

Durable and Regenerable Antibacterial Finishing of Fabrics with a New Hydantoin Derivative

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Durable and regenerable antibacterial fabrics were prepared by using an innovative chemical technology employing a precursor biocidal agent, dimethylol dimethylhydantoin (DMDMH), in a chemical finishing process. The method resulted in significant add-on rates of hydantoin groups on cellulose and established a durable antimicrobial functionality, once the grafted heterocyclic compounds were chlorinated by diluted chlorine bleaching. Both cotton fabrics and polyester/cotton fabrics exposed to treatment baths containing from 2 to 10% of DMDMH acquired a powerful inactivating capacity against a wide range of food-borne and water-borne infectious disease agents. The biocidal functions are regenerable by regular laundry exposure to chlorine bleach and can withstand over 50 standard machine washes without appreciable deterioration. In addition to their powerful antimicrobial efficacy, the fabrics exhibited improved wrinkle resistance and maintained appropriate mechanical properties, making them ideal for medical and hygienic textile applications. In this article we report the results from biocidal tests and durability evaluations and provide data characterizing physical attributes of the treated fabrics.

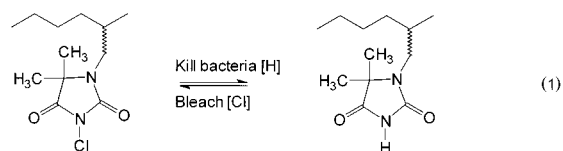
Introduction

Transmission of infectious disease agents, particularly antibiotic-resistant strains, in health-care facilities is an increasingly important concern to medical providers and the public.^{1–4} Survival of drug-resistant microorganisms has occurred on textile materials and plastics,³ and transmission has been demonstrated as a result of surface contact with hands, cloths, and hospital devices such as surgeon gowns and nurses' clothing.^{5–6} Currently, physical barriers to microorganisms are relied upon through the use of disposable nonwoven garments, and these are widely employed in operating and emergency rooms. There has been no practical way until now to provide an enhanced level of antimicrobial protection to healthcare providers who wear garments made of woven reusables.⁷ Effective biocidal materials for reusable clothing could find a place in hospitals, operating rooms, and other related work environments involving exposure to disease agents.

A number of methods for incorporating antimicrobial functions into textile materials have been developed elsewhere.^{8–9} Agents used to date include quaternary ammonium salts,^{10–11} metal ions,⁹ and antibiotics.¹² Despite the variety of systems reported in the literature, most treated textiles lack durability in their antimicrobial function, are poorly effective against many microbes, or have a capacity that is nonregenerable and subject to rapid decline when used. The production of durable, refreshable biocidal textile materials has not been reported previously by using any of these approaches. However, in pursuit of a standard theory, laid down several decades ago by Gagliardi,¹³ we recently developed a novel method of conferring cotton-contain-

ing fabrics with durable and regenerable antimicrobial functions.^{14–15}

The method employs a hydantoin derivative, monomethylol-5,5-dimethylhydantoin (MDMH), as a precursor for generation of a biocidal halamine structure on cellulose by exposure of the modified fabric to a laundering process involving a chlorine bleach rinse.¹⁴ During the chemical finishing process, hydantoin rings are covalently incorporated onto cellulose. The linkage between the heterocyclic ring and cellulose units is unaffected by repeated laundry and bleaching operations.¹⁵ The hydantoin halamine chemistry is best described as a reversible redox reaction (eq 1),



which also illustrates the regeneration capability in the presence of free chlorine, and the results are due to the outstanding stability of the hydantoin rings. The biocidal effect of the fabrics prepared with MDMH is controllable, so as to generate rapid killing of *Staphylococcus aureus* and *Escherichia coli* on the fabric surfaces

In this article, we report data on additional development with this system, with another hydantoin derivative, dimethylol-5,5-dimethylhydantoin (DMDMH), bearing the same functional group as MDMH, utilized as a grafting agent. Structurally similar to dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), DMDMH is a bi-functional compound and is able to establish both cross-linkages between cellulose molecules and grafting on cellulose. When fully constituted as a cross-linking agent, all of the reactive sites responsible for redox reactions on hydantoin rings are blocked by cellulose intermolecular linkages (Scheme 1). Then, the DMDMH

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Chemical Finishing of Fabrics. The chemical finishing process employed in the treatment is the same

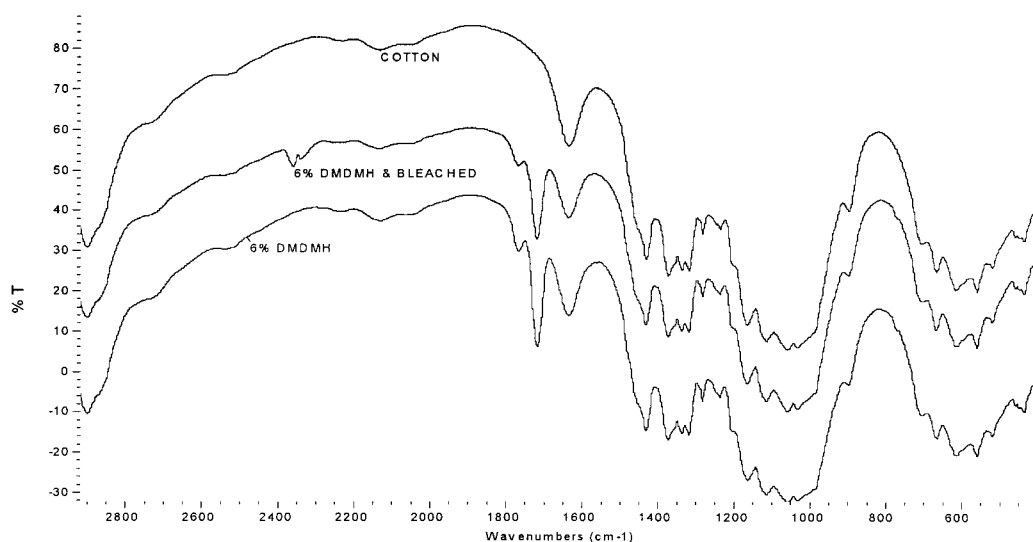


Figure 1. FTIR spectra of untreated, DMDMH-treated, and DMDMH-treated and bleached cotton fabrics.

as for wrinkle-free finishing, except that DMDHEU is replaced by DMDMH. The chemical structures of the finished fabrics were confirmed with FTIR spectra. Hydantoin compounds have unique structural characteristics, bearing two carbonyl groups in the ring and showing two prominent bands at 1720 and 1780 cm^{-1} .¹⁷ These bands can then be employed to confirm the presence of hydantoin rings on cellulose. Figure 1 shows the FTIR spectra of the treated fabric samples. Both the precursor and halogenated fabrics exhibited two bands in the carbonyl region. The carbonyl bands of the DMDMH-treated fabrics were identical to those of MDMH-treated ones, but the intensities of the bands were stronger than with MDMH-treated fabrics, indicating a better grafting rate of the hydantoin ring in the DMDMH treatment.¹⁵

The antibacterial properties of textile materials, in general, depend on the structures and amounts of biocidal groups incorporated on their surface. It should be pointed out that it is the *N*-halamine group and not the free chlorine that provides the inactivation of microorganisms.^{18–19} By incorporating different amounts of *N*-halamine biocidal groups, ranging degrees of efficacy, namely, biocidal (lethal) and biostatic (inhibitory) functions, can be acquired. With more concentrated biocides on the surface, fabrics will inactivate bacteria rapidly, whereas less biocidal sites might result in slower inactivation of microorganisms or might only cause inhibition to bacteria growth. The concentration of DMDMH in the finishing baths varied from 2 to 10%, and the corresponding add-on rates of the agent are listed in Table 2. Fabric #400 (100% cotton) samples showed higher add-on rates than fabric #7409 (polyester/cotton = 65/35) over the whole range of finishing bath concentrations because of the higher cellulose contents, and the results were consistent with those for the MDMH-treated fabrics.¹⁴

The add-on rates of DMDMH on fabrics were greater than those of MDMH. This was also indicated by the appearance of two stretching bands of DMDMH on treated fabrics at 1720 and 1780 cm^{-1} that were stronger than those seen for the fabrics treated with MDMH.¹⁵ The difference in add-on rates can be attributed to the structural characteristics of DMDMH, whose two similar reactive groups can potentially double the possibilities of the grafting reaction on cellulose (Scheme 1).

Table 2. Add-on Rates of Treated Fabrics^a

conc of DMDMH (%)	fabric ^b	add-on (%) ^c
2	400	0.85
	7409	0.84
6	400	2.22
	7409	1.62
10	400	3.52
	7409	2.61

^a Wet pick-up was 80–90%, and pH was below 4. ^b #400 is a plain woven pure cotton fabric, and #7409 is a blend of polyester/cotton (65/35) plain woven fabric. ^c Add-on values of fabrics are determined by the weight increase after the treatment divided by the original weight of the fabric.

However, because of the low efficiency of the catalyst (pure MgCl_2) used in the finishing, the overall fixation rates of the finished products were lower than expected (Table 2). Low fixation rates in chemical finishing are a serious concern to the textile industry and potential scale-up tests. The catalytic efficiency and fixation rates can be improved by using different catalysts and by varying chemical finishing conditions. These influences have been studied recently in order to optimize the chemical treatment conditions, with improved overall fixation rates achieved as well.

Efficacy against Various Microorganisms. The fabrics treated by DMDMH were activated with a diluted laundry bleach through a reversible redox reaction, as shown in eq 1. Then, the activated fabrics were challenged with both gram-positive and gram-negative bacteria for routine evaluations serving as an indication of successful chemical finishing. Tests of the biocidal functions against a broad range of microorganisms including pathogenic and nuisance species such as methicillin-resistant *Staphylococcus aureus*, *Candida albicans*, and *Brevibacterium*, which are of particular interest for potential medical and hygiene textile users, were also performed on the treated fabrics. The tests were conducted following AATCC test method 100, a quantitative evaluation test for antimicrobial properties of the fabrics, and the contact time was limited to 2 min, as preliminary experiments had demonstrated the rapid onset of biocidal functions.

Fabrics treated with both 2 and 6% DMDMH finishing baths, whether 100% cotton or polyester cotton blends, showed high levels of efficacy against all of the

Table 3. Biocidal Results of Fabrics Treated by 2 and 6% of DMDMH^a

fabric ^b	time of exposure	microorganism	log reduction of bacterial challenge	
			2% DMDMH	6% DMDMH
400	2 min	<i>E. coli</i>	6	6
7409			6	6
400	2 min	<i>Staph. aureus</i>	6	6
7409			6	6
400	2 min	<i>Salmonella choleraesuis</i>	6	7
7409			7	6
400	2 min	<i>Shigella</i>	6	6
7409			6	7
400	2 min	<i>Candida albicans</i>	2	6
7409			6	6
400	2 min	<i>Brevibacterium</i>	8	8
7409			8	8
400	2 min	<i>Pseudomonas aeruginosa</i>	6	6
7409			6	6
400	2 min	methicillin-resis.	/	3
7409		<i>Staph. aureus</i>	/	6
400	2 min	vancomycin-resis.	/	6
7409		<i>Enterococcus</i>	/	6

^a AATCC test method 100. ^b #400 is a plain woven pure cotton fabric, and #7409 is a blend of polyester/cotton (65/35) plain woven fabric.

tested microorganisms after 2-min exposures (Table 3). Test results also confirmed that finishing baths containing only 2% DMDMH could produce a uniformly high biocidal activity on both pure cotton and cotton blends. There were no significant differences in biocidal functions against the tested species between the fabrics used such as poly/cotton (7409) and pure cotton (400) fabrics, except in the case of the superior efficacy of polyester cotton blends in inactivating *Candida albicans* and methicillin-resistant *Staph. aureus*.

Durability of Antimicrobial Functions. Extraordinarily durable biocidal functions on the finished fabrics were revealed in a series of laundering tests. The tests were conducted by exposure of treated fabrics to repeated washing and bleaching cycles in such a way that, after every five machine washes, the fabrics were recharged by bleaching in a diluted chlorine solution, rinsed in deionized water, and then examined again for biocidal properties. Both pure cotton and polyester/cotton fabrics exhibited equal efficacies against gram-positive (*Staph. aureus*) and gram-negative (*E. coli*) bacteria at every level of DMDMH finishing concentrations, exhibiting six log reduction to both bacteria throughout the testing period of 50 machine washes. Compared to 2% DMDMH-treated cotton and polyester/cotton blend samples, DMDMH finishes showed more durable antimicrobial functions against *E. coli* and *S. aureus* after being subjected to laundering. For example, the efficacy of 2% DMDMH-treated fabrics against *S. aureus* declined after 25 machine washes,¹⁴ whereas that of the DMDMH-treated fabric was unchanged even after 50 washes.

The increased durable antibacterial functions of the DMDMH-treated fabrics contribute to increased addition of the functional hydantoin groups on cellulose, which then leads to more available biocidal halamine structures after bleaching. DMDMH has a higher tendency to react with cellulose than MDMH because of its two reactive groups, thus demonstrating increased add-on rates and improved efficacy against microorganisms. However, it was also found that the durability of the biocidal functions is associated with another reaction

in which the two methylol groups could have initiated a cross-linking reaction. Such cross-linking can result in random breakdown of one side of the cross-link and opening up for chlorination, which will be discussed in the following sections.

Similar to the results obtained from the MDMH study, DMDMH-treated polyester/cotton samples still showed outstanding biocidal properties even though they contained fewer functional groups per unit of fabric weight than pure cotton. This extraordinary property is possibly a result of a stabilization effect on halamine structures mediated by phenyl rings in polyester fibers.¹⁵

Halamine Content of Fabrics. The oxidative ability of the halamine structure is theoretically weaker than that of free chlorine according to their reduction potentials, but it is powerful enough to be biocidal.^{18–20} Obviously, the number of chloramine functions and not free chlorine atoms on the surface of the fabrics is responsible for the inactivation of microorganisms. The halamine bonds (N–Cl) or so-called combined chlorine were undetectable by FTIR analysis on the treated fabrics because the bonds are substantially less concentrated than unhalogenated structures (N–H) on the treated fabrics (Figure 1). However, N-chloramine (N–Cl) can be reduced to N–H and chloride by reaction with a reducing agent such as sodium thiosulfate. This reaction permits iodometric titration to provide an indirect measurement of N–Cl bonds. The combined chlorine contents on the fabrics before and after laundering titrated by this method are shown in Figure 2. It can be seen that the contents were not immediately reduced after extensive washing; instead, they generally rose to a certain level and then declined for most of the samples during repeated laundering.

The chemical linkages between the fibers and the DMDMH are quite stable because of the feature of covalent acetal bonds; thus, cannot be easily damaged by washing and bleaching. However, some DMDMH that had formed cross-linking bonds with cellulose would probably open up as a result of laundering, particularly on the imide side connections that are less stable to chemical attack (Scheme 1). Theoretically, concentrated active chlorine, acting as a strong oxidant in excess amounts, could be powerful enough to damage this chemical linkage between hydantoin and cellulose, resulting in the reduced durability of the functions. However, because of a high percentage of unreacted N–H sites, which remained available to absorb and react with the excess amount of active chlorine,²¹ together with the low concentrations of the chlorine solutions usually used in bleaching processes, oxidative damage to the linkages appeared to be minimal, and the chlorine contents on the fabrics after each recharging did not decrease. However, the dramatic increase in the chlorine contents on almost all of the fabrics, after the washing and recharging practice, were quite abnormal if only the grafting reaction is considered. They are reasonable, however, if the breakage of imide connections formed through cross-linking is considered. This phenomenon can be clearly demonstrated by the reactions in Scheme 1 and supported by the following discussion.

Wrinkle Resistance of the Treated Cotton Fabrics. It is clear that DMDMH cross-linking should improve the wrinkle resistance of cellulose. However, if DMDMH is tied up as a cross-linking agent, it will lose reactive sites with chlorine, and this would make

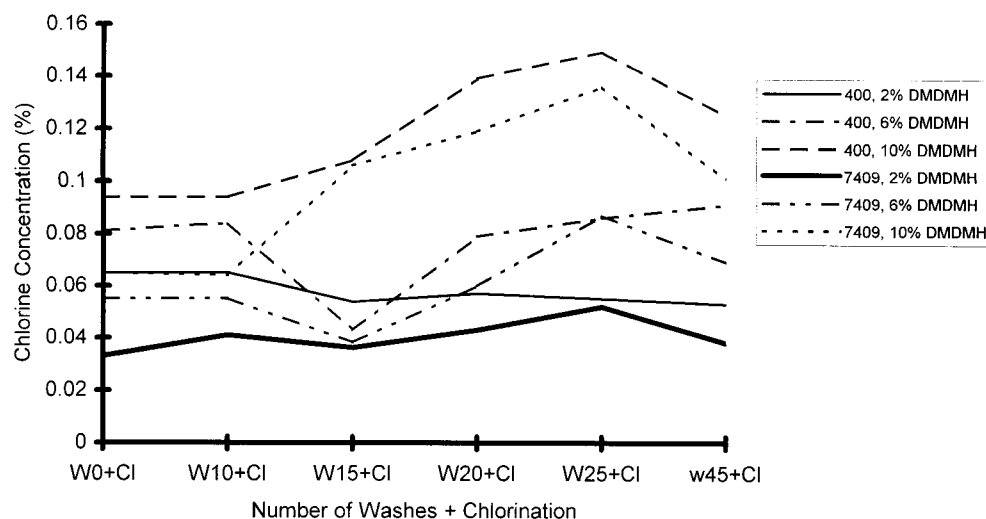


Figure 2. Chlorine contents on fabrics after washing and bleaching.

Table 4. Wrinkle Recovery Angles of DMDMH-Treated Cotton Fabrics (#400)^a

DMDMH %	before bleach	W5 + bleach	W10 + bleach	W15 + bleach	W20 + bleach	W25 + bleach	W30 + bleach	W40 + bleach	W50 + bleach
2	88.25	97.2	100.42	96.0	97.75	103.0	99.17	94.33	93.08
6	115.42	111.8	108.58	111.17	111.0	111.17	109.75	107.25	106.0
10	120.0	117.8	114.83	112.08	114.83	113.75	112.67	107.17	112.33

^a A bleaching solution containing 0.01% Cl was used in the activation and regeneration processes. Machine washing at 160 F for 30 min with 92 g of AATCC detergent 124.

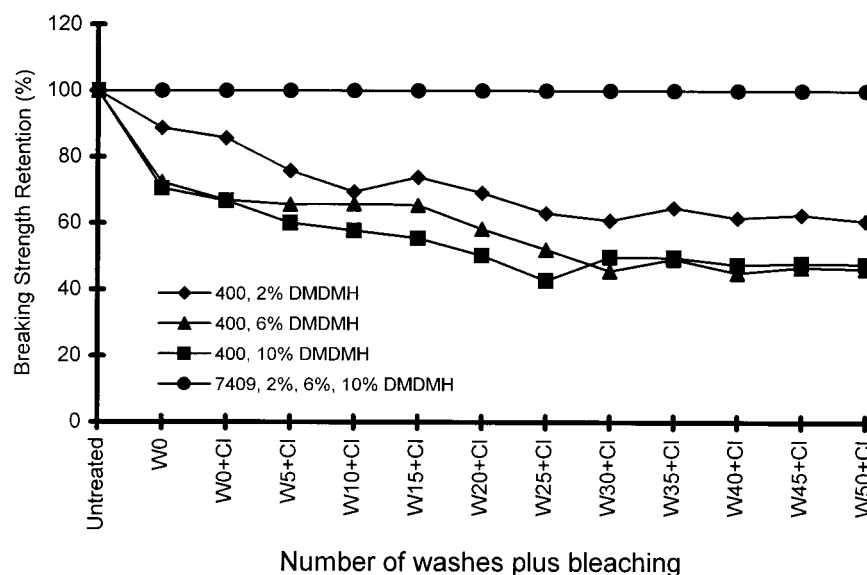


Figure 3. Breaking strength retentions of DMDMH-treated cotton fabrics (#400) and polyester/cotton fabrics (#7409) after treatment, washing, and bleaching.

the fabric less biocidal. Therefore, the reaction needs to be carefully controlled to minimize occurrence of cross-linking reactions in order to achieve the best biocidal effect. Nevertheless, cross-linking cannot be eliminated and is always associated with the grafting reaction with a bifunctional compound. However, it could be an extra benefit to some fabrics, particularly when durable press properties are desired. To quantify the cross-linking function of DMDMH, the wrinkle recovery angles of cotton fabrics (#400) treated with different concentrations of DMDMH were measured. The results are shown in Table 4. The wrinkle resistance of the fabrics improved as the concentration of DMDMH was increased, together with increased addition rates of DMDMH on the fabrics. However, the

wrinkle resistance was reduced substantially after 50 machine washes, indicating that the DMDMH cross-linking is not very durable. The wrinkle recovery angles of the fabrics treated with concentrated DMDMH dropped by almost 10%, a clear indication of some breakage of the chemical linkages between the agent and cellulose. This could be attributed to the breakage of the weak linkages between DMDMH and cellulose, particularly the weak imide bond connection (Scheme 1). When one side of the DMDMH connections to cellulose is broken, leaving the amide bonds intact, the cross-linking effect is lost, and the wrinkle-free properties are damaged. In this manner, the opened imide sites can accept more chlorine and thus be converted to biocidal halamine structures. The loss of wrinkle resis-

tance of the fabrics accounts for the increased chlorine content of the fabrics after repeated washing (Figure 2).

Mechanical Properties of the Fabrics. The breaking strengths of finished fabrics are closely related to the finishing agents and finishing conditions, especially to the acidity of the finishing baths and curing temperatures. More acidic finishing solutions and higher curing temperatures result in more serious damages to the fabrics. Figure 3 shows the breaking strength retentions of both pure cotton print cloth and polyester/cotton fabrics finished with different concentrations of DM-DMH, after extensive washes and bleaching cycles with a chlorine bleach. The finishing, washing, and chlorination conditions were same as those listed in Table 4. The breaking strengths of the pure cotton samples were substantially reduced after treatment and repeated washing and bleaching. Higher concentrations of DM-DMH in the finishing bath led to a decline in breaking strengths. The pattern of tensile strength reduction caused by different concentrations of DM-DMH finishing solutions is very similar to that observed on MDMH-treated fabrics.²²

On the other hand, polyester/cotton fabrics exhibited excellent breaking strength retention after chemical treatment and chlorination (Figure 3). Even after 50 washes and more than 10 recharges, there was no reduction in their breaking strengths. This is advantageous because most protective clothing is made of blends of polyester and cotton fibers. Because of the structure of the blend, only the cotton cellulose is damaged by the finishing conditions, whereas polyester, conferring mechanical properties, is unaffected by the chemical exposure. More importantly, the polyester/cotton blend fabrics showed excellent biocidal properties, sometimes exceeding those of pure cotton (Table 3).

Conclusions

Durable and regenerable antibacterial functions can be chemically imparted onto cotton- and cellulose-containing fabrics by treatment with dimethylol dimethylhydantoin (DMDMH), followed by chlorine bleaching. The methylol groups on DMDMH can either form cross-links with cellulose with both functional sites reacted or graft onto cotton with only one reactive site consumed. The biocidal effect of the treated fabrics results from grafted DMDMH, but the cross-linked DMDMH could provide additional active sites for conversion to halamine structures through the weaker imide bond connections to cellulose. The biocidal efficacy of such fabrics is high against a wide range of microorganisms with a contact time of only 2 min. The biocidal effect persists through at least 50 machine washing cycles and can be regenerated by exposure to diluted chlorine solutions for more than 10 times. The concentration of the DMDMH in the finishing bath can be dropped to as low as 2%, without affecting the antibacterial functions of the treated fabrics significantly. Cotton/polyester blends retain durable and regenerable biocidal properties better than pure cotton without deterioration of mechanical properties. DM-DMH-treated cotton fabrics also displayed durable press characteristics because of the cross-linking reaction of DMDMH with the cellulose.

Acknowledgment

This research is supported by a CAREER award from National Science Foundation (DMI-9733981). Halo-

Source Corporation of Seattle, WA, financially sponsored the research of antimicrobial textiles.

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Received for review July 13, 2000

Revised manuscript received November 20, 2000

Accepted November 20, 2000

IE000657T