyes was low. To prevent dye desorption, the separation of dye exhaustion and dye fixation would be beneficial. So in this study, an exhaust-pad-steam procedure was designed with the cationic cotton. In the procedure, sodium carbonate for dye fixation was directly padded on cotton, and a steam



**TABLE II**  
Comparison of the Colorimetric and Fastness Properties of the Three Reactive Dyes in Salt-Free and Conventional Dyeing

Dye	Process	K/S			L*	a*	b*
		After soap-off	After DMF extraction	K/S			
RR 195	2	17.1	17.0	0.1	41.1	59.4	-1.0
	3	16.3	16.1	0.2	41.5	59.6	-0.9
RY 145	2	10.0	9.9	0.1	71.5	29.4	70.6
	3	8.2	8.0	0.2	72.0	29.1	71.4
RB 19	2	25.2	25.0	0.2	27.6	6.8	-39.6
	3	23.1	22.7	0.4	28.5	6.8	-41.9

2, nonsalt exhaust-pad-steam dyeing with cationic cotton; 3, conventional exhaust dyeing with untreated cotton in the presence of salt.

process was used to promote dye penetration and dye fixation. As the results present for this dyeing method, the dye fixation of salt-free dyeing was very satisfactory. Accordingly, in the following study, a conventional exhaust dyeing method was used with untreated cotton, and the designed exhaust-pad-steam dyeing procedure was used with the cationic cotton.

#### Colorimetric and fastness properties in salt-free and conventional dyeing

The colorimetric and fastness properties of RR 195, RY 145, and RB 19 in salt-free and conventional dyeing are shown in Tables II and III.

It can be seen from Table II that the  $K/S$  values of the dyed fibers after soap-off and DMF extraction in procedure 2 were all higher than those in procedure 3.  $\Delta K/S$  is the difference between  $K/S$  after soap-off and that after DMF extraction. It was observed that the  $\Delta K/S$  values in salt-free dyeing were 0.1, 0.1, and 0.2 for RR 195, RY 145, and RB 19, respectively, whereas these values in conventional dyeing were all higher. They were 0.2, 0.2, and 0.4 for RR 195, RY 145, and RB 19, respectively. This indicated that by the common soap-off procedure, color staining on cotton with a salt-free dyeing method could be eas-

ily removed; this would be very convenient for the rinsing process of dyeing. Good color yield with salt-free dyeing was presumably attributed to both a high dye fixation and easy removal of the hydrolyzed dyes due to hydrolysis of ester bonds within PAOTAC.

In addition, the corresponding colorimetric data for the dyed samples in different dyeing procedures revealed that only a small difference existed in the lightness ( $L^*$ ), redness ( $a^*$ ), and blueness ( $b^*$ ) of color between the conventional dyeings and the salt-free ones; this indicated that cationization of cotton did not affect the color of the dyeings much.

The fastness properties of RR 195, RY 145, and RB 19 on cationic and untreated cotton were determined, as shown in Table III.

It shows that colorfastness of the salt-free dyeings was good for all three dyes. When RR 195 was used, the dyeings with cationic cotton showed equivalent rubbing fastness, washfastness, and lightfastness compared to those with untreated cotton. When RY 145 was used, salt-free dyeing showed better wet rubbing fastness, color staining on adjacent cotton, and lightfastness compared to conventional dyeing; For RB 19, the rubbing fastness and washfastness of the salt-free dyeings reached 4-5 grade, and lightfastness reached 6 grade; this was fairly good for this

**TABLE III**  
Comparison of the Fastness Properties of the Three Reactive Dyes in Salt-Free and Conventional Dyeing

Dye	Process	Rubbing fastness		Washfastness			Lightfastness
		Dry	Wet	Staining			
				Change	Cotton	Wool	
RR 195	2	4-5	4	4-5	4	4-5	4
	3	4-5	4	4-5	4	4-5	4
RY 145	2	4-5	4-5	4-5	4-5	4	5
	3	4-5	4	4-5	4	4	4-5
RB 19	2	4-5	4-5	4-5	4-5	4-5	6
	3	4	4	4-5	4-5	4	5-6

2, nonsalt exhaust-pad-steam dyeing with cationic cotton; 3, conventional exhaust dyeing with untreated cotton in the presence of salt.

**TABLE IV**  
***K/S* of the Dyed Fibers in Different Regions of the Fibers**

Dye	<i>K/S</i>			
	<i>K/S</i> <sub>1</sub>	<i>K/S</i> <sub>2</sub>	<i>K/S</i> <sub>3</sub>	<i>K/S</i> <sub>4</sub>
RR 195	17.08	17.10	17.10	17.13
RY 145	10.01	10.00	10.03	10.01
RB 19	25.21	25.19	25.23	25.20

dye. Such good fastness properties of all three dyes in salt-free dyeing demonstrated both the formation of chemical bonding between dyes and fibers and the complete removal of staining color on the cotton.

### Levelness dyeing analysis

The levelness of the dyes on the fibers is another important property for the evaluation of a dyeing process. The measurement of the *K/S* values at different regions of one dyed fabric can be used to evaluate the levelness of the dyes. If the difference among the *K/S* values is quite small, it demonstrates that the dyeing is level; namely, the dyes are jointed to the fibers homogeneously. The measurement results of *K/S* with the salt-free dyeing method are shown in Table IV. It can be seen from Table IV that the difference among the four *K/S* values was less than 0.3%; this indicated good levelness of the dyes on the cationic fibers. The levelness of the dyes also demonstrated the levelness of the cationic agent pretreated on cotton.

### Microscopic analysis

Microscopic photos of the cross sections of the cationic cotton fibers dyed with RR 195 are given in Figure 3. It can be seen that the inside of the cationic fibers was all colored, which indicated that the reac-

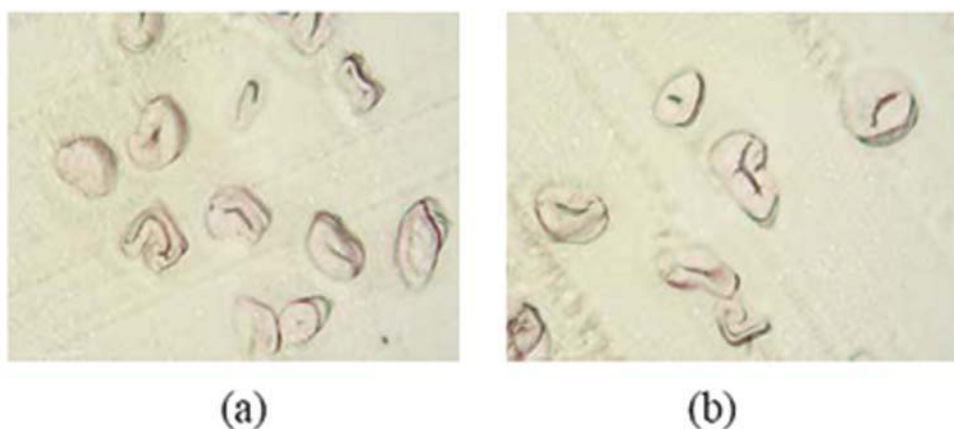
tive dyes had penetrated into the center of the fibers under the experimental dyeing conditions. As a result, it would be beneficial for covalent bonding between the reactive dyes and the cotton and be favorable to the retention of good colorfastness.

### Proof of the hydrolysis of ester bonds of PAOTAC on cotton

As the quantity of PAOTAC pretreated on cotton was small, to prove the hydrolysis of ester bonds of PAOTAC on cotton, we first investigated the hydrolysis conditions of PAOTAC in aqueous solution and characterized the hydrolyzed products (in the section on Hydrolysis of PAOTAC in Solution) by FTIR. The hydrolysis process of PAOTAC with the addition of Na<sub>2</sub>CO<sub>3</sub> is shown in Figure 4.

As the IR spectrum of PAOTAC in Figure 5 shows, the characteristic adsorption peak of ester groups appeared at 1735 cm<sup>-1</sup>. When the hydrolysis of PAOTAC was carried out with  $n_{\text{PAOTAC}}:n_{\text{Na}_2\text{CO}_3} = 1 : 0.25$ , PAOTAC could be partially hydrolyzed. The IR spectrum of the product showed besides the peak at 1735 cm<sup>-1</sup>, another peak at 1567 cm<sup>-1</sup>, which was attributed to the stretching vibration of carbonyl groups in sodium carboxylate (—COONa). This indicated that within the hydrolysis product, ester bonds and sodium carboxylate existed at the same time. When hydrolysis of PAOTAC was carried out with  $n_{\text{PAOTAC}}:n_{\text{Na}_2\text{CO}_3} = 1 : 0.5$ , PAOTAC could be completely hydrolyzed. Its IR spectrum showed that only the characteristic peak of sodium carboxylate appeared at 1567 cm<sup>-1</sup> and the peak at 1735 cm<sup>-1</sup> disappeared; this demonstrated that the ester bonds had been totally hydrolyzed to sodium carboxylate.<sup>19</sup>

On the basis of the results of hydrolysis of PAOTAC in aqueous solution, the structure change of PAOTAC on cotton treated with a 2 g/L Na<sub>2</sub>CO<sub>3</sub>



**Figure 3** Microscopic photos of the cotton fibers dyed with RR 195: (a) conventional dyeing and (b) salt-free dyeing, fibers pretreated with PAOTAC. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

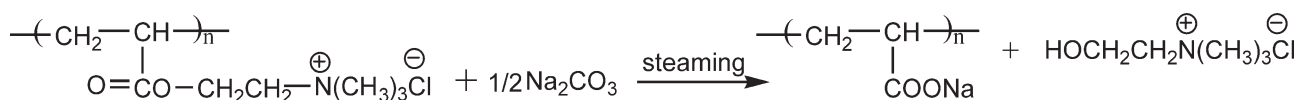


Figure 4 Hydrolysis of PAOTAC.

solution and steamed in the absence of reactive dyes (samples a and b in the section on Hydrolysis of PAOTAC on the Cotton) was examined by FTIR (see Fig. 6).

In comparison to IR of the untreated cotton (in Fig. 6), a new adsorption peak at  $1735\text{ cm}^{-1}$  appeared in the IR spectrum of sample a in Figure 6, which was in agreement with the characteristic peak of carboxylic groups in PAOTAC (in Fig. 5). It proved that PAOTAC successfully adhered to cotton fibers by pretreatment. However, after the cationic cotton was treated with  $\text{Na}_2\text{CO}_3$  solution under steam, IR of sample b in Figure 6 showed that the adsorption peak at  $1735\text{ cm}^{-1}$  disappeared, and a new adsorption peak at  $1567\text{ cm}^{-1}$  appeared. In combination of the analysis results of the hydrolysis product of PAOTAC in solution, this new peak was assigned to stretching vibration of carbonyl groups in polyacrylate sodium.<sup>19</sup> This result indicated that PAOTAC was hydrolyzed.

The previous results showed that  $2\text{ g/L Na}_2\text{CO}_3$  could well hydrolyze PAOTAC on cotton under steam conditions; in the salt-free dyeing process,  $10\text{ g/L Na}_2\text{CO}_3$  was used in the dye fixation step. It was far more enough for the hydrolysis of PAOTAC, although partial  $\text{Na}_2\text{CO}_3$  was consumed for dye fixation. Thus, the hydrolysis of the ester bonds of PAO-

TAC in the salt-free dyeing process was testified. Because of the hydrolysis of ester bonds, the cationic groups, together with the adsorbed hydrolyzed dyes, were much easier to remove from the cotton by the soap-off procedure. Thus, colorfastness with cationic cotton could remain good, compared with the untreated cotton.

## CONCLUSIONS

Application of PAOTAC to the cationization of cotton realized good dyeing properties by an exhaust-steam dyeing method. Higher dye fixation and  $K/S$  values were obtained with cationic cotton. When 2% PAOTAC with a weight-average molecular weight of  $8700\text{ g/mol}$  was used, the  $F\%$  values of RR 195, RY 145, and RB 19 reached 88.4, 87.1, and 86.4%, respectively. Those values were 8.2, 9.8, and 17.1% higher than those obtained from conventional dyeings. The color staining was easy to remove in the salt-free dyeing via a common soap-off procedure. We were pleased to find that the colorfastness properties, including rubbing fastness, washfastness, and lightfastness, in the salt-free dyeing were equivalent with or even better than those obtained in conventional dyeing. These good dyeing properties were mainly due to good dye penetration and easy removal of the hydrolyzed dyes from cotton.

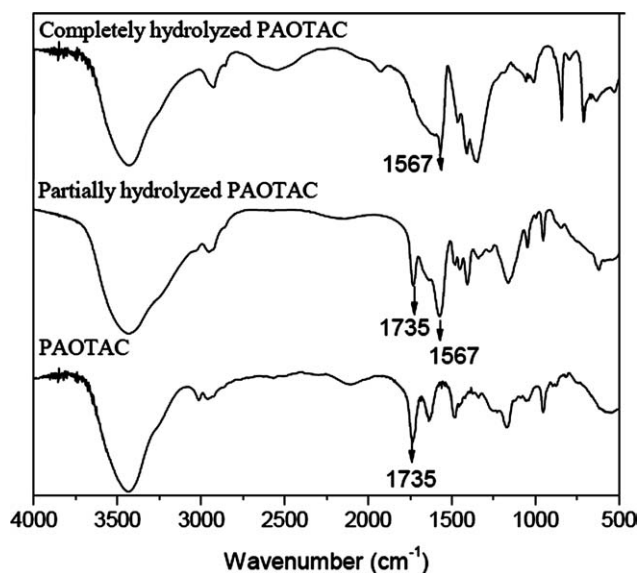


Figure 5 FTIR spectra of PAOTAC and the hydrolysis product with the addition of different amounts of  $\text{Na}_2\text{CO}_3$  (partially hydrolyzed PAOTAC,  $n_{\text{PAOTAC}}:n_{\text{Na}_2\text{CO}_3} = 1 : 0.25$ ; completely hydrolyzed PAOTAC,  $n_{\text{PAOTAC}}:n_{\text{Na}_2\text{CO}_3} = 1 : 0.5$ ).

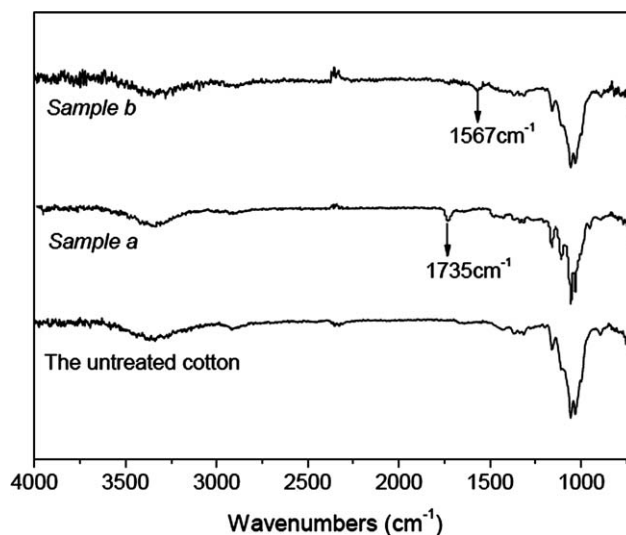


Figure 6 FTIR spectra of the cationic and untreated cotton fibers (sample a: the cotton pretreated with PAOTAC; sample b: the cotton pretreated with PAOTAC and then treated with  $2\text{ g/L}$  of  $\text{Na}_2\text{CO}_3$  solution and steam conditions).

Besides, the levelness properties of the dyes on the cationic cotton were very good. Therefore, it could be concluded that PAOTAC containing hydrolyzable ester bonds could be regarded as an improved cationic agent of cotton for salt-free reactive dyeing, and it also shows promising prospects for application.

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