An Effective Antimicrobial Treatment for Wool Using Polyhexamethylene Biguanide as the Biocide, Part 2: Further Characterizations of the Fabrics

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ABSTRACT: Part 1 of this study reported an effective antimicrobial treatment for wool, using a pretreatment of peroxymonosulfate and sulfite to facilitate the exhaustion of polyhexamethylene biguanide (PHMB), a biocide with a long history of safe use. Here, further studies were performed to examine whether this finishing would satisfy the requirements for commercial antimicrobial textile production in terms of washing durability, its compatibility with dyeing and its effects on textile physical properties. The finishing was found to be very durable, sustaining at least 25 washing cycles without significant reduction in the antimicrobial activity. The process was compatible with reactive dyes, although other types of dyes (acid dyes, chrome dyes, and Premetalized dyes) all reduced PHMB uptake by ~ 50%. The finishing had little adverse effect on the tensile strength, handle or whiteness of the fabrics. This process therefore meets the requirements of and holds promise for the commercial production of antimicrobial wool textiles.
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Key words: textile; wool; antimicrobial; polyhexamethylene biguanide; peroxymonosulfate

INTRODUCTION

Antimicrobial treatments of textiles prevent odor formation and microbe-associated deterioration of the textiles during use, especially under humid conditions.[1–3] The treatments use biocides to either inhibit the growth of bacteria or to kill them on the textiles. Commonly used biocides include silver (or its salts), quaternary ammonium compounds, polyhexamethylene biguanide (PHMB), triclosan, chitosan and regenerable *N*-halamine and peroxyacids. The treatments require the incorporation of a biocide into the fibers or its attachment to the fiber surface. Various methods are available to confer antimicrobial activity. For synthetic fibers, the antimicrobial agents, typically silver, can be incorporated into the polymer before extrusion. The conventional exhaust and pad-dry-cure processes have been used for antimicrobial finishing on cotton as well as synthetic fibers for the biocides such as triclosan[4] and PHMB.[5,6] Padding, spraying and foam finishing have been used for the silicone-based quaternary ammonium agent.[7] To improve washing durability, chemical bonding of the biocide with the fiber,[8,9] crosslinking on the fiber using a crosslinker[10,11] and polymerization grafting[12] have also been trialed in the laboratory.

While many antimicrobial treatments can deliver antimicrobial activity to the textiles, they may have little value for commercial production due to limited durability or other unwanted drawbacks. Purwar and Joshi (2004) outlined that an ideal antimicrobial treatment of textiles should satisfy a number of requirements.[1] The chemical used has to exhibit low toxicity to consumers, for example, not to cause toxicity, allergy or irritation to the user. The finishing should be durable to repeated laundering, have no negative effect on the quality (e.g., physical strength, handle or appearance) of the textile and be compatible with common textile processing such as dyeing. In addition, given the low profit margin of the textile industry, the process has to be as simple as possible and easily scalable to be economically viable.

In Part 1 of this study,[13] a novel and effective antimicrobial treatment for wool was demonstrated, using peroxymonosulfate (PMS) and sulfite in a pretreatment followed by the exhaustion of the biocide PHMB. It showed that such pretreated fabrics were able to exhaust up to 5% owf PHMB, and the finishing was able to kill >99% bacteria within a few minutes of contact.[13] For this process to have any commercial potential, it must meet the requirements mentioned earlier. The safety of PHMB has been well established, as it has been used as a disinfectant in the food industry and for sanitization of

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swimming pools[14] and has been being explored as a biocide in mouth washes[15] and wound dressings.[16] Here, the washing durability, the physical properties of the finished fabrics and the compatibility of the process with dyeing are examined.

EXPERIMENTAL

Materials

All fabrics and materials used have been described previously.[13] The wool fabric used in this study had a mass of 190 g/m^2. Fabric construction was 2 × 1 twill using untreated and unchlorinated Australian Merino wool. PMS (trade name Oxone) was purchased from Dupont. Sodium sulfite was from Sigma. PHMB in 20% (w/v) aqueous solution was purchased from Arch Chemicals and adjusted to pH 7 to pH 7.5 with NaOH before use.

Methods

Pretreatment and PHMB exhaustion

Pretreatment of wool fabrics with PMS and sodium sulfite, were described previously.[13] Briefly, fabrics were firstly treated with 2 g/L PMS containing 1 mL/L of the nonionic surfactant Triton X-100 at room temperature for 15 min, rinsed in water and subsequently treated with 10 g/L sodium sulfite (pH adjusted to 8.2–8.5 with 2 *M* sulphuric acid) at room temperature for 15 min and again rinsed in water. The liquor to wool ratio for both PMS and sulfite treatments was 40 : 1 The fabrics were dried in an oven at 80°C for 45 min and stored at room temperature before use. For PHMB exhaustion, wool fabrics were shaken in aqueous solutions in beakers containing 8% owf (on weight of fabric) PHMB, 0.1% (v/v) of Triton X-100 at 40°C (in a water bath) for up to 60 min. The liquor to fabric ratio was 50 : 1. The uptake of PHMB was calculated from the absorbance at 236 nm as described previously.[13] To examine the effects of curing on the finishing, fabrics were treated at 120°C for 5 min in an oven after PHMB exhaustion and rinsing.

Dyeing procedure

A Pretema Multicolor dyeing machine and standard dyeing procedures were used in the dyeing work. Untreated or PMS/sulfite pretreated fabrics (11.5–12.0 g each) were used for each dye. Four types of dyes were used, each with three different shades: (1) Reactive dyes (1% Lanasol Yellow 4G, 1% Lanasol Red 6G and 4% Lanasol Navy MBN), (2) Premetalized dyes (1% Lanaset Yellow 4G, 1% Lanaset Red G and 3% Lanaset Navy R), (3) Acid dyes (1.5% Sandolan Yellow MF-2GL, 1.5% Sandolan Red MF-GRL, 1.5% Sandolan Blue MF-2RL), and (4) Chrome dyes (0.5% Eriochrome Orange 2RL, 1% Eriochrome Red G, 1% Solochrome Azurine BS). The dyeing with each dye was successful as indicated by very good dye exhaustion, color depth and color fastness.

Physical properties of fabrics

Fabrics were conditioned at 65% relative humidity and 20°C for 48 h before tensile strength and bending rigidity tests. Tensile strength was tested using an Instron on fabrics of 50 mm × 140 mm in size. Bending rigidity was measured on a KES-FB2 Bending Tester on fabrics of 200 mm × 200 mm in size. Fabrics were tested in the warp and weft directions for bending rigidity and the average of the two was presented. Whiteness was measured using a Gretag-Macbeth™ Color-Eye 7000A spectrophotometer equipped with the Optiview ProPalette V2.0C software. All treatments had three replicates and values are expressed as means with standard errors.

Washing durability test

All washing tests were done at 40°C in a washing machine using 5A cycles according to the test method ISO 6330 : 2000. The load was made up to one kilogram using other fabric pieces and 10 g of washing powder was used.

Antimicrobial assays

Qualitative and quantitative antimicrobial assays on textiles were performed as per AATCC Test Methods 147-1998 (parallel streak method) and 100-1999, respectively, using the bacterial species *Escherichia coli* as described previously.[13] The appearance of bacterial growth in the qualitative test or the absence of bacterial reduction in the quantitative test indicated no antimicrobial activity in the fabrics.

RESULTS AND DISCUSSION

In Part 1 of this study,[13] an effective antimicrobial treatment for wool was reported, using the biocide PHMB in the finishing. Part 2 of this study further considered the washfastness of the finishing, its compatibility with dyeing and its effects on the physical properties of the fabrics. These issues are important in the development of antimicrobial textiles and poor performance in any of these areas may either make the process commercially unviable or restrict its applications.

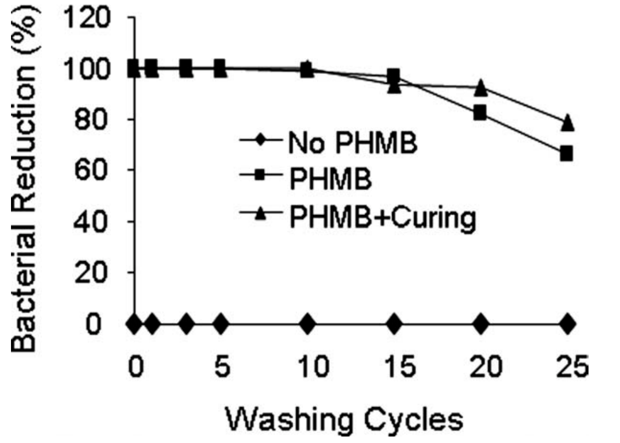

Figure 1 Washing durability of antimicrobial activity of wool fabrics that had been pretreated with PMS/sulfite, exhausted with PHMB or cured at 120°C for 5 min after PHMB exhaustion.

Washing durability of PHMB finishing

To examine the durability of PHMB finishing, treated wool fabrics were washed successively for a number of 5A wash cycles at 40°C. The washfastness of PHMB finishing was assessed by quantitative antimicrobial tests. Figure 1 shows that the PHMB-treated fabrics had strong antimicrobial activity, deactivating >99% of the *E. coli* inoculated to them. This ability was retained when the fabrics were washed up to 15 cycles. After 25 washing cycles, the fabrics had still had a bacterial reduction of 67%. These results indicated that the finishing was very durable. Curing (120°C for 5 min) was also investigated whether it would increase the durability. Curing has been reported not to have any effect on PHMB durability in cotton fabrics.[17] Consistent with these findings, our results revealed no difference between the fabrics with or without the curing

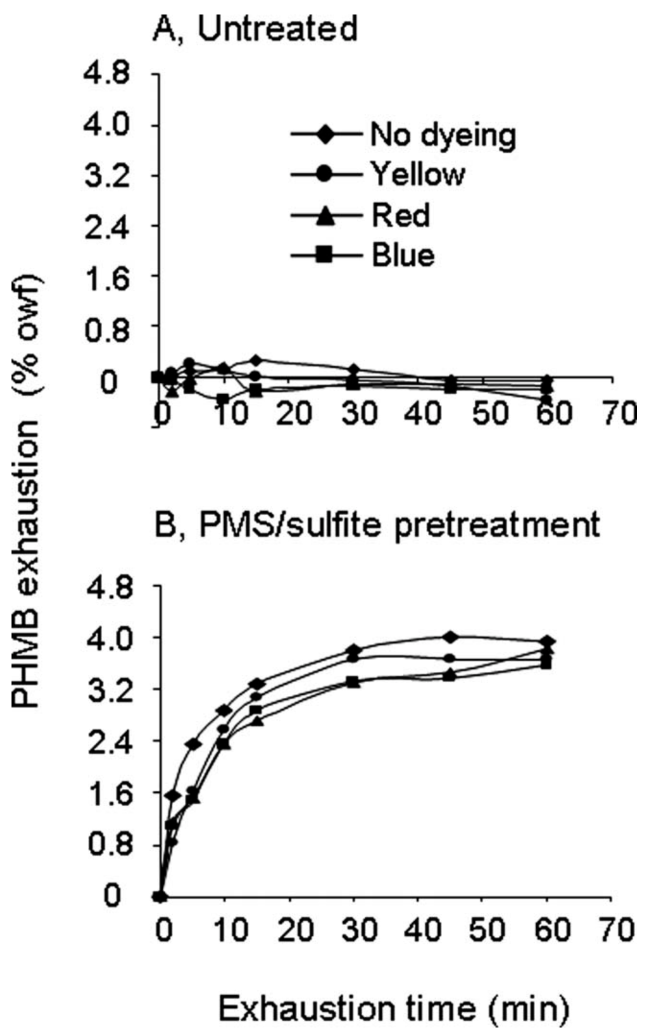

Figure 2 Effect of premetalized dyes on PHMB exhaustion. Untreated or PMS/sulfite pretreated wool fabrics were dyed with three shades of the dyes and used for PHMB exhaustion (8% owf in the bath) at 40°C.

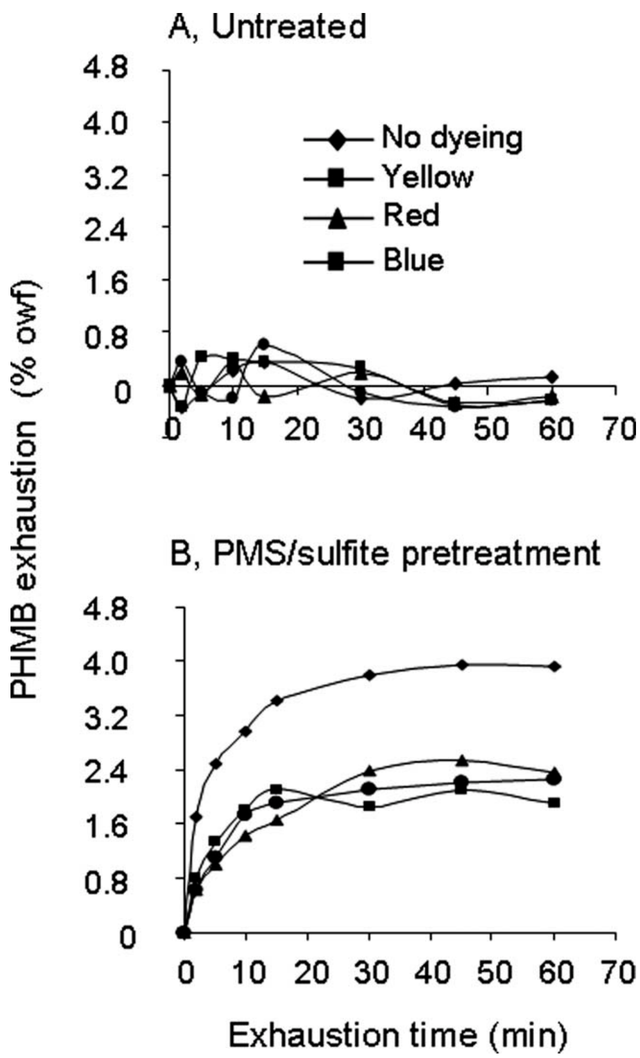

Figure 3 Effect of acid dyes on PHMB exhaustion of untreated and PMS/sulfite pretreated wool fabrics. Other conditions were the same as in Figure 2.

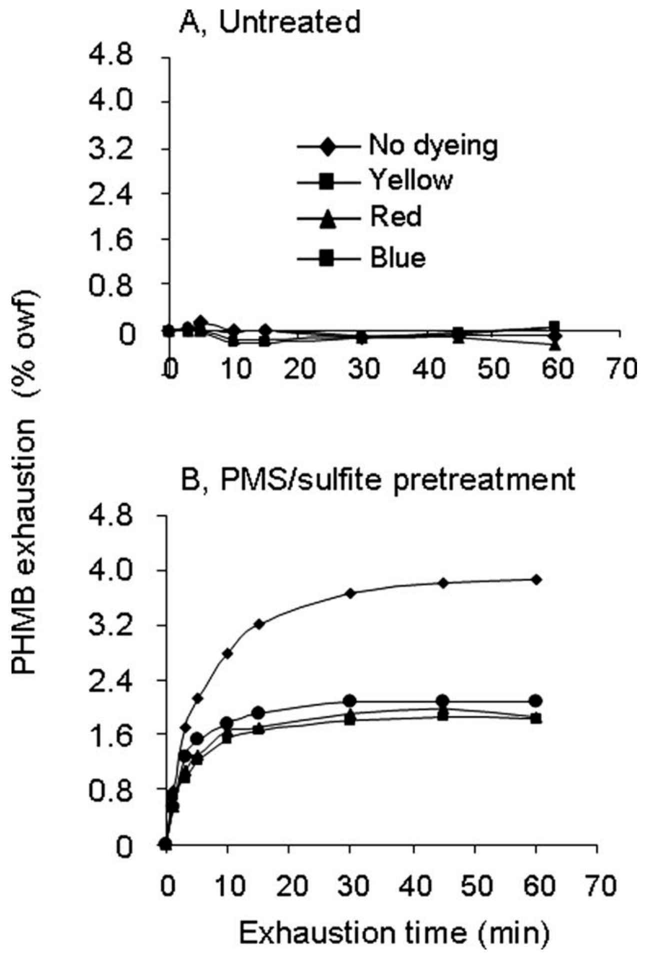

Figure 4 Effect of chrome dyes on PHMB exhaustion of untreated and PMS/sulfite pretreated wool fabrics. Other conditions were the same as in Figure 2.

treatment on wool (Fig. 1). These results indicate that the washfastness of PMHB finishing on wool is at least comparable to that of cotton reported in the literature. Cotton fabrics padded with 2–4% PHMB had a durability of up to 50 washing cycles against *Staphylococcus aureus* but very poor durability against *E. coli*.[17] In a separate study, it was found that cotton fabrics padded with 2.3% PHMB had a durability of 10 cycles against both *S. aureus* and *E. coli*, but the bacteriocidal activity was completely lost after 25 washing cycles.[6]

Effect of dyeing on PHMB exhaustion

For the PHMB antimicrobial finishing to have any industrial value, it must be compatible with common processing in the textile industry, for example, dyeing. It has been observed in cotton that PHMB finishing, if applied first, may affect subsequent dyeing [Arch Chemicals information on Reputex 20^{TM}]. Therefore, investigations were made to examine whether PHMB could be applied to wool fabrics that had been pretreated with PMS/sulfite and dyed. Four different types of dyes, i.e., premetalized dyes, chrome dyes, acid dyes, and reactive dyes, each with three shades, were used. The premetalized dyes (Fig. 2), chrome dyes (Fig. 3) and acid dyes (Fig. 4) all decreased PHMB exhaustion at 40°C by $\sim$ 50%, i.e., from 4% owf to $\sim$ 2% owf. Such a similar magnitude of reduction appeared to suggest that these dyes affected the exhaustion by a common underlying mechanism. In contrast, the three shades of reactive dyes had very little effect on PHMB exhaustion (Fig. 5). So for best results, PHMB should be used in conjunction with reactive dyes.

Wool fabrics without the PMS/sulfite pretreatment, either dyed or undyed, didn't take up any significant amounts of PHMB (Figs. 2–5).

It has been reported that dyeing cotton with reactive dyes enhances the uptake of PHMB through the introduction of additional anionic sites in the fiber.[18]

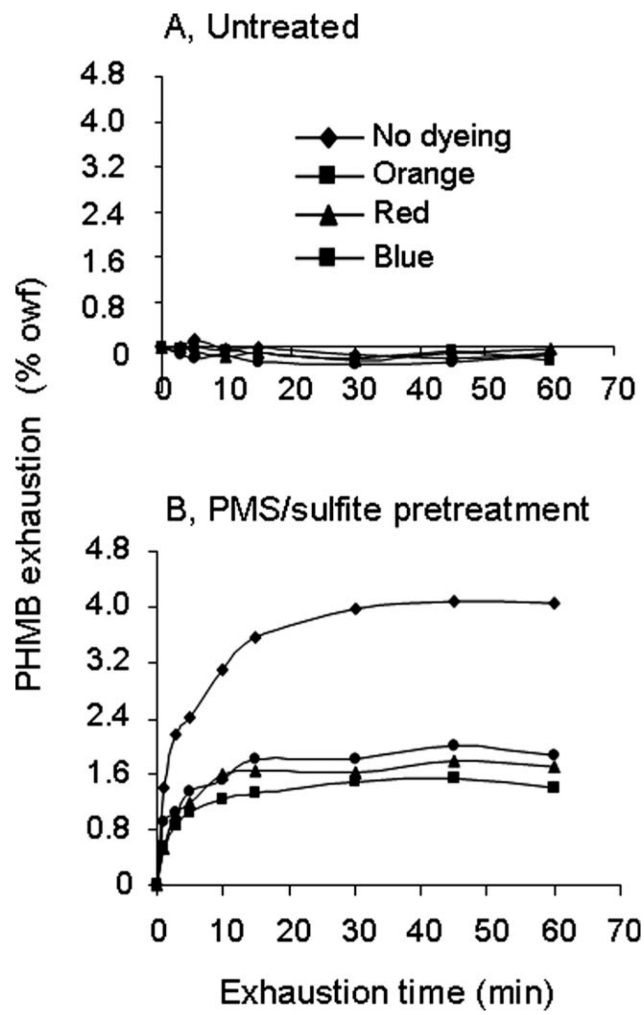

Figure 5 Effect of reactive dyes on PHMB exhaustion of untreated and PMS/sulfite pretreated wool fabrics. Other conditions were the same as in Figure 2.

TABLE I
Antimicrobial Ability of PMS/Sulfite Pretreated, Dyed and PHMB Finished Wool Fabrics Using *E. coli*

Pretreatment	Reactive dyes (shade)	PHMB treatment	Qualitative test (microbial growth)	Quantitative test (% reduction)
None	None	No	Yes	NR
None	Yellow	No	Yes	NR
None	Red	No	Yes	NR
None	Blue	No	Yes	NR
PMS/sulfite	None	No	Yes	NR
PMS/sulfite	Yellow	No	Yes	NR
PMS/sulfite	Red	No	Yes	NR
PMS/sulfite	Blue	No	Yes	NR
PMS/sulfite	None	Yes	No	99.9%
PMS/sulfite	Yellow	Yes	No	99.9%
PMS/sulfite	Red	Yes	No	99.9%
PMS/sulfite	Blue	Yes	No	99.9%

Wool fabrics were pretreated with PMS/sulfite and then dyed with one shade of the reactive dyes. PHMB exhaustion was carried out with 8% PHMB (owf) for 1 hour at 40°C. NR, no bacterial reduction.

However, this effect was not observed for wool in our study (Fig. 5). This appears to suggest that pretreated wool and cotton interact with PHMB through different mechanisms. The attachment of PHMB to cotton is believed to be via ionic interaction and hydrogen bonding.[19] It was previously found that PMS and chlorine oxidization, both of which generated large quantities of anionic cysteic acid on wool surface,[20] failed to improve PHMB. This observation led us to hypothesize that ionic interaction may not play a major role in the uptake of PHMB on PMS/sulfite pretreated wool.[13] The lack of effect of reactive dyes on the uptake further supports this notion.

Antimicrobial activity of dyed fabrics

As reactive dyes did not compromise PHMB exhaustion of the pretreated fabrics, they were used in antimicrobial studies. Fabrics without PHMB finishing, irrespective of the PMS/sulfite pretreatment or dyeing, did not inhibit bacterial growth by the qualitative and quantitative assays. This indicated that neither the pretreatment nor the dyes were detrimental to the bacteria (Table I). On the other hand, dyed or undyed fabrics after PHMB finishing killed all the bacteria that were applied to them in both qualitative and quantitative assays, demonstrating potent antimicrobial efficacy. This indicates that predyeing with reactive dyes does not interfere with PHMB antimicrobial properties.

Physical properties

An ideal antimicrobial finishing should not unacceptably affect the strength, handle or appearance of fabrics. While small biocides (metal, triclosan, QAC) generally have little adverse effect, the application of polymeric biocides (e.g., chitosan) or polymerization grafting may significantly impair the handle of the fabrics.[21,22]

Table II shows tensile strength, bending rigidity and whiteness of wool fabrics after PHMB finishing. Tensile strength was decreased (<10%) by the PMS/sulfite pretreatment, but finishing with PHMB did not alter it any further. Bending rigidity, which is a critical parameter of handle, was slightly increased by PHMB finishing over pretreated fabrics ($P < 0.05$ on Student's *t*-Test) but not over the untreated fabrics. This small increase was somewhat expected because of the presence of PHMB on the fabrics. Subjective assessment by several people indicated that the handle of PHMB-finished fabrics was indistinguishable to that of the untreated or pretreated fabrics. Finally, PHMB, which is a colorless solution at 20% (w/v), slightly increased the whiteness of the

TABLE II
Physical Properties of Wool Fabrics After the PMS/Sulfite Pretreatment and After PHMB Finishing. PHMB Exhaustion Was Carried Out With 8% PHMB (owf) for One Hour at 40°C

Treatments	Tensile strength (maximal loading, N)	Bending rigidity (μN m)	Whiteness (CIE Ganz 82 units)
Untreated	299.1 ± 1.3	6.93 ± 0.27	3.49 ± 0.24
Pretreatment only	273.2 ± 3.3	6.48 ± 0.10	8.90 ± 0.49
Pretreatment +PHMB	282.7 ± 4.1	7.27 ± 0.23	12.15 ± 0.60

fabrics although the difference was not visually apparent (Table II). Overall, the process had little adverse effect on the physical properties of the wool fabrics.

CONCLUSIONS

This report has demonstrated the washing durability, compatibility with dyeing and fabric physical properties of PHMB finished antimicrobial wool. PHMB finishing on PMS/sulfite pretreated wool fabrics was durable, sustaining at least 25 washing cycles without significant decrease in its antimicrobial efficacy. The finishing was compatible with reactive dyes, but other types of dyes (i.e., acid, chrome and premetalized dyes) reduced the uptake of PHMB by ~50%. So for best results reactive dyes should be used in conjunction with PHMB finishing. The finishing had no apparent adverse effect on the physical properties of the fabrics (i.e., tensile strength, handle and whiteness). These results, together with the record of safe use of PHMB, indicate that this treatment regime meets the requirements for the production of effective antimicrobial wool textile products.

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