Antimicrobial Finishing of Cellulose with Incorporation of Aminopyridinium Salts to Reactive and Direct Dyed Fabrics

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ABSTRACT: Three quaternary ammonium salts namely 4-amino-laurylpyridinium chloride, 4-benzoylamino-1-dodecylpyridinium bromide, and 4-(1-naphthoyl) amino-1-dodecylpyridinium bromide were employed in antimicrobial finishing of dyed and undyed cotton fabrics. The intermolecular interactions between the dyes and the aminopyridinium salts, and their impact on the exhaustions of salts on the dyed fabrics were discussed. The quaternary ammonium salts could form ionic interactions with sulfonate groups on the dyed cotton fibers, which contribute to higher exhaustion uptakes of the salts and better antimicrobial activities against *Escherichia coli* of the dyed cotton fabrics compared with that of the undyed sample. However, the washing durability of the antimicrobial functions on the finished cotton fabrics was still low because of easy dissociation of the ionic interactions in water. J Appl Polym Sci 106: 2634–2639, 2007

Key words: dyes/pigments; functionalization of polymers; fibers

INTRODUCTION

Cotton is the most popular fiber widely used in apparel and institutional textiles. Functionalization of cotton fabrics has been of utmost interest to textile scientists. Many methods have been developed to incorporate biocides such as quaternary ammonium salts, metal ions, phenols, and chloramines to cotton fabrics for the production of antimicrobial textiles.[1–4] The recent development of durable and regenerable biocidal cotton fabrics by grafting *N*-halamine structures on cellulose provides ideal materials for medical textiles.[5] However, the halamine structures impose certain limitations on dyes that are chlorine bleach sensitive to be employed on the fabrics. Reactive and direct dyes are the most popular ones used for cotton but most of them are not chlorine bleachable, which significantly restricts the applications of the technology in apparel products. Antimicrobial quaternary ammonium salts could be incorporated onto different fibers by ionic interaction between the fibers and the cationic salts. But there is lack of direct interactions between cellulose and quaternary ammonium salts, resulting in low durability of the antimicrobial functions. However, most reactive dye molecules contain reactive groups such as sulfonate, amino, and hydroxyl that can serve as linkers for attaching some functional moieties to the fibers. For example, some acid dyes have been used as bridges to bind quaternary ammonium salts to produce antimicrobial Nylons 66 and 6, and the functions were proven durable, surviving more than 25 times of home laundry.[6] Both reactive and direct dyes are anionic species usually containing sulfonate groups as solubilizing groups, and these groups can interact with cationic surfactants, which have been employed as a method to increase color washing-fastness of direct dyes.[7] According to this practice, the incorporated quaternary ammonium salts improved dye durability on cellulose through ionic interactions, and consequently the salts could provide durable antimicrobial functions on the materials.

Three aminopyridinium salts were synthesized and applied in antimicrobial finishing of wool fabrics.[8] The fabrics have demonstrated desired durable antimicrobial function because of ionic interactions of fibers and the salts. Practically, reactive dyes form covalent bonds with cotton fibers to get very good washing fastness. Direct dyes, though not having permanent connection, interact with cellulose through secondary interactions with cotton fibers such as van der Waals forces, dipole–dipole interactions, and hydrogen bonds and result in acceptable durability as well. Once these dyes are anchored to the cellulose, the existing sulfonate groups on the dyes can serve as reactive sites to bind quaternary ammonium salts. In

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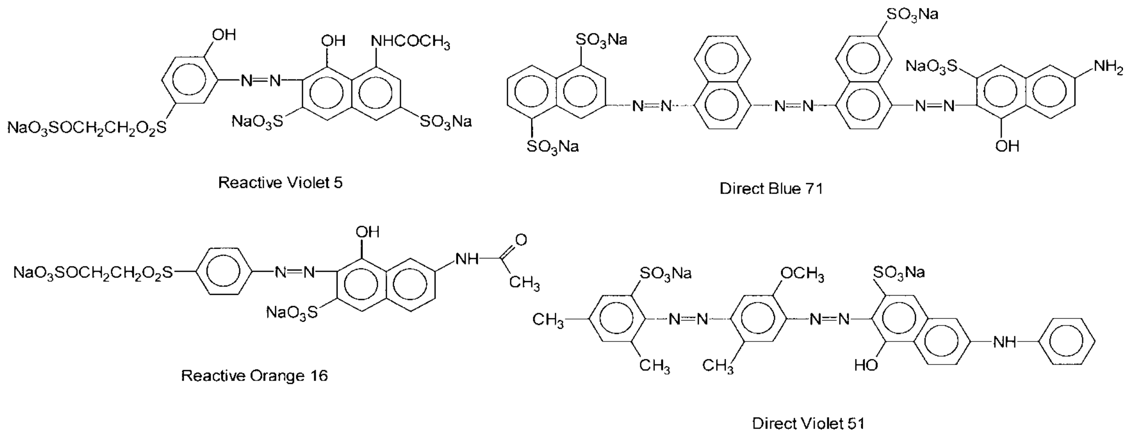

Figure 1 Structures of direct and reactive dyes.

this article, we report findings of incorporating quaternary groups by means of reactive and direct dye molecules on cellulosic fibers. The interactions between dyes and the aminopyridinium salts as well as impacts of chemical structures of dyes on the exhaustions of salts on the dyed fabrics are discussed. Besides, the durability of the antimicrobial functions of the treated fabrics was evaluated using standard Launder-Ometer washing and antimicrobial tests.

EXPERIMENTAL

Materials

Cotton fabrics, supplied by TestFabrics (Pittston, PA), were thoroughly scoured using an AATCC standard detergent WOB according to AATCC Test Method 124-1996, then rinsed thoroughly in tap water, and dried in air before use. C.I. Direct Violet 51, C.I. Direct Blue 71, and C.I. Reactive Orange 16 were supplied by Aldrich Chemical Company (Milwaukee, WI). C.I. Reactive Violet 16 was supplied by Dystar L. P. (USA). All of them were used without further purification (Fig. 1). Aminopyridinium salts, 4-amino-laurylpyridinium chloride (ALPC), 4-benzoylamino-1-dodecyl pyridinium bromide (BADPB), and 4-(1-naphthoyl) amino-1-dodecyl pyridinium bromide (NADPB) were prepared according to a described method.[9] The structures are shown in Figure 2.

The cotton fabrics were dyed in dye solutions with concentrations of 1.0 and 3.0% [on weight of fabrics (owf)], respectively. Liquor ratio (weight of dyeing solution/weight of fabric) was 50 : 1. Direct dyeing conditions were temperature = 95°C, sodium sulfate concentration = 20 g/L, dyeing time = 1 h (1.0% owf) and 2 h (3.0% owf). The fabrics were washed in 50°C hot water. Reactive dyeing conditions were exhaust dyeing temperature = 60°C, sodium sulfate concentration = 50 g/L, time = 0.5 h (1.0% owf) and 1 h (3.0% owf), fixation temperature = 70°C, fixation time = 1 h. The reactive dyed fabrics were washed with an AATCC standard detergent at 95°C.

Finishing of fabrics

The dyed cotton fabrics were immersed into a finishing bath containing one of the quaternary ammoniums salts under different temperatures from 30 to 100°C. The bath liquor ratio was 50 : 1. The pH values of the finishing baths were neutral. The quaternary salt concentration changes during the treatment were measured by taking 1 mL of the solution from the bath at different intervals. The UV absorbance of these solutions was then measured at λ_{max} values of 270.5 nm (ALPC), 263.5 nm (BADPB), and 264.5 nm (NADPB) in a quartz covet by using a UV–vis spectrophotometer (U-2000, Hitachi Instruments, Japan). The uptakes of the salts on cotton fabric were calculated by comparing the absorbance of the salt solutions at the beginning and the absorbance of salt solution at the finishing.

The CIE L^* (lightness), a^* (redness), b^* (yellowness), C^* (chroma), h° (hue) color coordinates, and

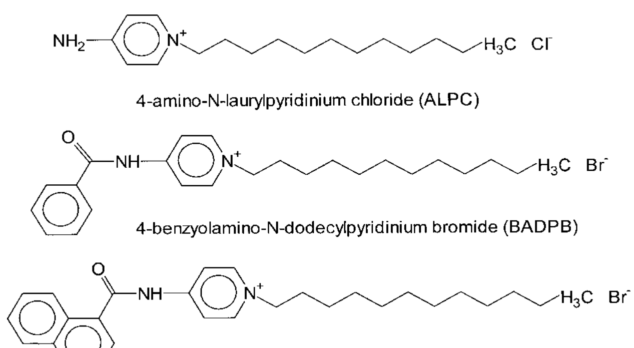

Figure 2 Structures of quaternary ammonium salts.

CIELab total color difference (ΔE) of the finished and unfinished color cotton fabrics were measured with a ColorEye 7000A (GretagMacbeth, USA) reflectance spectrometer under illuminant D65 and a 10° standard observer.

Assessment of antimicrobial properties

Antimicrobial activities of the treated cotton fabrics were quantitatively evaluated against *Escherichia coli* (*E. coli*; K 12, Microbiology Lab of University of California, Davis, Gram-negative) according to AATCC test method 100-1999. Circular fabric swatches (about 1.0 g) were challenged with 1.0 ± 0.1 mL of bacterial inoculums. The inoculum was a nutrient broth culture containing 1.0×10^5 to 1.0×10^6/mL colony-forming units of bacterium (*E. coli*). The inoculated fabric samples were then placed into a 250-mL container for a measured duration of 12 h (defined as the contact time). After the swatches were in contact with the bacterium for over 12 h, 100 mL of sterilized distilled water was added into the container, the mixture was vigorously shaken, and then the solution was diluted to 10^1, 10^2, 10^3, and 10^4 in series. One hundred microliters of each dilution was placed onto a nutrient agar and incubated for over 18 h at 37°C. Finally, viable bacteria colonies on the agar plate were counted, and the percentage reduction in numbers of bacteria was calculated using eq. (1)

$$R = \frac{A - B}{A} \times 100\% \tag{1}$$

where R is the percentage reduction of the bacterium, A represents the numbers of bacterial colonies from control fabric (an untreated fabric), and B represents the number of bacterial colonies from treated fabrics.

The treated cotton fabrics were washed in a Launder-Ometer (Atlas, USA) according to AATCC standard method 61-2005 to evaluate the washing durability of the treated fabrics, and then the antimicrobial properties of the washed fabrics were evaluated.

RESULTS AND DISCUSSION

Effect of treatment temperature on adsorption of aminopyridinium salts

In exhaustion finishing process, temperature plays an important role in the adsorption of the quaternary ammonium salts on the fibers. Figure 3 shows the uptakes of three aminopyridinium salts on Reactive Violet 5 dyed cotton fabrics in a temperature range of 30–100°C. With the temperature rising, the exhaustions of three agents showed initial increases, and after reaching a maximum then either reached

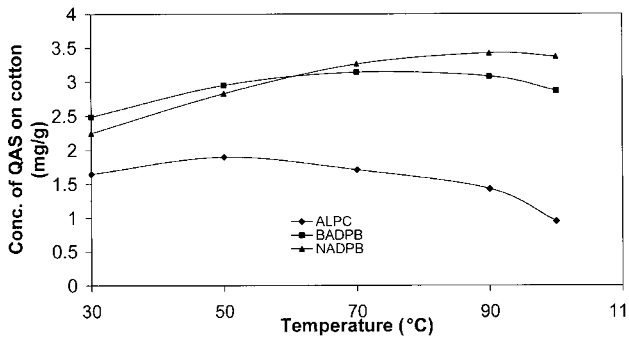

Figure 3 Effect of treatment temperature on absorption of quaternary ammonium salts (conc. 1% owf; time 120 min).

equilibrium or reduced under higher finishing temperatures. The reduction of exhaustions of ALPC on the dyed fabrics was most significant. These diverse differences of salt exhaustions are a reflection of adverse influences of increasing finishing temperature. Thermodynamically speaking, if the adsorption of a cationic salt on the anionic site of the dyed fabrics is exothermic higher temperature is not favored.[10] Increasing temperature also increases the solubility of the salts, which may enhance desorption of the agents. However, higher temperature accelerates diffusion of agents into fibers.

In addition, affinity of the agents with the dyed fibers is another parameter affecting the equilibrium exhaustion. The structures of the agents affected their affinities on the dyed fabrics. The hydrophilicity of the three compounds should be in such an order, i.e., ALPC > BADPB > NADPB, according to the structures. The maximum uptake of NADPB was the highest, more than doubled compared with that of ALPC on the fabric. Thus, the lower affinity to the fabrics and higher solubility in aqueous solution compared with other two compounds lowered the exhaustion of ALPC. On the other side, NADPB is the most hydrophobic compound among the three agents and has lower solubility in water. Increasing the temperature can promote NADPB deaggregation in the finishing solution, liberating more individual salt molecules to enter the fiber. The overall impact of the deaggregation and high affinity of NADPB with fibers make it high exhaustion rate on cellulose fibers.

Effect of dye and aminopyridinium salt structures on uptakes of salts on cotton fabrics

Anionic dyes contain negatively charged sulfonate groups that can interact with positively charged nitrogen ions in aminopyridinium salt molecules. These intermolecular interactions are primarily columbic forces. In addition, aminopyridinium salt may also form dipole–dipole or van der Waals inter-

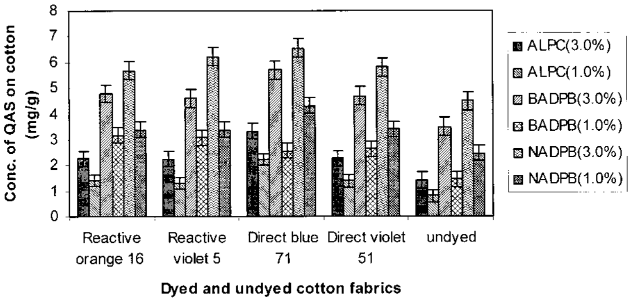

Figure 4 Effect of dye structures on absorption of quaternary ammonium salts (finishing temperature: ALPC 50°C, BADPB 70°C, and NADPB 90°C; time 120 min).

actions with cellulose molecules. These binding forces contribute to the affinity of the aminopyridinium salts on cellulosic fibers and enhance the durability of the antimicrobial functions. Figure 4 shows exhaustions of ALPC, BADPB, and NADPB on cotton fabrics dyed with several reactive and direct dyes as well as that on undyed ones. The exhaustions of the three salts on all dyed cotton fabrics were higher than those on the undyed cotton fabrics, a clear indication of increased interactions between the salts and the dyes. The more dyes incorporated onto cotton fibers, the more ALPC could be absorbed onto the fibers consequently. The amounts of the cationic salts exhausted on the dyed cotton fabrics were also different under different structured dyes. Generally speaking, the direct dyed fabrics should show higher salt exhaustions than the reactive dyed ones since these direct dyes all contain more sulfonate groups than the reactive dyes. However, the results indicated that the salts exhaustions on both reactive and direct dyes were basically similar, not showing the difference based on sulfonate anionic groups on the dyes.

Although the exhaustion levels of three salts on the dyed and undyed fabrics are obviously different, because of the existence of ionic interactions, the undyed cotton fabrics also demonstrated certain levels of exhaustion of three quaternary ammonium salts. Such a result is possibly because of dipole–dipole or van der Waals interactions between the salts and the cellulose. Cellulose exhibits anionic characters in aqueous solution, which might be another reason for the uptakes. However, these interactions are expected to be much weaker compared with ionic interactions, which is consistent with the observed lower exhaustions of the salts on the undyed cotton than that of the dyed samples.

Another interesting phenomenon observed from Figure 4 was that the exhaustions of the salts on all dyed and undyed cotton are related to hydrophobicity of the salts. The NADPB always showed the highest uptakes on the fabrics, whereas the ALPC the lowest, among the fabrics under the same dyed or undyed condition. Since the treatments of the fabrics with the agents were conducted under temperatures at which the maximum exhaustions of the dyes were obtained, the overall dye exhaustion of the three agents are similar to the observation in Figure 3.

Antimicrobial assessment

Antimicrobial functions of ALPC, BADPB, and NADPB treated dyed and undyed cotton fabrics were evaluated against *E. coli* following AATCC Test Method 100. The results are shown in Table I. The undyed and dyed cotton fabrics that were treated with these salts all demonstrated very effective antimicrobial activities. The undyed samples exhibited only small difference in antibacterial functions compared with the dyed samples, a result of adsorptions of the quaternary ammonium salts on the cellulose. This result also indicates that regular rinsing of the finished fabrics in water was insufficient to remove any physically adsorbed cationic species.

Washing durability of antimicrobial functions

The washing durability of the antimicrobial functions on the treated cotton fabrics are shown in

TABLE I
Antimicrobial Functions of Treated Cotton Fabrics

QAS conc. (owf) (%)	Log reduction[a] of *E. coli*														
	Direct Violet 51			Direct Blue 71			Reactive Violet 5			Reactive Orange 16			Undyed		
	A[b]	B[b]	N[b]	A	B	N	A	B	N	A	B	N	A	B	N
0.5	6	6	6	6	6	6	6	6	6	6	6	6	2	3	3
1.0	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
2.0	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
3.5	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6

E. coli concentration: 10^6–10^7 CFU/mL; contact time: 15 h.
[a] One log reduction means 90% kill, two log reduction equals 99% kill, and six log reduction equals 99.9999% kill.
[b] A, B, and N represent ALPC, BADPB, and NADPB respectively.

TABLE II
Durable Antimicrobial Functions of the Treated Cotton Fabrics

	Percentage reduction of *E. coli* (%)								
	Water washing[b]			One time washing[c]			Two times washing[c]		
Sample[a]	A	B	N	A	B	N	A	B	N
Direct Violet 51	97.01	98.40	99.89	22	24	22	0	0	0
Direct Blue 71	98.35	98.78	99.97	24	25	25	0	0	0
Reactive Violet	97.56	98.13	98.05	24	26	22	0	0	0
Reactive Orange	98.29	99.11	99.36	26	27	25	0	0	0
Undyed	83.43	88.42	88.57	0	0	0	0	0	0

E. coli concentration: 10^6–10^7 CFU/mL; contact time: 5 h.
[a] ALPC concentration was 3.0% on weight of cotton fabrics.
[b] Washing time was 5 min at 26°C.
[c] Washing tests were performed in a Launder-Ometer using AATCC 1993 standard reference detergent.

Table II. After cold water washing, the fabrics still retained the functions, and dyed fabrics showed more than 98% kill of *E. coli*. But the undyed fabrics displayed much lower antibacterial activities compared with the dyed fabrics, an indication of weak interactions between the salts with the fabrics. After some time Launder-Ometer washing the fabrics lost the function dramatically, and the dyed samples showed less than 30% kill of *E. coli*. The undyed fabric totally lost the antimicrobial properties. The second Launder-Ometer washing completely removed the imparted antimicrobial functions of all fabric samples. To further confirm the loss of the antimicrobial functions, the samples after second Launder-Ometer washing were put into the hot water (80°C) and stirred for 5 min, and the aqueous solution was evaluated with a UV–vis spectrophotometer. No obvious peak was detected, indicating no residual salt left on the treated fabrics after two Launder-Ometer washings. Although each Launder-Ometer washing is equivalent to five times of home laundering, such performance is still below our expectation. The washing durability of the antimicrobial functions depends on the bonding of the quaternary ammonium salts with dyes in the fibers. Because the ionic bonding between sulfonate and pyridinium groups can dissociate in water, the quaternary ammonium salts could still be washed off in water and the durability of antimicrobial functions would be low.

On the other hand, the structural characteristics of dyes played a major role in exhaustion of the salts but did not provide enhanced washing durability of the salts on the fabrics. Obviously, antimicrobial properties of the dyed fabrics were a little better than the undyed fabrics after Launder-Ometer washing, showing improved durability. Repeated laundering still could completely remove all three quaternary ammonium salts. Since the increased exhaustion of the slat on the dyed cellulose was a result of ionic interactions between the sulfonate and quaternary ammonium species, dissociation of the ionic interactions in water is relatively easier and quicker, resulting in low washing durability.

TABLE III
CIELAB Color Difference of Unfinished and Finished Fabrics

Fabrics	*L**	*a**	*b**	*C**	*h*°	Δ*E*	Grade[a]
Direct Violet 51[b]	30.634	16.781	−27.669	32.360	301.236	0	1–2
Direct Violet 51[c]	32.733	25.862	−22.629	34.364	318.815	10.596	
Direct Blue 71[b]	30.988	−1.584	−23.262	23.316	266.104	0	3–4
Direct Blue 71[c]	30.949	−3.036	−25.486	25.666	263.207	2.656	
Reactive Orange 16[b]	60.851	44.483	24.086	50.586	28.434	0	4
Reactive Orange 16[c]	60.106	43.947	22.864	49.539	27.487	1.529	
Reactive Violet 5[b]	56.830	21.298	−22.796	31.197	313.054	0	4
Reactive Violet 5[c]	56.850	19.971	−21.777	29.548	312.523	1.673	

*L** measures lightness and varies from 100 for perfect white to zero for black; *a** measures redness when positive, gray when zero, and greenness when negative; *b** measures yellowness when positive, gray when zero, and blueness when negative; *C** (chroma), *h*° (hue) color coordinates, and Δ*E* is total color difference.
[a] AATCC evaluation procedure 1 (2002).
[b] Unfinished fabric.
[c] Finished fabric.

Color difference of finished fabrics

Table III presents the results of the CIELab coordinates and color differences before and after the salt treatment of the reactive and direct dyed cotton fabrics. The fabrics dyed with Reactive Violet 5, Reactive Orange 16, and Direct Blue 71 showed slight color variations before and after the salt treatments, while for the fabrics dyed with Direct Violet 51, there is a relatively higher color change in hue that greatly impedes shade correction and color matching. Direct Violet 51 is an exception; the hues of other three dyed fabrics were not significantly affected according to AATCC colorfastness grade.[11] So the ionic bonds formed between the quaternary ammonium salts and dyes did not affect chromogens of the dyes.

CONCLUSIONS

Three quaternary ammonium salts ALPC, BADPB, and NADPB were successfully incorporated into reactive and direct dyed cotton fabrics using ionic interactions between salts and the dyes. The chemical structures of the three salts can significantly affect its uptake on the cotton fabrics. Higher hydrophobicity of the salts results in stronger intermolecular interactions and higher uptakes. NADPB has the maximum exhaustion uptakes on cotton because of the hydrophobic naphthyl group in the molecules. The number of sulfonate groups in dye molecules could affect exhaustions of the salts. The finished cotton fabrics demonstrated antimicrobial functions. The ionic interactions between quaternary ammonium salts and the dyes on the dyed fabrics have certain impact on colors of certain dyes. The durability of the antimicrobial properties was improved for the dyed fabrics but still relatively low because of easy dissociation of the ionic bonds in water.

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