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# Synthesis and antimicrobial applications of 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin]

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**Abstract**

A novel, durable, long lasting, *N*-halamine siloxane monomer precursor, 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin] has been prepared and characterized by $^{1}$H-NMR and FTIR for the purpose of functionalizing the surfaces of various materials. In this work, the precursor *N*-halamine moiety was attached by siloxane covalent bonding to surfaces of cotton fibers. Simulated laundering tests indicated that the chlorinated *N*-halamine structure could survive many repeated home launderings. The materials were rendered biocidal after exposure to oxidative halogen solutions, i.e. dilute household bleach. Once chlorinated, these materials were biocidal against *Staphylococcus aureus* and *Escherichia coli*. Upon loss of the halogen from either long-term use or consumption by the microbes on the surfaces, they could be simply recharged by further exposure to dilute bleach to regain biocidal activity.


*Keywords:* Biocides; Bioactivity; *N*-halamine; Siloxane

## 1. Introduction

Recently there has been a growing concern about how to reduce or eliminate infections completely, especially those caused by antibiotic-resistant, Gram-positive bacteria, such as methicillin-resistant *Staphylococcus aureus* (MRSA), and vancomycin-resistant *Enterococci* (VRE). These bacteria have been shown to have long survival times on commonly used hospital fabrics, such as hospital privacy drapes, scrub suits, and lab coats [1,2]. The survival and transfer of microorganisms between patients and health care workers have been documented [3–6]. The medical gowns and uniforms used currently have been proven to provide ineffective barriers for health care workers in numerous studies [7–11]. This demonstrates a great need for antimicrobial textiles and polymers that are able to protect against all major pathogens [12–14]. *N*-halamine compounds could provide such protection since they have shown excellent biocidal functions against a wide range of microorganisms such as fungi, bacteria, viruses, and yeasts [15–17]. In addition, *N*-halamines have demonstrated the capability of rapid and total inactivation of various microorganisms without causing the microorganisms to develop resistance to them [18]. The stability of *N*-halamines is directly related to their structures, which is evidenced by their dissociation constants in solution [19]. Furthermore, *N*-halamine structures are capable of killing microorganisms directly without the release of free chlorine into the system [20]. *N*-halamines can be composed of amine, amide, and imide halamine bonds, the dissociation constants for which are presented in Table 1 [19]. It is thought that those structures containing amide halamine bonds are of the most practical use since they exhibit a moderate rate of transfer of active chlorine from the *N*-halamine structures in aqueous solution to cells of organisms and provide reasonably rapid biocidal activity. The equilibrium of dissociation of a halamine

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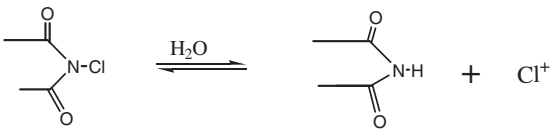
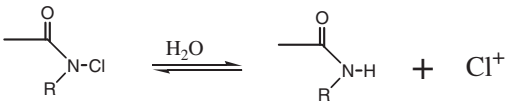
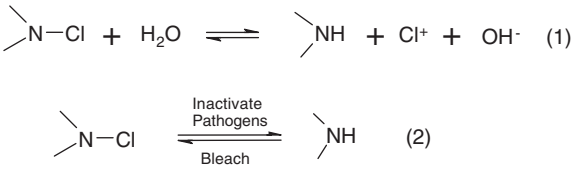
Table 1
Stability of *N*-halamine structures [19]

| Dissociation reaction | Dissociation constant for example |
|---|---|
| Imide structure  | $1.6 \times 10^{-12}$–$8.5 \times 10^{-4}$ trichlorocyanuric acid $2.54 \times 10^{-4}$ 1,3-dichloro-5,5-dimethylhydantoin |
| Amide structure  | $2.6 \times 10^{-8}$ 1,3-dichloro-2,2,5,5-tetramethylimidazolidin-4-one $2.3 \times 10^{-9}$ 3-chloro-4,4-dimethyl-2-oxazolidinone |
| Amine structure  | $<10^{-12}$ 1-chloro-2,2,5,5-tetramethylimidazolidin-4-one |

in aqueous solution can best be understood from Eqs. (1) and (2).



The amine halamine bonds are the most stable, but offer a slower kill rate than do the amide halamines, and although the imide halamine offers a very rapid kill rate, it is the least stable structure and can rapidly lose active chlorine. Thus, the amide function seems to be a reasonable compromise between stability and biocidal efficacy. With this in mind, the precursor 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin] was designed so that once chlorinated, it would provide an effective biocide which would be capable of having two or more siloxyl bonds to surfaces. This could enable a textile coated with it to withstand numerous home laundering cycles, providing a durable and effective broad-spectrum biocidal textile. Examples of surfaces and materials which can be rendered biocidal with the *N*-halamine siloxanes include cellulose, synthetic fibers, ceramics, plastics, polyurethanes, and metals [17]. In the case of cellulose, the binding to the surface is almost certainly covalent in nature due to a condensation reaction of the OH groups on the siloxane with those on the cellulose. Upon loss of the halogen from either long-term use or consumption by the microbes on the surfaces, surfaces such as for textiles can be simply recharged by further exposure to dilute bleach and thus regain their biocidal activity [21–23]. The limiting factor of the biocidal efficacy ultimately is how readily the *N*-halamine, and/or the precursor, can be washed off the surfaces of the materials due to hydrolysis of the formed silyl ether linkages. Prior work on a lower molecular-weight monomer 3-triethoxysilylpropyl-5,5-dimethylhydantoin has shown excellent biocidal efficacy on textiles, but a tendency to hydrolyze off the fabrics after extended machine washings [22]. Therefore, it seemed reasonable that increasing the molecular weight, hydrophobicity, and the number of chemical bonds to the surface would provide for an effective and durable antimicrobial coating for various materials.

## 2. Experimental

### 2.1. Materials

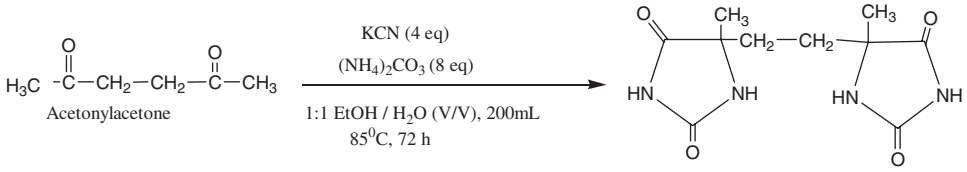
All chemicals were purchased from the Aldrich Chemical Company, Milwaukee, WI and used as they were received without further purification unless otherwise noted. The fabric used was (Style 400 Bleached 100% Cotton print Cloth, Testfabics, Inc., West Pittston, PA). The household bleach was Clorox® brand (Clorox, Inc., Oakland, CA). The bacteria used were *S. aureus* ATCC 6538 and *Escherichia coli* O157:H7 ATCC 43895 (American Type Culture Collection, Rockville, MD). The Trypticase soy agar employed was from (Difco Laboratories, Detroit, MI).

### 2.2. Instruments

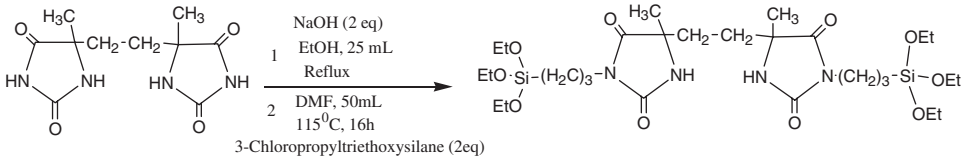
The NMR spectra were obtained using a Bruker 400 MHz spectrometer; the IR data were obtained with a Shimadzu IR Prestige-21 FTIR. Tensile strengths were measured with a model 1122 Instron Universal Materials Testing Machine. The reactor used was a Parr 4841 high-pressure reactor.

### 2.3. Preparation of 5,5′-(1,2-ethanediyl)bis[5-methylhydantoin] Scheme 1

Preparation of 5,5′-(1,2-ethanediyl)bis[5-methylhydantoin] was carried out, for example in one experiment, by adding 5.71 g (0.05 mol) of 97% acetonylacetone to a 250 mL stainless steal vessel, along with 13.02 g (0.20 mol) of 97% potassium cyanide and 38.44 g (0.40 mol) of 98% ammonium carbonate in 200 mL of a 1:1 (v/v) mixture of ethanol and water as solvent. This mixture was then sealed and heated to 85 °C with constant stirring for 72 h. The reactor vessel was then allowed to cool to room temperature, and the reaction mixture was poured into a 500 mL beaker containing 300 mL of water. The precipitate formed was then vacuum filtered from the mother liquor which was then neutralized to a pH ≈ 7 by drop wise addition of a 6 N HCl acid solution over a period of




Scheme 1. Preparation of 5,5′-(1,2-ethanediyl)bis[5-methylhydantoin].




Scheme 2. Preparation of 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin].

90 min. The precipitate was the desired product, which was dried in a vacuum oven overnight at 45 °C. A light-tan solid was weighed, and (6.41 g, 50.4% yield) was obtained. Spectroscopic data obtained for 5,5′-(1,2-ethanediyl)bis[5-methylhydantoin] were: $^1$H NMR ($d_6$ DMSO) $\delta$ 1.27 (s, 6 H), 1.58 (m,4 H), 7.97 (s, 1 H), 7.99 (s, 1 H), 10.60 (s, 2 H); IR (KBr) 1715, 1735, 3207 cm$^{-1}$.

### 2.4. Preparation of 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin] Scheme 2

Prparation of 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin] was carried out, for example in one experiment, by first preparing the sodium salt of 5,5′-(1,2-ethanediyl)bis[5-methylhydantoin]. This was done by mixing 1.00 g ($3.90 \times 10^{-3}$ mol) of 5,5′-(1,2-ethanediyl)bis[5-methylhydantoin] in a 100 mL round bottom flask with 0.159 g ($3.90 \times 10^{-3}$ mol) of 98% sodium hydroxide and 25 mL of absolute ethanol as solvent. This solution was then refluxed for 30 min with constant stirring. The sodium salt was isolated by removing the ethanol under reduced pressure and was then placed in a vacuum oven overnight at 45 °C to remove any water produced as a byproduct. Once 1.17 g of sodium salt were obtained, 50 mL of anhydrous DMF were added as solvent. When the salt had been dissolved, the reaction solution was heated to 45 °C, and 1.94 g ($7.80 \times 10^{-3}$ mol) of 97% 3-chloropropyltriethoxy silane were added drop wise over a period of 25 min. Once all of the 3-chloro propyltriethoxysilane had been added, the temperature was then raised to 115 °C, and the reaction mixture was stirred constantly overnight. After cooling to ambient temperature, the KCl produced in the reaction and the DMF solvent were removed by filtration and evaporation, respectively. The KCl was then dried in an oven and weighed as one method to determine the percent yield of the reaction. Any DMF residual was removed with a hexane extraction, and the dark gold oil left behind was the desired product with a mass of 2.54 g which corresponded to a 97.7% yield. The mass of the KCl was 0.273 g which corresponded to a 94% yield. Some spectroscopic data for 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin] were: $^1$H NMR ($d_6$ DMSO) $\delta$ 0.58 (4 H), 1.19 (18 H), 1.20 (6 H), 1.36 (4 H), 1.37 (4 H), 3.7 (4 H), 3.9 (12 H), 7.31 (1H), 7.96 (1 H); IR (KBr) 773, 862, 1080, 1167, 1713, 1769, 2887, 2974, 3289, 3520 cm$^{-1}$.

### 2.5. Coating procedure

The 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin] monomer was coated onto the surfaces of cotton swatches by soaking the swatches in baths containing 5% by weight of the crude product of the aforementioned monomer dissolved in a 1:1 (w/w) mixture of ethanol and water. After the soaking procedure, the coated swatches were cured at 95 °C for 1 h. Then, the swatches were soaked in 0.5% detergent solution for 15 min, followed by several water rinses to remove any weakly bonded coating. Add-on weights for the coated swatches were measured after drying at about 110 °C for 90 min followed by cooling for 60 min in a desiccator. Also, FTIR spectra were observed for the dried swatches after the coating process, and tensile strengths of the fibers were measured in order to assess any loss of strength of the fibers induced by the coating procedure.

### 2.6. Chlorination procedure

The coated cotton swatches were chlorinated by soaking them in a 10% aqueous solution of NaOCl household bleach buffered to pH 7 at ambient temperature for 30 min. The Chlorinated swatches were washed with water and dried at 45 °C for 1 h to remove any occluded free chlorine. The loading of bound chlorine on the swatches was determined as described in the analytical titration procedure.

### 2.7. Analytical titration procedure

For the determination of oxidative chlorine ($Cl^+$) content, a standard iodometric/thiosulfate titration procedure was employed. For example, about 0.3 g of coated and chlorinated cotton swatch material was suspended in 50 mL of 0.1 N acetic acid solution. After addition of 0.3 g KI, and starch as an indicator, the solution was titrated with 0.0375 N sodium thiosulfate until the blue color disappeared at the end point. The weight percent $Cl^+$ on the cotton swatches could then be determined from the equation below:

$$\%Cl^+ = [N \times V \times 35.45/(2 \times W)] \times 100\%, \quad (3)$$

where $N$ and $V$ are the normality (eqv/L) and volume (L), respectively, of the $Na_2S_2O_3$ consumed in the titration, and $W$ is the weight in grams of the cotton swatch sample.

### 2.8. Biocidal efficacy testing

One inch square cotton swatches, some uncoated to serve as controls, others coated with 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin] monomer, but unchlorinated, to serve as a second type of control, and others coated with chlorinated 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin] monomer were prepared. Dried swatches were then challenged with either *S. aureus* ATCC 6538 or *E. coli* O157:H7 ATCC 43895 using a "sandwich test". In this test, 25 μL of bacterial suspension were placed in the center of a swatch, and a second identical swatch was laid upon it, which was held in place by a sterile weight to insure good contact of the swatches with the inoculum. The bacterial suspensions employed for the tests contained from $10^6$ to $10^7$ colony forming units (CFU), the actual number determined by counting after

spread plating on Trypticase soy agar plates. After contact times of 5.0, 10.0, and 30.0 min, the various swatches were placed in sterile conical centrifuge tubes, each containing 5.0 mL of sterile 0.01 M sodium thiosulfate to quench any oxidative-free chlorine which might have been present, and vortexed for 150 s to remove bacteria. Then the swatches were removed, and serial dilutions of the quenched solutions were plated on Trypticase soy agar. The plates were incubated at 37 °C for 24 h and then counted for viable CFU of bacteria.

### 2.9. Washing and durability of coatings

Laundering tests were performed on swatches of cotton coated with the 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin] monomer prepared as detailed above. Then one half of the swatches were chlorinated following the aforementioned procedure. All types of coated swatches were subjected to laundry washing cycles using AATCC Test Method 61 (Test 2A Procedure). Samples were evaluated after 5, 10, 25, and 50 washing cycles for retention of the coatings. Those samples not chlorinated before washing were chlorinated by the procedure described above in order to assess how much chlorine could be loaded after variable numbers of washing cycles. Those chlorinated before washing were divided into two groups, with half being assessed for chlorine loading without rechlorination, the other half being rechlorinated and then assessed for chlorine loading.

## 3. Results and discussion

For cotton swatches treated with 5,5′-ethylenebis [5-methyl-3-(3-triethoxysilylpropyl)hydantoin] monomer as described in the experimental section, it was found that there was no significant loss of tensile strength of the fibers. Typically an add-on weight gain of 7.5% was measured for the swatches. The FTIR spectra of the coated swatches exhibited a band at 1072 $cm^{-1}$ characteristic of an Si–O–C vibrational mode which was not observed for an uncoated cotton control. This provides evidence for covalent bonding of the new monomer to the cellulose. Upon chlorination, it was found that the average oxidative chlorine loading on the swatches was 0.66% by weight. The treated cotton swatches were challenged with *S. aureus* and *E. coli* O157: H7 at a concentration between $10^7$ and $10^8$ CFU/mL in pH 7 phosphate buffer solution using a modified version of AATCC method 100. It was found that all *S. aureus* colonies (>6.0 logs) were inactivated by the swatches treated with chlorinated 5,5′-ethylenebis [5-methyl-3-(3-triethoxysilylpropyl)hydantoin] monomer in the contact interval of 10–30 min, whereas the swatches treated with the unchlorinated monomer experienced only a 0.2 log reduction at 30 min (Table 2). The control sample (untreated cotton swatches) gave only a 0.2 log reduction as well for the 30 min interval. It was also found that all *E. coli* (7.5 logs) were inactivated by the swatches treated with the chlorinated 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin] monomer in the contact interval of 10–30 min, whereas the unchlorinated monomer and the untreated swatches experienced only a 0.15 log reduction in the same contact time interval (Table 3). Thus, it can be determined that the cotton cloth treated with 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin] monomer, once chlorinated, became capable of rapid and total inactivation of both Gram positive and Gram-negative bacteria. In comparison, the siloxane monomer described previously [22] was found to have deactivated >5.7 logs of *S. aureus* in a contact interval of 10–30 min, while a contact interval of 60–120 min was necessary to inactivate >5.9 logs of *E. coli*.

Finally, the results of the wash test performed on swatches of cotton containing the monomer coating, some chlorinated as outlined in the chlorination procedure, and

Table 2
The efficacies of coated cotton swatches against *S. aureus*

| Sample coating | Log reduction in a contact time of (min) | | |
|---|---|---|---|
| | 1.0 | 10.0 | 30.0 |
| Exp. 1[a] | | | |
| Cotton control | 0.26 | 0.30 | 0.29 |
| Unchlorinated monomer[b] | 0.04 | 0.10 | 0.21 |
| Chlorinated monomer[c] | 2.04 | 3.52 | 6.90 |
| Exp. 2[d] | | | |
| Cotton control | 0.09 | 0.18 | 0.20 |
| Unchlorinated monomer[b] | 0.02 | 0.07 | 0.06 |
| Chlorinated monomer[e] | 2.82 | 3.89 | 6.62 |

[a]Inoculum concentration was $8.00 \times 10^6$ CFU.
[b]Cotton treated with 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin], but not chlorinated. The percent add-on weight was about 7.5%.
[c]Cotton treated with 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin], and then chlorinated to a loading of 0.634% (6340 ppm active $Cl^+$ on the fabric).
[d]Inoculum concentration was $4.17 \times 10^6$ CFU.
[e]Cotton treated with 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin], and then chlorinated to a loading of 0.691% (6910 ppm active $Cl^+$ on the fabric).

Table 3
The efficacies of coated cotton swatches against *E. coli* O157:H7

| Sample coating | Log reduction in a contact time of (min) | | |
|---|---|---|---|
| | 1.0 | 10.0 | 30.0 |
| Exp. 3[a] | | | |
| Cotton control | 0.02 | 0.03 | 0.15 |
| Unchlorinated monomer[b] | 0.07 | 0.11 | 0.15 |
| Chlorinated monomer[c] | 0.39 | 4.18 | 7.56 |
| Exp. 4[d] | | | |
| Cotton control | 0.04 | 0.13 | 0.22 |
| Unchlorinated monomer[b] | 0.17 | 0.21 | 0.29 |
| Chlorinated monomer[e] | 4.86 | 6.68 | 6.68 |

[a]Inoculum concentration was $3.63 \times 10^7$ CFU.
[b]Cotton treated with 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin], but not chlorinated. The percent add-on weight was about 7.5%.
[c]Cotton treated with 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin], and then chlorinated to a loading of 0.634% (6340 ppm active $Cl^+$ on the fabric).
[d]Inoculum concentration was $4.83 \times 10^6$ CFU.
[e]Cotton treated with 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin], and then chlorinated to a loading of 0.691% (6910 ppm active $Cl^+$ on the fabric).

Table 4
Durability of *N*-halamine siloxane coating on the surfaces of cotton

| Number of laundering cycles | $Cl^+$ % when chlorinated before laundering[a] | $Cl^+$ % when chlorinated after laundering[b] | $Cl^+$ % when chlorinated after recharge[c] |
|---|---|---|---|
| 0 | 0.62 | 0.62 | 0.62 |
| 5 | 0.53 | 0.52 | 0.62 |
| 10 | 0.48 | 0.45 | 0.59 |
| 25 | 0.37 | 0.37 | 0.47 |
| 50 | 0.32 | 0.28 | 0.42 |
| Number of laundering cycles | % $Cl^+$ remaining on the cotton surfaces | | |
| 0 | 100 | 100 | 100 |
| 5 | 85 | 84 | 100 |
| 10 | 77 | 73 | 95 |
| 25 | 60 | 60 | 76 |
| 50 | 52 | 45 | 68 |

[a]The treated cotton swatches were chlorinated before they were laundered, i.e. 0.62% $Cl^+$ is equivalent to 6200 ppm active $Cl^+$ on the fabric.
[b]The treated cotton swatches were chlorinated after they were laundered.
[c]The treated cotton swatches were chlorinated, laundered, and then rechlorinated.

others unchlorinated for comparison purposes, are presented in Table 4. The average oxidative chlorine loading for the monomer-coated sample was 0.62% by weight. Three observations are clearly evident from the data in Table 4. First, the monomeric coatings are partially washed off the surfaces upon successive laundering cycles. Second, prechlorination reduces the rate of loss, perhaps due to the increased hydrophobicity of the chlorinated surfaces. Third, it is evident for all of the coating conditions that a sufficient biocidal efficacy could be regenerated upon rechlorination even after 50 laundering cycles. Furthermore, a low concentration of bleach added to the laundering cycles could possibly maintain biocidal activity of the cotton material for its lifetime. In comparison, the 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilyl propyl) hydantoin] monomer has a retention of 68% on the cotton surfaces after 50 laundering cycles, whereas the 3-triethoxysilylpropyl-5,5-dimethylhydantoin monomer only had 22% retention after 50 laundering cycles [22]. As a result, the novel compound discussed herein is a much more effective and durable coating for textile fabrics.

## 4. Conclusion

The postulate proposed herein, i.e. that increasing the potential covalent bonding to the surface by use of the 5,5′-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin] instead of the lower molecular weight monomer 3-triethoxysilylpropyl-5,5-dimethylhydantoin, has been validated.

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