



AFRL-RX-TY-TR-2012-0027

**A CONTINUED STUDY OF POLYMERIC
MATERIALS FOR PROTECTION AGAINST
CHEMICAL AND BIOLOGICAL CONTAMINANTS
AND HALOGEN OXIDANTS FOR
IMMOBILIZATION IN PROTECTIVE MATERIALS
AND COATINGS**

S. D. Worley
Department of Chemistry and Biochemistry
Auburn University
Auburn, AL 36849

R. M. Broughton
Department of Polymer and Fiber Engineering
Auburn University
Auburn, AL 36849

Contract No. FA8650-07-1-5908

March 2013

DISTRIBUTION A. Approved for public release; distribution unlimited.
88ABW-2013-1126, 8 March 2013.

**AIR FORCE RESEARCH LABORATORY
MATERIALS AND MANUFACTURING DIRECTORATE**

DISCLAIMER

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not constitute or imply its endorsement, recommendation, or approval by the United States Air Force. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Air Force.

This report was prepared as an account of work sponsored by the United States Air Force. Neither the United States Air Force, nor any of its employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

NOTICE AND SIGNATURE PAGE

Using Government drawings, specifications, or other data included in this document for any purpose other than Government procurement does not in any way obligate the U.S. Government. The fact that the Government formulated or supplied the drawings, specifications, or other data does not license the holder or any other person or corporation; or convey any rights or permission to manufacture, use, or sell any patented invention that may relate to them.

This report was cleared for public release by the 88th Air Base Wing Public Affairs Office at Wright Patterson Air Force Base, Ohio available to the general public, including foreign nationals. Copies may be obtained from the Defense Technical Information Center (DTIC) (<http://www.dtic.mil>).

AFRL-RX-TY-TR-2012-0027 HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION IN ACCORDANCE WITH ASSIGNED DISTRIBUTION STATEMENT.

WANDER.JOSEP
H.D.1230231660

Digitally signed by
WANDER.JOSEPH.D.1230231660
DN: c=US, o=U.S. Government, ou=DoD, ou=PKI,
ou=USAF, cn=WANDER.JOSEPH.D.1230231660
Date: 2013.01.24 13:21:31 -0600

JOSEPH D. WANDER, PhD
Work Unit Manager

HENLEY.MICHAEL.V.1231823332
L.V.1231823332

Digitally signed by HENLEY.MICHAEL.V.1231823332
DN: c=US, o=U.S. Government, ou=DoD, ou=PKI,
ou=USAF, cn=HENLEY.MICHAEL.V.1231823332
Date: 2013.01.30 12:25:46 -0600

MICHAEL V. HENLEY, DR-III
Program Manager

RHODES.ALBERT
.N.III.1175488622

Digitally signed by
RHODES.ALBERT.N.III.1175488622
DN: c=US, o=U.S. Government, ou=DoD, ou=PKI,
ou=USAF, cn=RHODES.ALBERT.N.III.1175488622
Date: 2013.02.12 12:29:29 -0600

ALBERT N. RHODES, PhD
Chief, Airbase Technologies Division

This report is published in the interest of scientific and technical information exchange, and its publication does not constitute the Government's approval or disapproval of its ideas or findings.

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 01-MAR-2013		2. REPORT TYPE Final Technical Report		3. DATES COVERED (From - To) 23-FEB-2007 -- 28-FEB-2013	
4. TITLE AND SUBTITLE A Continued Study of Polymeric Materials for Protection Against Chemical and Biological Contaminants and Halogen Oxidants for Immobilization in Protective Materials and Coatings				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA8650-07-1-5908	
				5c. PROGRAM ELEMENT NUMBER 0909999F	
				5d. PROJECT NUMBER GOVT	
6. AUTHOR(S) *Worley, S. D.; **Broughton, R. M.				5e. TASK NUMBER L0	
				5f. WORK UNIT NUMBER X0C2 (QL102002)	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) *Department of Chemistry and Biochemistry, Auburn University, Auburn, AL 36849 **Department of Polymer and Fiber Engineering, Auburn University, Auburn, AL 36849				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory Materials and Manufacturing Directorate Airbase Technologies Division 139 Barnes Drive, Suite 2 Tyndall Air Force Base, FL 32403-5323				10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/RXQL	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-RX-TY-TR-2012-0027	
12. DISTRIBUTION/AVAILABILITY STATEMENT Distribution A: Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES Ref Public Affairs Case # 88ABW-2013-1126, 8 March 2013. Document contains color images.					
14. ABSTRACT This report highlights major findings of a six-year project exploring preparation and use of <i>N</i> -halamines, a class of compounds that can be employed to prepare polymeric materials and coatings for disinfection and detoxification applications: - Novel halogenated hydantoinyl polystyrene beads quickly disinfect potable water. The new beads are less expensive to prepare than an earlier version prepared by functionalizing polystyrene, but equally effective in gravity-feed water filters. As mild oxidizing agents, they can also be used to detoxify water and to neutralize HD or VX. - Several <i>N</i> -halamine coating materials regenerable with hypochlorite were prepared and tested that involve attachment of <i>N</i> -chlorohydantoin moieties to surfaces such as cellulose, polyurethanes, and acrylic paints through siloxane and epoxide tethering groups. 6 -7 log kills of <i>S. aureus</i> and <i>E. coli</i> O157:H7 in <10 min contact are typical. - A new acrylamide monomer capable of loading large amounts of halogen and being copolymerized with a variety of other monomers to create a variety of disinfection applications is described. Coatings so prepared showed considerably better resistance to photodecomposition by sunlight than typical <i>N</i> -halamides. - The mechanism of photodecomposition of <i>N</i> -halamine siloxanes was thoroughly investigated both theoretically and experimentally, and was shown to occur by a Hoffmann -Loeffler rearrangement. This limits the utility of siloxane-tethered <i>N</i> -halamine materials. - <i>N</i> -Halamine polymers can be made water soluble by copolymerization with materials containing charged groups like quaternary ammonium salts, an important step for industrial coating processes as it avoids the use of organic solvents in coating baths.					
15. SUBJECT TERMS chloramides, decontamination, disinfection, hydantoin, hypochlorite, photodecomposition, synthesis, water purification					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Joseph D. Wander
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER (Include area code)

Reset

TABLE OF CONTENTS

LIST OF FIGURES	ii
LIST OF TABLES	ii
PREFACE	iii
ACKNOWLEDGEMENTS	iv
1. SUMMARY	1
2. INTRODUCTION	2
3. METHODS AND PROCEDURES.....	4
4. RESULTS AND DISCUSSION	5
4.1. Major Findings.....	5
4.1.1. Water Disinfection by <i>N</i> -Halamine Polymers	5
4.1.2. Development of <i>N</i> -Halamine Antimicrobial Coatings	6
4.1.3. Development of a Novel <i>N</i> -Halamine Monomer for Antimicrobial Coatings	12
4.1.4. Photolytic Decomposition of <i>N</i> -Halamine Antimicrobial Coatings	13
4.1.5. Oxidation of Mustard Simulant	16
4.2. Other Findings	16
5. CONCLUSIONS.....	17
6. RECOMMENDATIONS.....	18
7. REFERENCES	19
Appendix: Publications and Presentations Referencing F08637-02-C-7020 and FA8650-07-1-5908	21
LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS	29

LIST OF FIGURES

	Page
Figure 1. A Disinfecting <i>N</i> -Halamine Polymer for Water Disinfection and Detoxification.....	3
Figure 2. An Improved Disinfecting <i>N</i> -Halamine Polymer for Water Disinfection and Detoxification	6
Figure 3. Concept for Preparation of an Antimicrobial Polyurethane	7
Figure 4. Preparation of an Antimicrobial <i>N</i> -Halamine Diol	7
Figure 5. Preparation of an <i>N</i> -Halamine Precursor Silane and Polymeric Siloxane	8
Figure 6. Preparation from a Precursor of a Water-soluble <i>N</i> -Halamine Copolymer	10
Figure 7. Synthesis of an <i>N</i> -Halamine Epoxide Monomer and Formation of Antimicrobial Cellulose	11
Figure 8. Preparation of a Precursor Epoxide Copolymer	11
Figure 9. An Antimicrobial <i>N</i> -Halamine Epoxide Polymer Coating	12
Figure 10. Preparation of a Novel Hydantoinyl Acrylamide Monomer.....	13
Figure 11. Antimicrobial Paint ($m = 7$; $n = 3$).....	13
Figure 12. Intramolecular Photorearrangement of Acyclic <i>N</i> -Halamides (1,5-Hydrogen Atom Transfer).....	15
Figure 13. Structures of Synthesized Siloxane Coating Materials and Model Compounds	15
Figure 14. Possible Photolytic Rearrangements for 3-Butyl-1-chlorohydantoins	15
Figure 15. Proposed Sequence for Decomposition of an <i>N</i> -Chlorohydantoinylsiloxane.....	16

LIST OF TABLES

	Page
Table 1. Stability Toward UVA Light of HASA on a Polyester Transparency Slide	14

PREFACE

This document represents the final report for a decade of work at Auburn University on contracts FO8637-02-C-7020 and FA8650-07-5908 sponsored by the Air Force Research Laboratory, (AFRL) at Tyndall Air Force Base (AFB). The technical managers at Tyndall AFB were Drs. Joseph Wander and Jeffery Owens. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily the official policies or endorsements, either expressed or implied, of AFRL or the U. S. Government.

ACKNOWLEDGEMENTS

Drs. Worley and Broughton gratefully acknowledge the work of and collaboration with microbiologists Dr. J. F. Williams of HaloSource, Inc. of Seattle, WA, and Professor T. S. Huang of the Department of Poultry Sciences at Auburn University. Also, they thank Professors M. McKee and O. Acevedo of the Department of Chemistry and Biochemistry at Auburn University for their assistance with theoretical computations during the course of the work. Thanks are also accorded to Drs. Joseph Wander and Jeffery Owens of AFRL at Tyndall Air Force Base for helpful discussions and some laboratory testing of materials developed during the project, as well as to Dr. M. E. Shirtliff at the Center for Biofilm Engineering at Montana State University for laboratory testing. Immense gratitude is owed to post-doctoral fellows A. Chen, J-W. Wang, J. Liang, X. Ren, A. Akdag, H. Kocer, I. Cerkez and to the numerous graduate students (listed as authors in the Appendix) who worked diligently to collect the data for the project.

1. SUMMARY

The work discussed in this final report and in the publications, patents, and presentations cited in the Appendix concerns the use of a class of compounds known as *N*-halamines, which can be employed to prepare polymeric materials and coatings for use in disinfection and detoxification applications.

The report highlights the major findings of the work, but details of the work have been discussed extensively in the publications cited in the Appendix. A major finding was that novel halogenated hydantoinyl polystyrene beads can be used to disinfect potable water. The beads discussed are an improvement over prior ones developed in these laboratories in that they are less expensive to prepare than were those developed herein before the start of the project; yet they function equally well in their application for gravity-feed water filters. Because they are mild oxidizing agents, they can also be employed in water detoxification applications.

Several *N*-halamine coating materials are discussed. All of these involve attachment of *N*-chlorohydantoin moieties to surfaces such as cellulose, polyurethanes, and acrylic paints through tethering groups such as siloxanes and epoxides. The materials generally provide 6–7 log disinfections of *Staphylococcus aureus* and *Escherichia coli* O157:H7 within 5–10 min of contact. Furthermore, they are capable of recharge by simply exposing them to dilute aqueous household bleach.

A new acrylamide monomer capable of loading large amounts of halogen and being copolymerized with a variety of other monomers to create a variety of disinfection applications is described.

Although *N*-halamines are somewhat subject to photolytic decomposition in the presence of direct sunlight or ultraviolet radiation, an *N*-halamine copolymer utilizing the acrylamide monomer exhibited minimal decomposition in an acrylic paint application.

The mechanism of photodecomposition of *N*-halamine siloxanes has been thoroughly investigated experimentally and with theoretical computations. Our evidence shows that it follows a well-known photorearrangement process known as a Hoffmann–Loeffler rearrangement. This suggests that tethering groups other than siloxanes are probably preferable for use with *N*-halamine materials.

It was shown that *N*-halamine polymers can be made water soluble by use of copolymers containing charged groups like quaternary ammonium salts of alkali sulfonates. This was an important finding because, for industrial coating processes, one prefers to avoid organic solvents in coating baths.

The *N*-halamines employed in these laboratories are less active as oxidizers than other halogenating compounds. They convert organic sulfides into less-toxic sulfoxides rather than to more-toxic sulfones. This finding is important for the detoxification of chemical agents, particularly mustard agent.

2. INTRODUCTION

Work concerning antimicrobial materials has progressed in the laboratories of the principal investigator S. D. Worley and his collaborators for over three decades. Most of this work has focused upon a class of chemical compounds termed *N*-halamines or, more precisely, *N*-halamides. All compounds developed at Auburn University have been organic and generally heterocyclic, with nitrogen atoms that could be reacted with free chlorine or free bromine to form nitrogen–halogen moieties. In these types of molecules the N–Cl or N–Br bond is polarized such that the halogen is in a +1 oxidation state. Hence the compounds would be expected to (and indeed do) inactivate pathogenic microorganisms and viruses. The compounds studied at Auburn University are generally mild oxidizing agents, which could potentially deactivate chemical agents as well as inactivate pathogens.

The first decade of research at Auburn University focused upon small, water-soluble, monomeric *N*-halamine compounds. The thrust of the research was to develop compounds that were very stable in aqueous solution over time, i.e., those with very low hydrolysis constants (e.g., less than 10^{-11}), which released negligible amounts of corrosive free halogen into their water solutions. It was found that derivatization of the *N*-halamine heterocyclic structure adjacent to the N–X moiety with alkyl groups (generally methyl groups) considerably enhanced the stability of the N–X bond toward release of free halogen. There are at least three reasons for this. One, alkyl groups are electron donors which push electron density toward the developing negative charge on the nitrogen as the positive halogen atom is released. This is a destabilizing interaction which causes a strengthening of the N–X bond. Second, the alkyl groups in close proximity to the N–X moiety sterically hinder the approach of solvent water molecules. And third, and probably most important, two alkyl groups adjacent to the N–X moiety prevent all possibilities of a dehydrohalogenation reaction, i.e., loss of HX, which would consume the oxidative halogen and destroy any chance of an antimicrobial event. Several such monomeric *N*-halamine compounds were developed at Auburn University which were very stable in water, killed various species of bacteria, and, in fact, detoxified toxic mustard agent.¹ The mechanism of action of the *N*-halamine compounds was thought to be a direct transfer of the oxidative halogen atom to a receptor site in a cell, followed by inactivation by oxidation, as would be the case for free halogen, e.g., hypochlorite in household bleach.

In about 1990, we realized that commercialization of the water soluble *N*-halamine materials was problematic, since numerous expensive toxicity tests would be necessary to secure governmental regulatory approval, as disinfected water would indeed contain the soluble compounds. Yet, development of new disinfecting materials for potable water was the primary goal in these laboratories at the time given that water-borne disease was (and still is) a principal cause of mortality in developing nations. Thus the decade of the '90s was devoted to creating an insoluble *N*-halamine material that could be employed in water-disinfecting filtration applications. The obvious choice was an insoluble *N*-halamine polymer. This part of the work was a tremendous success, as we were able to derivatize polystyrene with a hydantoin moiety that could be reacted with solutions containing chlorine or bromine as shown in Figure 1 and thus rendered antimicrobial.

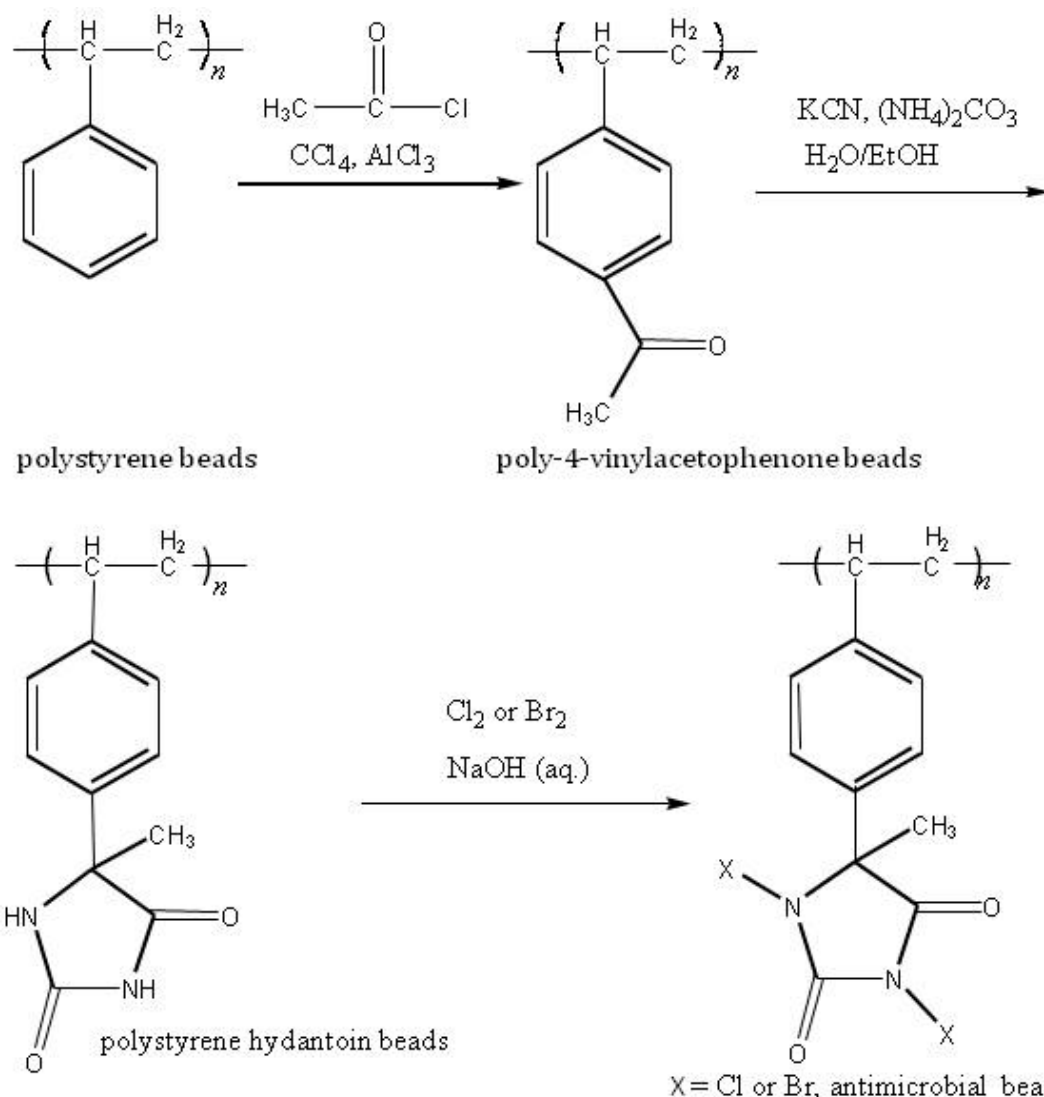


Figure 1. A Disinfecting *N*-Halamine Polymer for Water Disinfection and Detoxification

Extensive testing of filters containing the new material (in either bead form or as an amorphous solid) showed that it could kill all bacterial species and viruses tested in a few seconds of contact time in a gravity feed application.^{2,3} Once the halogen was exhausted through antimicrobial events or reaction with impurities and reducing agents in the water, the polymer could be replenished by merely exposing it to a solution of free halogen. The material is currently being marketed by HaloSource, Inc., in disinfecting gravity-feed water filtration devices in several developing nations.

Once it was evident that an *N*-halamine polymer could provide useful disinfecting applications for water, we began to explore the possibility of extending the work to polymer coatings of various materials for which a disinfection or detoxification event would add value. The new applications—all of which should be of use to the military—then became the focus for the work discussed in this final report.

3. METHODS AND PROCEDURES

In this project the synthetic methods employed were all straightforward and will be elaborated upon where necessary in the next section. Characterization of the various materials developed was generally performed by ^1H and ^{13}C nuclear magnetic resonance (NMR) using a Bruker 400-MHz spectrometer, Fourier-transform infrared spectroscopy (FTIR) using a Nicolet 6700 FTIR spectrometer with an attenuated total reflectance accessory, thermal analyses using TA Instruments Q500 and Q2000, and scanning electron microscopy (SEM) using a Zeiss DSM 940. Coatings on materials, e.g., cotton, were commonly created from synthesized polymers by dipping the material in a solution of the polymer—in some cases in water, in others cases in an organic solvent—for a prescribed amount of time, removing the wet material, drying at ambient temperature, curing at elevated temperature, rinsing with tap water, drying in air, and then further treatment with aqueous bleach (or not for controls). Halogenation was commonly effected by soaking the cured, coated material in 10 % by weight aqueous household bleach in water at a pH controlled at 7–10, or in a dilute solution of bromine. The loading of the halogen on the coatings was determined using iodometric/thiosulfate titration. Weight percent Cl^+ on the samples was calculated using Equation 1 below:

$$\text{wt-\% Cl}^+ = (35.45 NV) \times 100/(2 W) \quad (1)$$

where N and V are the normality (equiv/L) and volume (L) of the sodium thiosulfate titrant, and W is the weight of the sample (g). For wt-% Br^+ 79.90 replaces 35.45 in Equation (1). Typically, for cellulose as an example, W is 0.1~0.15 g, N is 0.00375 equiv/L, and V is of the order of 5 mL. For nonporous samples the halogen loadings were determined as Cl^+ or Br^+ atoms per unit surface area.

Stability testing for the halogen on the coatings was generally conducted by three means: with light exclusion, under laboratory lighting, and in an accelerated weathering tester (Q-Panel Co., Cleveland, OH). The latter testing was done to evaluate stability of the halogen in the presence of UVA photons at controlled temperature (37.6 °C) and humidity (17 %).

For microbiology testing, generally Gram-positive *S. aureus* (ATCC 6538) and Gram-negative *E. coli* O157:H7 (ATCC 43895) were employed as pathogens. A “sandwich test” was used for fabrics, in which 25 μL of a known concentration ($10^6 \sim 10^7$ CFU) of bacteria was placed in the center of a small swatch, typically 2.54×2.54 cm, and an identical swatch was placed on top. After a given contact time under a sterile weight employed to hold the swatches in close contact with the bacteria, the swatches were placed into a sterile tube containing 0.02 N sodium thiosulfate to quench any further disinfectant action, and the mixture was vortexed to remove the bacterial cells. Then serial dilutions were prepared using 100 mM phosphate buffer solution (pH 7) and plated onto trypticase soy agar plates, which were incubated at 37 °C for 24 h, and the viable bacteria were counted for antimicrobial assessment. Nonporous solid samples were handled in a similar manner.

4. RESULTS AND DISCUSSION

4.1. Major Findings

4.1.1. Water Disinfection by *N*-Halamine Polymers

Refinements to the hydantoinyl polystyrene bead system were made in hopes that a disinfecting, detoxifying potable water filter could be developed for use by the military in remote locations. It was found that the weight percent loading of halogen was very dependent upon the pH at which the beads were treated with halogen.^{3,4} For example, it was found that a dichlorohydantoinyl polystyrene bead containing about 20 wt-% chlorine could be formed by chlorination at pH lower than 8.0. However, beads with this high a chlorine loading can be hazardous in terms of flammability in contact with moisture upon storage. If the chlorination was performed between pH 8–8.5, the chlorine loading was 14–18 wt-%, which is a safer loading for use, although these beads should be kept dry in storage. Beads chlorinated with sodium hypochlorite at a pH above 8.8 were monosubstituted with about 13 wt-% chlorine content. The FTIR spectrum of these beads (prominent band at 1602 cm⁻¹) showed them to be the sodium salt (at the imide nitrogen) with the chlorine bonded to the amide nitrogen, the thermodynamically more stable position. These beads were hygroscopic, but could be treated with dilute acid to protonate the imide nitrogen, which rendered them easier to maintain dry. Dibromo and monobromo beads were prepared by similar pH-controlled methods. This was significant because the monobromo beads were shown to be as effective antimicrobials as the dichloro beads. It was demonstrated in the 1980s in these laboratories that bromine is about 50 times more effective in a biocidal event than is chlorine.¹ In practice, the monobromo beads are the form that has been commercialized by HaloSource, Inc., and is being marketed in developing nations. The beads elute only 0.1~0.2 mg/L of free halogen into flowing water—well below the U.S. Environmental Protection Agency standard requirement for safe drinking water. The antimicrobial event occurs within the bead bed itself through a direct contact mechanism that transfers oxidative halogen to pathogenic cells.

It was recognized that the polymer beads illustrated in Figure 1, albeit very effective in an antimicrobial potable water application, are fairly expensive to produce, primarily because of the use of cyanide in the synthetic process. Thus considerable effort was expended to develop an alternate polymer that worked as well in an antimicrobial application, but avoided the use of cyanide in the industrial synthesis process. The result was the development of a hydantoinyl polystyrene bead material utilizing the reaction scheme shown in Figure 2.^{5,6} In this case commercial chloromethylated polystyrene beads (Merrifield resin) were reacted with the potassium salt of 5,5-dimethylhydantoin.

Because the Friedel–Crafts acylation reaction and the use of cyanide (Figure 1) are avoided for the synthesis of this polymer, the expense of the industrial process is reduced by about two-thirds. The performances of the two types of halogenated hydantoinyl polystyrene beads in antimicrobial events are equivalent, although the new polymer does liberate slightly more free halogen. HaloSource, Inc., is scaling up the new process for commercialization in gravity-feed water filtration devices. During the course of the research the analogous polymeric quaternary ammonium salt was produced by reacting the Merrifield resin beads with methyldodecylamine. Whereas complete (5–6 log) reductions of *S. aureus* and *E. coli* were obtained within 1~2 s for the *N*-chloramine functionalized beads, only ~1.5-log kill of *S. aureus* and almost no attenuation

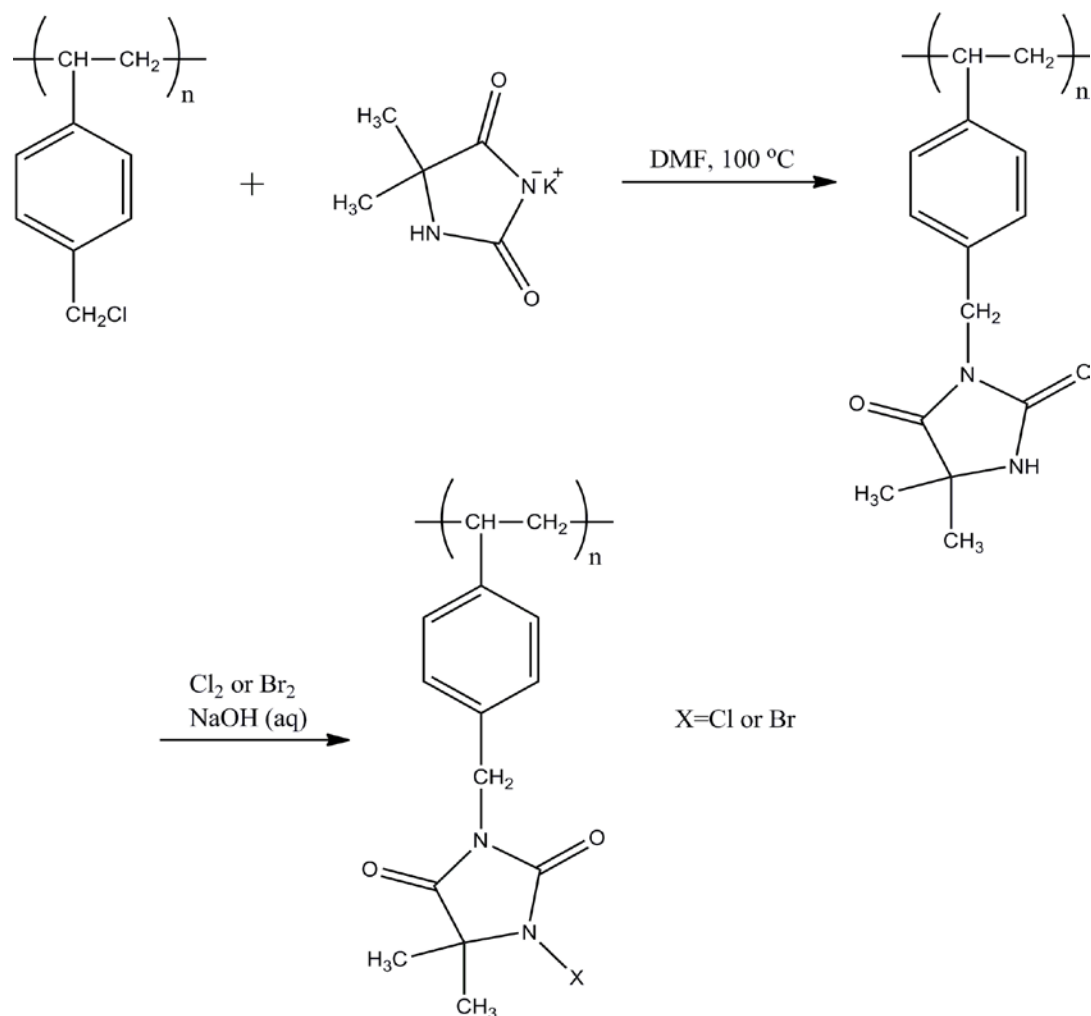


Figure 2. An Improved Disinfecting *N*-Halamine Polymer for Water Disinfection and Detoxification

of *E. coli* were observed after 5 s of contact time in a flowing water experiment for the quaternary-ammonium-functionalized derivative.⁵ This illustrated the superior antimicrobial performance of an *N*-halamine polymer compared to an analogous quaternary ammonium polymer.

4.1.2. Development of *N*-Halamine Antimicrobial Coatings

Given the success experienced in *N*-halamine antimicrobial polymers for potable water disinfection, we decided to attempt to extend the technology to the preparation of *N*-halamine antimicrobial coatings for a variety of surface applications.

4.1.2.1. Polyurethane Coatings

The first successful effort involved preparation of an *N*-halamine monomer that could be formulated into a commercial, water-borne, acrylic polyol, thus producing a polyurethane for use in paints that, upon treatment with dilute bleach, became antimicrobial.⁷ The general concept for

production of an antimicrobial polyurethane is shown in Figure 3; the preparation scheme for the actual *N*-halamine precursor diol is shown in Figure 4.

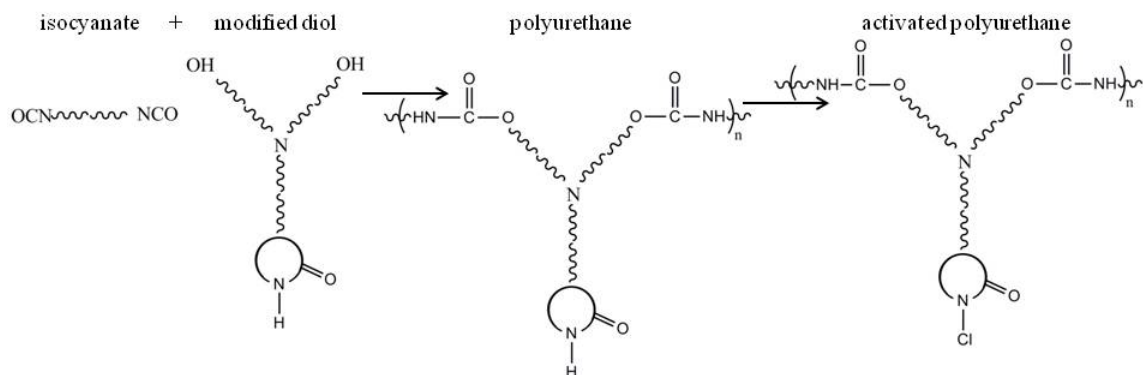


Figure 3. Concept for Preparation of an Antimicrobial Polyurethane

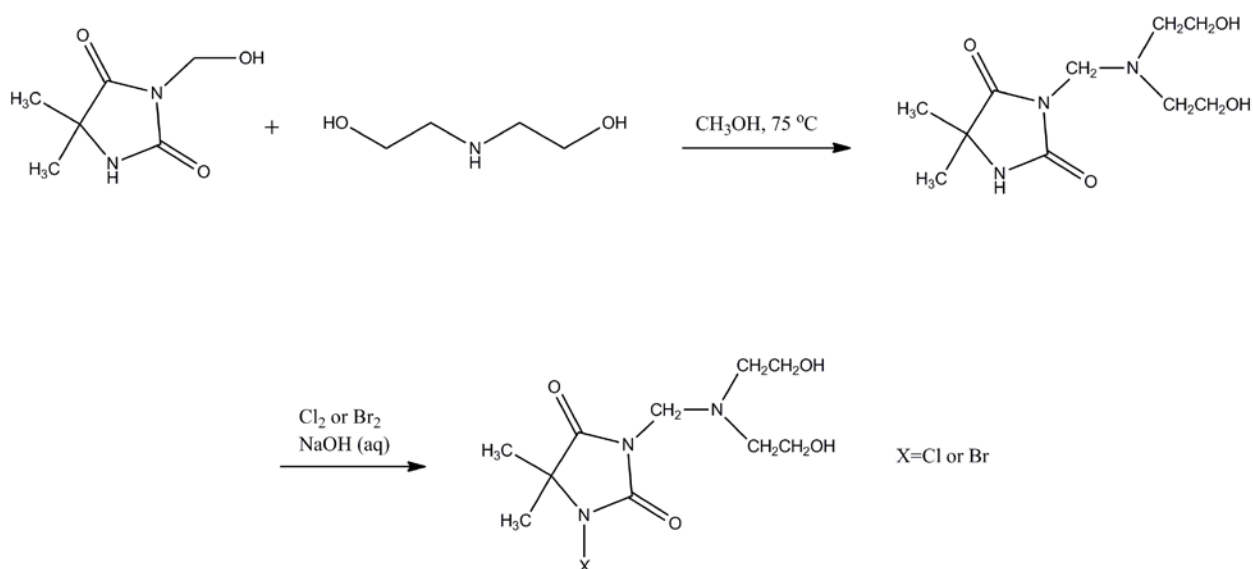


Figure 4. Preparation of an Antimicrobial *N*-Halamine Diol

The synthesis involved reaction of commercial 3-hydroxymethyl-5,5-dimethylhydantoin with diethanolamine in methanol solvent at 75 °C. The viscous residue produced after removal of the methanol was dissolved in ethyl acetate and precipitated as a white solid at 4 °C. The solid was stirred into the water-borne acrylic at a weight ratio of 0.7 g to 10 g. The formulation was spread onto various surfaces and allowed to dry. Chlorination with a 10 % aqueous household bleach solution (about 0.5 % sodium hypochlorite) provided a Cl^+ loading of about 1.3×10^{17} atoms/cm². This chlorinated surface achieved a complete reduction (>4.5 logs) of *S. aureus* over a 2-h contact period. Scientists at Tyndall AFB performed an experiment with the material in which they painted portions of a restroom stall door, chlorinated portions leaving other portions as unchlorinated controls, and three months later challenged the surfaces with about 10^6 CFU of *Pseudomonas pseudoalcaligenes*. After a 5-min contact time, the bacteria on the chlorinated surfaces were completely inactivated. The experiment was repeated after six months (without rechlorination) with the same result.⁷ In another experiment scientists at the Center for Biofilm

Engineering at Montana State University coated polycarbonate slides with our material and tested them (chlorinated versus unchlorinated) in a biofilm reactor. With about 1 mg/L free chlorine present, the slides containing the chlorinated polyurethane coating yielded 1–2 logs fewer biofilm organisms than did slides not containing the coating.

4.1.2.2. Siloxane Coatings

We have found that *N*-halamine siloxanes are very versatile building blocks for antimicrobial surface coatings. Alkoxysilanes, upon conversion into hydroxysilanes in the presence of moisture and traces of acid, can react with any surface containing oxide or –OH moieties, e.g., cellulose; they also undergo facile homopolymerization and co-polymerization with other monomers. Thus they are logical candidate antimicrobial coatings. Our first effort to exploit these materials involved the reaction of the potassium salt of 5,5-dimethylhydantoin with 3-chloropropyltriethoxysilane in dimethyl formamide at 60–90 °C using the procedure of Berger.⁸ The monomeric product, 3-triethoxysilylpropyl-5,5-dimethylhydantoin (Figure 5), has often been nicknamed BA-1 in these laboratories and elsewhere. The monomer can be homopolymerized as shown in Figure 5. Alternatively, the starting material 3-chloropropyltriethoxysilane can be homopolymerized in the presence of HCl, followed by a nucleophilic substitution reaction using the potassium salt of 5,5-dimethylhydantoin. The monomer BA-1 and the two versions of polymer can all be reacted with surfaces such as cellulose to produce *N*-halamine precursor structures, which, upon exposure to dilute aqueous bleach, become antimicrobial.⁹

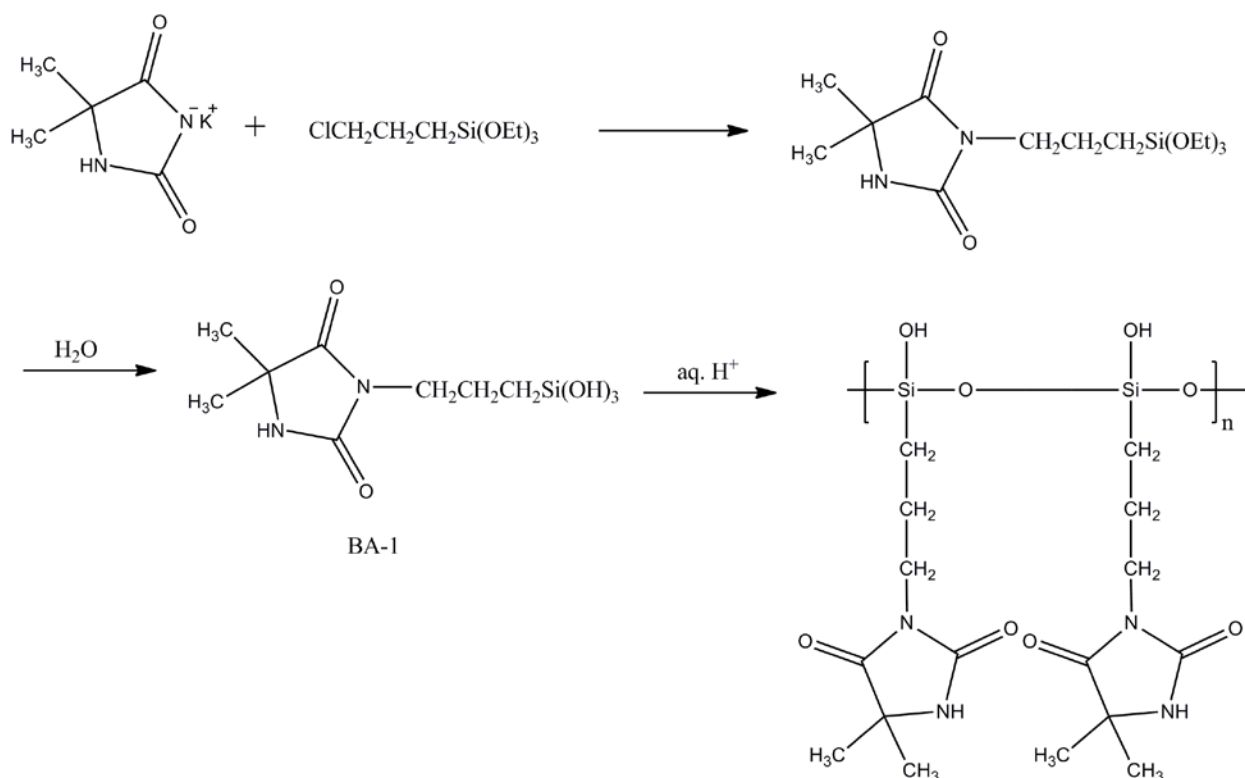


Figure 5. Preparation of an *N*-Halamine Precursor Silane and Polymeric Siloxane

BA-1 or its polymers could be dissolved in ethanol/water mixtures (50/50) and then applied to surfaces such as cotton fabric by dipping the fabric into a bath of the dissolved material. Alternatively the material in solution could be sprayed onto the surface of the substrate. The treated surfaces were then cured at elevated temperature, e.g., 130–150 °C. Halogenation then was accomplished at ambient temperature followed by rinsing and then drying at a temperature no higher than 45 °C.

Office paper treated with chlorinated BA-1 (0.5–0.8 wt-% Cl⁺) completely inactivated *S. aureus* (>5.4 logs) within 10 min of contact. The treated paper lost only 5 % of its chlorine upon storage under ambient conditions during a 36-d period. *S. aureus* was inactivated (>5.7 logs) on treated cotton fabric (at a chlorine loading of about 0.4 wt-%) in the contact time interval 10–30 min; for *E. coli* O157:H7 the time interval for equivalent performance was about 60 min. Testing in a Launder-Ometer showed that the coatings, especially the polymeric ones, were fairly stable to repeated washing cycles. For example, a polymer-coated sample chlorinated before and after washing lost only about 42 % of its coating during 50 washing cycles; in contrast, a monomer-coated sample treated identically lost about 64 % of its coating, implying that the polymer is bound more strongly to the cotton than is the monomer. It was also shown that the BA-1 technology could be utilized with silicon dioxide and silica gel to produce antimicrobial sand and silica gel antimicrobial water filters, albeit chlorine loadings are much lower (0.3–2.0 wt-% Cl⁺) leading to considerably longer contact times for flowing water (min) to achieve antimicrobial activity than was the case for the hydantoinyl polystyrene beads (~1 s) discussed above.^{10,11}

A possible limitation of the BA-1 technology is the fact that its utilization requires a solvent containing alcohol, which can cause problems in industrial settings. Thus, an effort was made to so modify the compound as to render it soluble in water. The successful reaction scheme is shown in Figure 6. The homopolymer of 3-chloropropylsilane was synthesized as shown in Figure 6. It was then reacted with the potassium salt of 5,5-dimethylhydantoin and trimethylamine, either sequentially or in one pot, to produce the hydantoin/quaternary ammonium copolymer. The values of *n* and *m* in Figure 6 were easily controlled by setting the feed ratios. It was found that the copolymer that contained the largest proportion of *N*-halamine precursor for disinfection, together with an adequate proportion of quaternary ammonium groups to achieve water solubility for practical uses, had values of *n* and *m* of 9 and 1, respectively.¹² This copolymer could be loaded onto cotton with 0.69 wt-% Cl⁺ from a 5 wt-% coating solution. Its performance when bonded to cotton was very good, providing a 7-log reduction of both *S. aureus* and *E. coli* O157:H7 after a contact time interval of 1–5 min. Its stability on the surface of the cotton to washing was similar to that for the BA-1 homopolymer.¹²

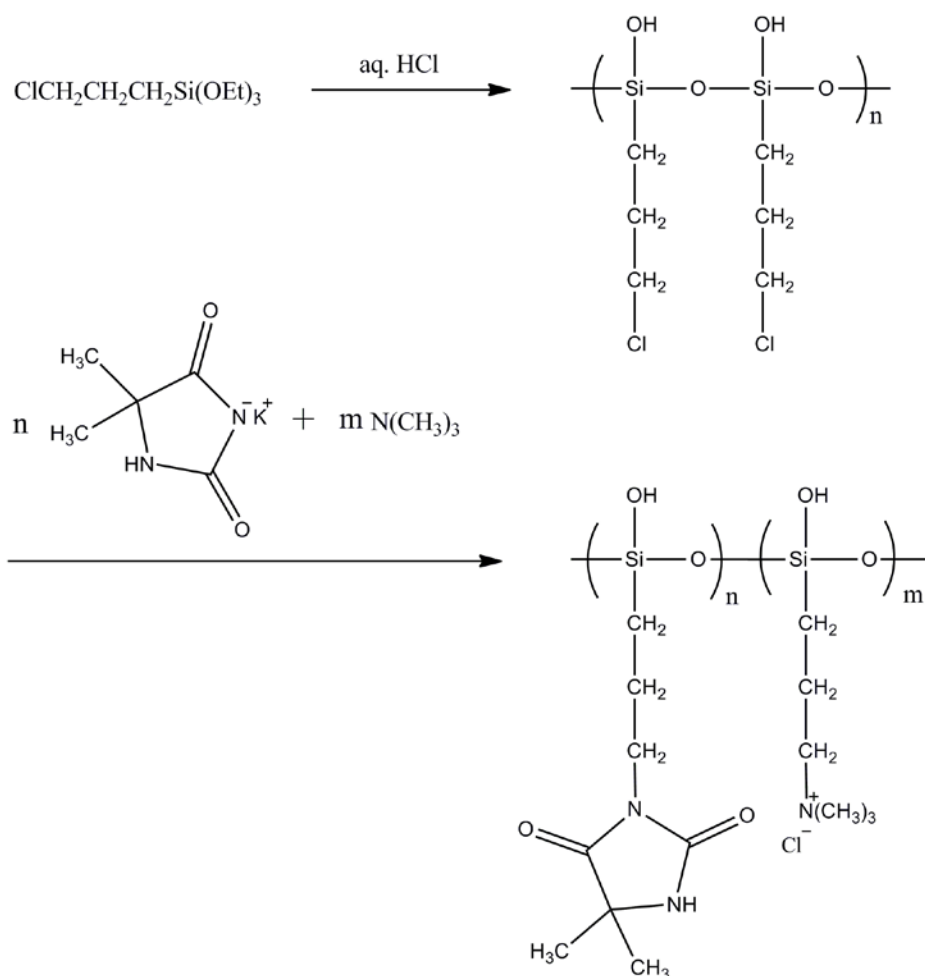


Figure 6. Preparation from a Precursor of a Water-soluble *N*-Halamine Copolymer

4.1.2.3. Epoxide Coatings

Another logical path for producing an *N*-halamine functionalized surface, particularly on cellulose, is the use of epoxide derivatives. Our first entry into this area is illustrated by the reaction scheme in Figure 7.¹³ First, 5,5-dimethylhydantoin was converted into its potassium salt by stirring in an aqueous solution of KOH. Then, an equimolar concentration of commercial epichlorohydrin was added to the solution followed by simply stirring at ambient temperature for 10 h. After removal of most of the water by evaporation, the product was extracted from the remainder of the water with acetone. After evaporation of the acetone, the hydantoinyl epoxide was obtained as an oil.

Extensive purification of the product yielded a white solid. However, the oil could be used for coating, thus eliminating the need of a tedious chromatographic purification step. For treatment of cotton, an aqueous coating bath containing 5 wt-% of the epoxide was prepared. Cotton swatches were held in the bath for 15 min, followed by drying at 95 °C for 1 h, and curing at 145 °C for 20 min. After rinsing, the swatches were chlorinated with 10 % aqueous bleach at pH 7 and ambient temperature for 45 min. Drying at 45 °C was performed to remove any occluded free chlorine. Testing included stability in storage of the treatment solution and stability toward

washing and antimicrobial efficacy for the coated swatches. The treatment solution performed the same, i.e., led to the same chlorine loadings on the swatches, after 30 d as on day 1. Washing stability for the coatings was excellent, as the same chlorine loadings could be obtained after 50 washing cycles as were obtained before washing. Complete inactivation of *S. aureus* and *E. coli* O157:H7 occurred within 10–30 min contact time.

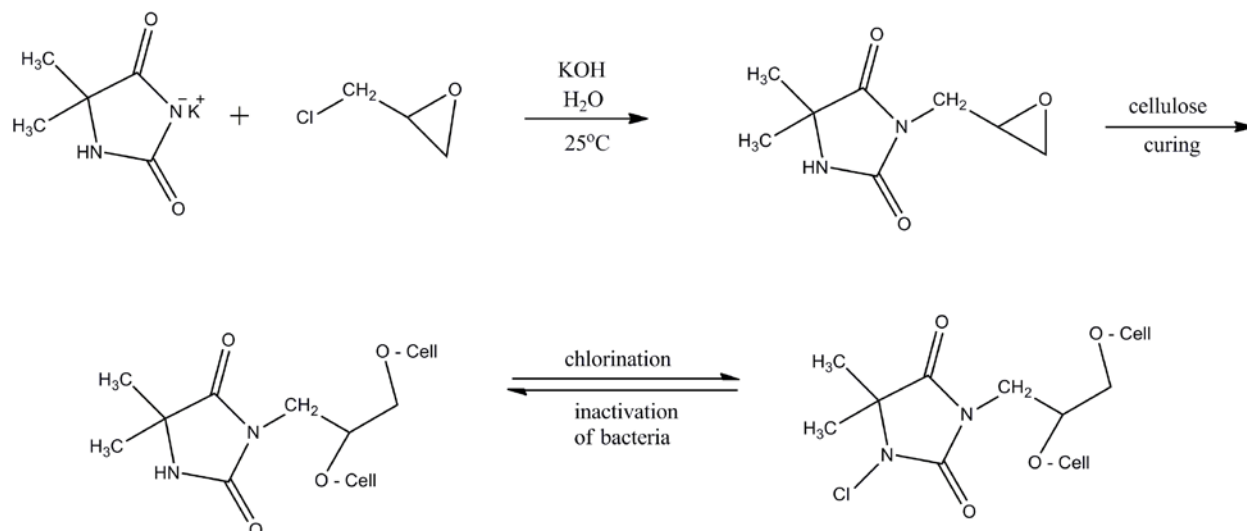


Figure 7. Synthesis of an *N*-Halamine Epoxide Monomer and Formation of Antimicrobial Cellulose

In general, polymers provide more-stable coatings than do monomers. A polymeric *N*-halamine epoxide that was developed during this project is shown in Figure 8 and Figure 9.¹⁴

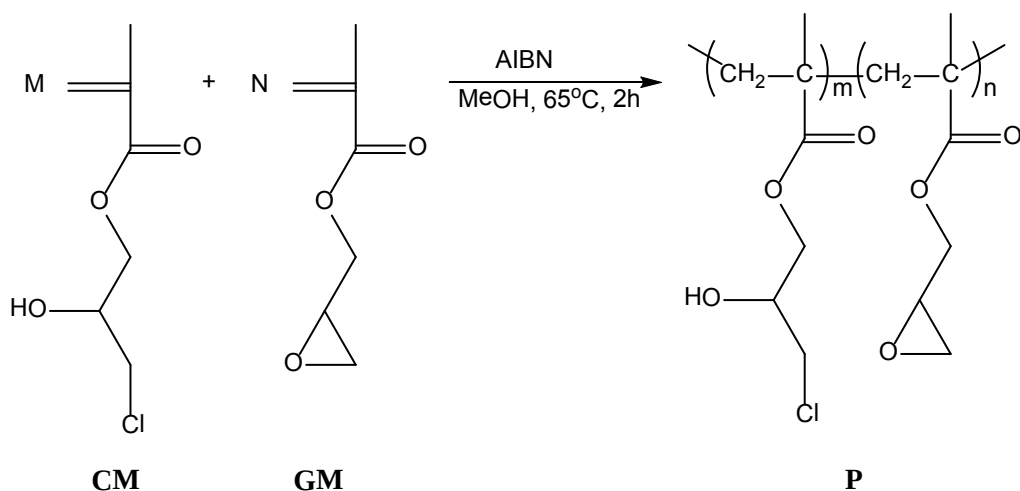


Figure 8. Preparation of a Precursor Epoxide Copolymer

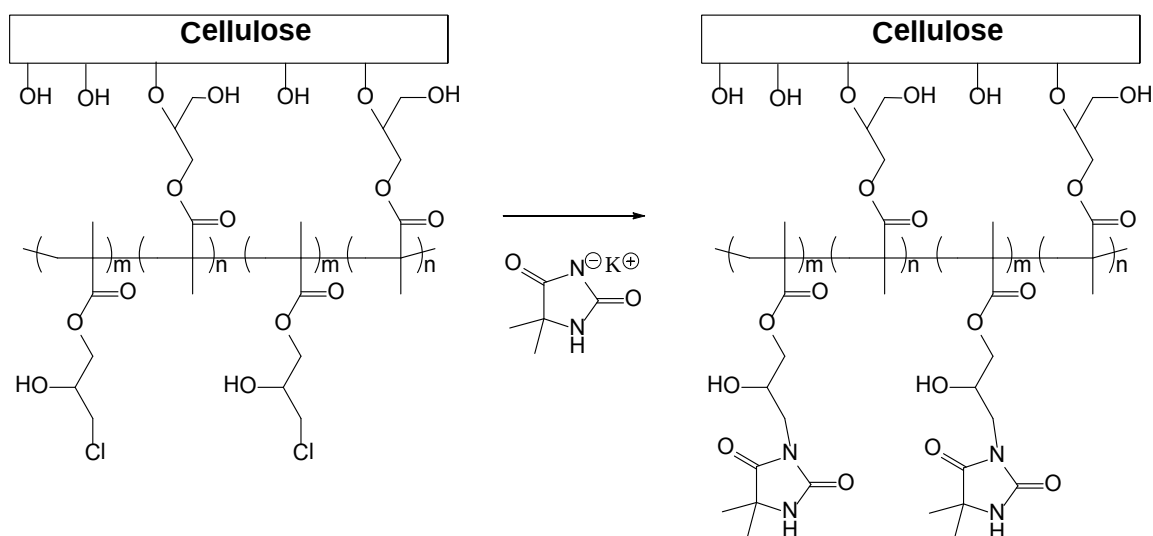


Figure 9. An Antimicrobial *N*-Halamine Epoxide Polymer Coating

A commercial monomer (3-chloro-2-hydroxypropyl methacrylate, CM) was copolymerized with glycidyl methacrylate (GM) in methanol at 65 °C for 2 h. The product copolymer in acetone was padded onto cotton using a laboratory wringer, and then was cured at 165 °C for 1 h. The coated cotton was then immersed in a solution of the potassium salt of 5,5-dimethylhydantoin in ethanol for 5 min under reflux. After chlorination at pH 7 for 1 h, rinsing in water, and drying at 45 °C for 1 h, stability toward washing and exposure to UVA light and antimicrobial efficacy were tested. The coated material showed remarkable stability toward washing; no coating was lost in 50 machine washing cycles, i.e., the same chlorine loading was obtained at the end as at the beginning. Although the samples lost most of their chlorine content over a period of 120 h of exposure to UVA, 94 % of the chlorine could be recovered after the exposure upon rechlorination. Complete inactivation of both *S. aureus* and *E. coli* O157:H7 (6.75 logs) were obtained within 5 min of contact.

4.1.3. Development of a Novel *N*-Halamine Monomer for Antimicrobial Coatings

Recent work in these laboratories focused on a new hydantoin acrylamide monomer (Figure 10), which can copolymerize with a variety of other monomers for use in novel applications.¹⁵ This monomer, which contains three nitrogen atoms that can be halogenated—none of which is subject to a dehydrohalogenation process—was prepared by reacting commercial *N*-(1,1-dimethyl-3-oxobutyl)acrylamide with KCN and ammonium carbonate in ethanol–water (1:1 by volume) solvent. The white solid product was formed with the vinyl group intact (proof by NMR and FTIR) and thus could be copolymerized with other monomers useful for tethering to surfaces such as siloxanes and epoxides.^{15,16} Of particular interest to us was copolymerization with a water-soluble acrylamide for use in a latex paint (Figure 11).¹⁷ Different feed ratios (*m* and *n* in Figure 11) were used. Optimum values of *m* and *n* proved to be 7 and 3, respectively. This formulation was soluble in water and thus provided excellent dispersion in a commercial latex paint. The treated paint was spread on a polyester transparency slide surface and allowed to dry. Chlorination was effected with dilute bleach (10 wt-% in aqueous solution). Chlorine loadings of the order of 10¹⁷ chlorine atoms/cm² were obtained. The painted surface provided > 6-log inactivation of both *S. aureus* and *E. coli* O157:H7 within 5 min contact. In contrast, unchlorinated control coatings provided less than 0.2-log inactivations at the same contact time.^{17,18}

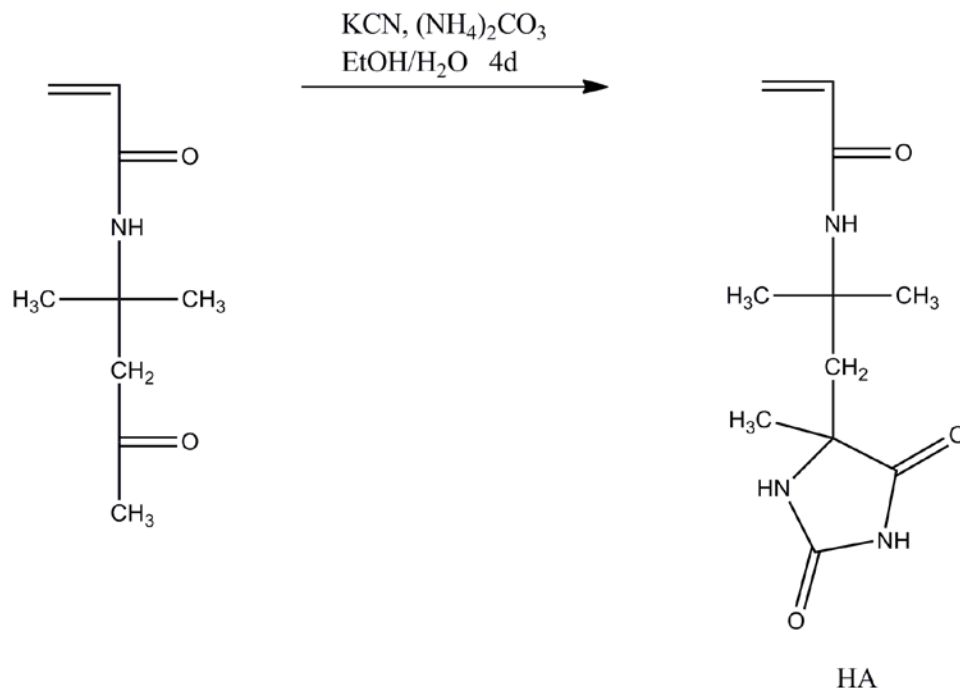


Figure 10. Preparation of a Novel Hydantoinyl Acrylamide Monomer

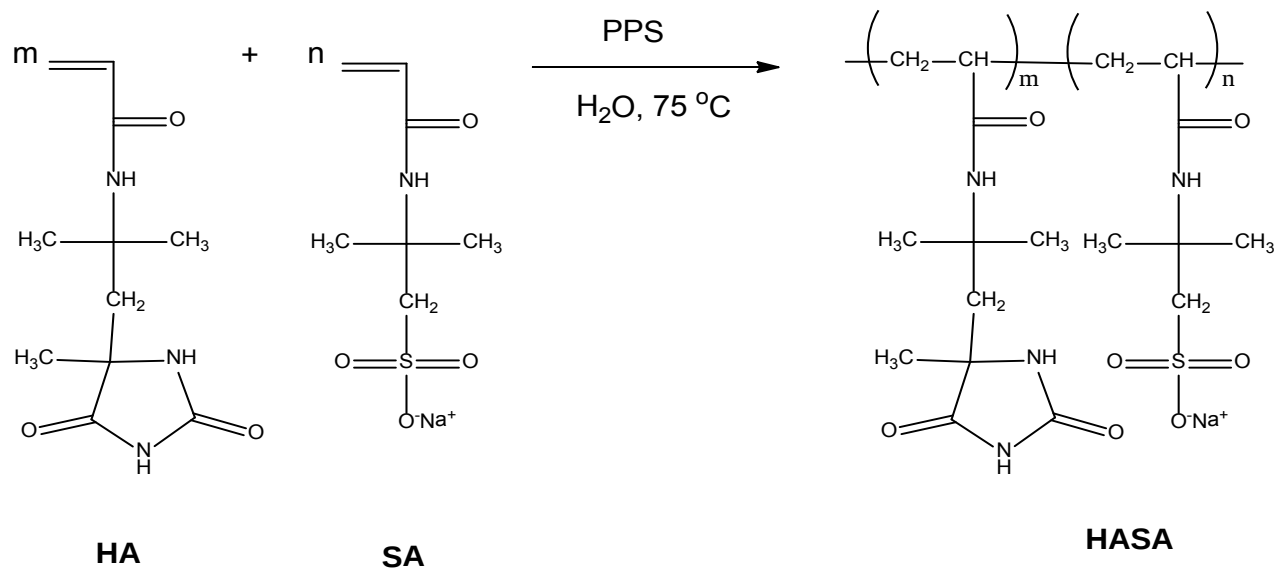


Figure 11. Antimicrobial Paint ($m = 7$; $n = 3$)

4.1.4. Photolytic Decomposition of *N*-Halamine Antimicrobial Coatings

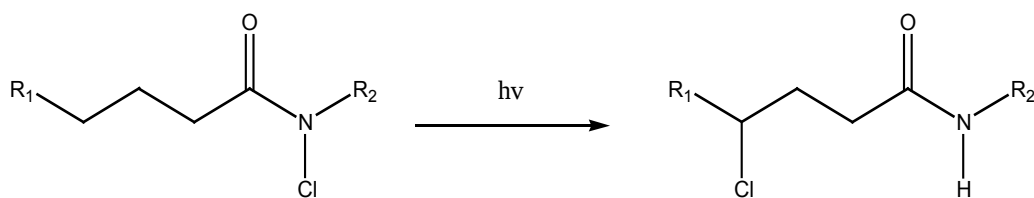
The primary limitation of *N*-halamine coatings and materials is slow decomposition in the presence of ultraviolet photons. This, of course, limits their use in direct sunlight. Not only is the nitrogen–halogen bond sensitive to dissociation accelerated by UV photons, most of the materials themselves decompose slowly over time of exposure. This can be shown by repeated UV exposure and *N*-halamine regeneration cycles, as the halogen loadings slowly decrease with

the cycling. The mechanism of this decomposition process seems to be dependent upon the tethering group, e.g., siloxane, epoxide, etc. One of the materials studied in these laboratories that showed better stability toward UV decomposition is the paint labeled HASA in Figure 11. Its performance during repeated UVA–rechlorination cycles is shown in Table 1. This could be because the paint matrix partially protects the *N*-halamine from decomposition. However, some of the materials such as the siloxanes are less stable toward UV exposure. For example, BA-1 loses all of its chlorine within 24 h exposure to UVA photons and can be only partially regenerated (to about 35 % of its initial value) at that time.¹⁹ We decided to perform an experimental/theoretical study of this decomposition process.

Table 1. Stability Toward UVA Light of HASA on a Polyester Transparency Slide

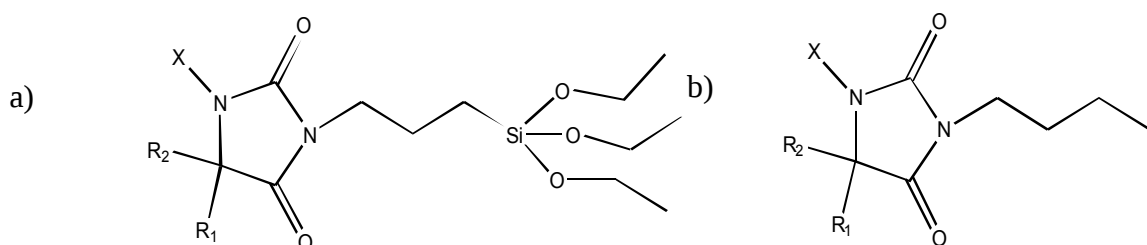
Exposure Time (d)	% Cl ⁺ Remaining
0	0.30
1	0.21
2	0.19
3	0.18
4	0.18
5	0.13
6	0.13
7	0.13
14	0.12
Rechlorination	0.28
28	0.16
Rechlorination	0.30
42	0.16
Rechlorination	0.27
70	0.11
Rechlorination	0.26

N-Halamine precursor coatings exhibit little or no decomposition upon exposure to UV light, so obviously the presence of halogen accentuates the process. A search of the literature revealed that acyclic *N*-halamides are subject to an intramolecular photorearrangement process known as the Hoffmann–Loeffler rearrangement (Figure 12).²⁰ We thought that the cyclic *N*-halamide BA-1 might undergo a similar photorearrangement. Thus we initiated a model compound study using mass spectrometry to identify products produced under UV photolysis and Density Functional Theory *ab initio* computations.²¹ The structures in the study are shown in Figure 13. We found that compounds identified in Figure 14 as A and B were isolated in the model compound study (mass spectral identification), and the computations showed the transition states represented by 1,5- or 1,6- hydrogen transfer to be energetically favorable. Thus it is likely that under UV photolysis the N–Cl bond breaks in a radical process, followed by a hydrogen atom migration from C₇ and/or C₈ (Figure 15). Subsequent recombination of the radical centers with chlorine



$R_1 = R_2 = \text{alkyl}$

Figure 12. Intramolecular Photorearrangement of Acyclic N-Halamides (1,5-Hydrogen Atom Transfer)



R_1 / R_2	X=H	X=Cl	X=H	X=Cl
Methyl / Methyl	MM	MM-Cl	MMm	MMm-Cl
Methyl / Phenyl	MP	MP-Cl	MPm	MPm-Cl
Phenyl / Phenyl	PP	PP-Cl	PPm	PPm-Cl

Figure 13. Structures of Synthesized Siloxane Coating Materials and Model Compounds

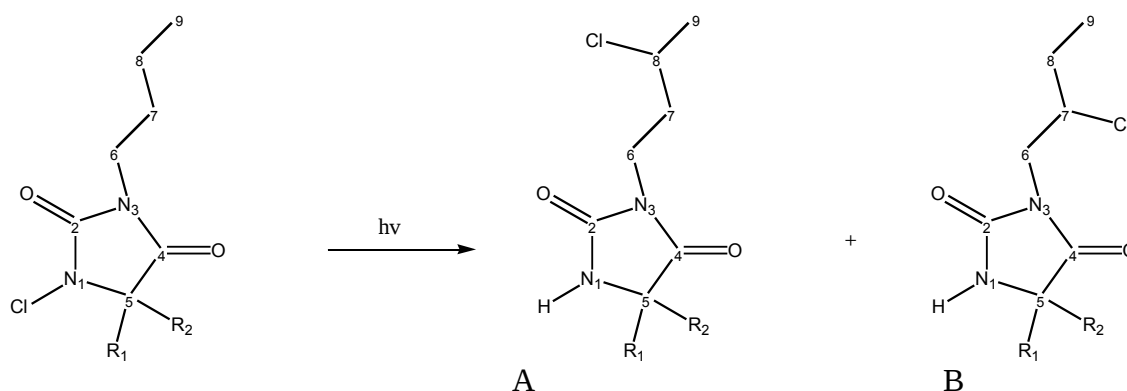


Figure 14. Possible Photolytic Rearrangements for 3-Butyl-1-chlorohydantoin

atoms would leave the products illustrated in Figure 14. Thus for the BA-1-derived siloxane the chlorine atom would migrate to positions either α or β relative to the silicon atom. It is well known that when halogen atoms are bonded to carbon atoms in α or β positions relative to a silicon atom, the C–Si bond is notoriously susceptible to bond scission.²² Thus, the hydantoin group would be lost before and during an attempted rechlorination, accompanied by loss of antimicrobial efficacy as illustrated in Figure 15.

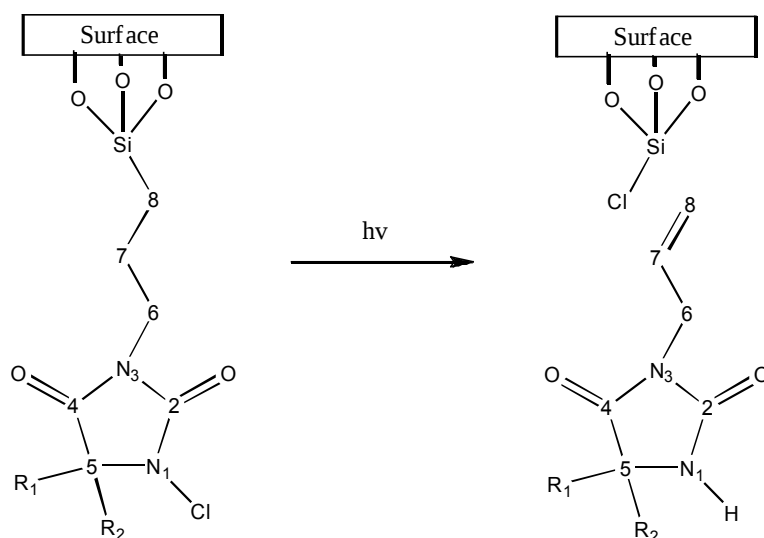


Figure 15. Proposed Sequence for Decomposition of an *N*-Chlorohydantoinylsiloxane

4.1.5. Oxidation of Mustard Simulant

It was shown that *N*-halamine compounds, such as the chlorinated polystyrene hydantoin beads, oxidize organic sulfides, such as mustard simulant, to the less toxic sulfoxides rather than to the more toxic sulfones, as other halogenating agents, such as free chlorine, do.²³ The various *N*-halamine coatings discussed in this report should do the same.

4.2. Other Findings

This report has emphasized certain major findings during the project. However, much other work was accomplished during the 10-year period including both experimental and theoretical studies. All of the studies have been published, and full citations are given in the Appendix.

5. CONCLUSIONS

A massive amount of work has been performed on the various projects supported by contract F08637-02-C-7020 and grant FA8650-07-1-5908. The work has demonstrated that *N*-halamine chemistry can be of great benefit to the military. It has been shown that the *N*-halamine technology can be employed for disinfection of potable water, and because the materials are oxidizing agents, they can also be used for detoxification of contaminated water. Much of the work on the project has focused on antimicrobial coatings for such surfaces as cellulose, but paints and fabrics such as polyester can also be rendered antimicrobial by the *N*-halamine materials. Various polymerization techniques such as admicellar polymerization and layer-by-layer deposition of *N*-halamine materials have also been addressed in publications cited in the Appendix. Likewise, theoretical studies have been conducted to support the experimental work and rationalize observations. Sixty-one publications/patents and numerous presentations at national and international meetings have highlighted the work and are referenced in the Appendix. Furthermore, the work has served as a training ground for several post-doctoral fellows and graduate students at Auburn University. Several of the materials developed during the study such as BA-1, the antimicrobial polyurethane, and some alkylated hydantoin compounds have been supplied to the U.S. Air Force for testing and evaluation.

6. RECOMMENDATIONS

We recommend that the military seriously consider adaptation of the halogenated hydantoinyl polystyrene beads for disinfection and detoxification of potable water in remote locations. The beads have been proven to work well in developing nations by HaloSource, Inc., the company which markets them. They would be far superior to the methods currently used by the military in remote locations. Also, work on actual applications of the *N*-halamine coatings should be pursued by the U.S. military services with the intent of adopting them for real field use. At one time the BA-1 technology seemed to be moving toward adoption by the military. We do not know where that stands at this time, but during the project we have developed *N*-halamine coatings superior to BA-1 in terms of photostability, washing fastness, and antimicrobial efficacy.

7. REFERENCES

- 1) S. D. Worley and D. E. Williams, "Halamine Water Disinfectants," *Crit. Rev. Environ. Control*, *18*, 133 (1988).
- 2) G. Sun, W. B. Wheatley, and S. D. Worley, "A New Cyclic *N*-Halamine Biocidal Polymer," *Ind. Eng. Chem. Res.*, *33*, 168 (1994).
- 3) Y. Chen, S. D. Worley, J. Kim, C-I. Wei, T-Y. Chen, J. I. Santiago, J. F. Williams, and G. Sun, "Biocidal Polystyrenehydantoin Beads for Disinfection of Water," *Ind. Eng. Chem. Res.*, *42*, 280 (2003).
- 4) Y. Chen, S. D. Worley, J. Kim, C.-I. Wei, T.-Y. Chen, J. Suess, H. Kawai, and J. F. Williams, "Biocidal Polystyrenehydantoin Beads. 2. Control of Chlorine Loading," *Ind. Eng. Chem. Res.*, *42*, 5715 (2003).
- 5) Y. Chen, S. D. Worley, T. S. Huang, J. Weese, J. Kim, C-I. Wei, and J. F. Williams, "Biocidal Polystyrene Beads. III. Comparison of *N*-halamine and Quat Functional Groups," *J. Appl. Polym. Sci.*, *92*, 363 (2004).
- 6) Y. Chen, S. D. Worley, T. S. Huang, J. Weese, J. Kim, C-I. Wei, and J. F. Williams, "Biocidal Polystyrene Beads. IV. Functionalized Methylated Polystyrene," *J. Appl. Polym. Sci.*, *92*, 368 (2004).
- 7) S. D. Worley, F. Li, R. Wu, J. Kim, C-I. Wei, J. F. Williams, J. R. Owens, J. D. Wander, A. M. Bargmeyer, and M. E. Shirliff, "A Novel *N*-Halamine Monomer for Preparing Biocidal Coatings," *Surf. Coat. Intern. Part B Coat. Trans.*, *86*, B4,273 (2003).
- 8) A. Berger, "Hydantoinylsilanes," US Patent 4,412,078, 1983.
- 9) S. D. Worley, Y. Chen, J-W. Wang, R. Wu, U. Cho, R. M. Broughton, J. Kim, C-I. Wei, J. F. Williams, J. Chen, and Y. Li, "Novel *N*-Halamine Siloxane Monomers and Polymers for Preparing Biocidal Coatings," *Surf. Coat. Intern. Part B. Coat. Trans.*, *88*, 93 (2005).
- 10) J. Liang, R. Wu, T. S. Huang, "Polymerization of a Hydantoinylsiloxaneon Particles of Silicon Dioxide to Produce a Biocidal Sand," *J. Appl. Polym. Sci.*, *97*, 1161 (2005).
- 11) J. Liang, J. R. Owens, T. S. Huang, and S. D. Worley, "Biocidal Hydantoinylsiloxane Polymers. IV. *N*-Halamine Siloxane-Functionalized Silica Gel," *J. Appl. Polym. Sci.*, *101*, 3448 (2006).
- 12) L. Kou, J. Liang, X. Ren, H. B. Kocer, S. D. Worley, Y-M. Tzou, and T. S. Huang, "Synthesis of a Water Soluble Siloxane Copolymer and Its Application for Antimicrobial Coatings," *Ind. Eng. Chem. Res.*, *48*, 6521 (2009).
- 13) J. Liang, Y. Chen, X. Ren, R. Wu, K. Barnes, S. D. Worley, R. M. Broughton, U. Cho, H. Kocer, and T. S. Huang, "Fabric Treated with Antimicrobial *N*-Halamine Epoxides," *Ind. Eng. Chem. Res.*, *46*(20), 6425 (2007).
- 14) H. B. Kocer, I. Cerkez, S. D. Worley, R. M. Broughton, and T. S. Huang, "Polymeric Antimicrobial *N*-Halamine Epoxides," *ACS Appl. Mat. Interf.*, *3*, 2845 (2011).

- 15) H. B. Kocer, S. D. Worley, R. M. Broughton, and T. S. Huang, "A Novel *N*-Halamine Acrylamide Monomer and Its Copolymers for Antimicrobial Coatings," *Reac. & Func. Polym.*, *71*, 561 (2011).
- 16) I. Cerkez, H. B. Kocer, S. D. Worley, R. M. Broughton, and T. S. Huang, "*N*-Halamine Copolymers for Biocidal Coatings," *Reac. Func. Polym.*, *72*, 673(2012).
- 17) H. B. Kocer, I. Cerkez, S. D. Worley, R. M. Broughton, and T. S. Huang, "*N*-Halamine Copolymers for Use in Antimicrobial Paints," *ACS Appl. Mat. Interf.*, *3*, 3189 (2011).
- 18) H. B. Kocer, "Residual Disinfection with *N*-Halamine Based Antimicrobial Paints," *Prog. Org. Coat.*, *74*, 100 (2012).
- 19) X. Ren, L. Kou, J. Liang, S. D. Worley, Y. M. Tzou, and T. S. Huang, "Antimicrobial Efficacy and Light Stability of *N*-Halamine Siloxanes Bound to Cotton," *Cellulose*, *15*, 593 (2008).
- 20) R. C. Petterson and A. Wambsgans, "Photochemical Rearrangement of *N*-Chloroimides to 4-Chloroimides. A New Synthesis of γ -Lactones," *J. Amer. Chem. Soc.*, *86*, 1648 (1964).
- 21) H. B. Kocer, A. Akdag, S. D. Worley, O. Acevedo, R. M. Broughton, and Y. Wu, "Mechanism of Photolytic Decomposition of *N*-Halamine Antimicrobial Siloxane Coatings," *ACS Appl. Mat. Interf.*, *2*(8), 2456 (2010).
- 22) L. H. Sommer, G. M. Goldberg, E. Dorfman, and F. C. Whitmore, "Organosilicon Compounds. V. β -Eliminations Involving Silicon," *J. Amer. Chem. Soc.*, *68*, 1083(1946).
- 23) A. Akdag, J. Liang, and S. D. Worley, "Oxidation of Organic Sulfides by *N*-Halamine Compounds," *Phosphorus, Sulfur, and Silicon*, *182*, 1525 (2007).

Appendix: Publications and Presentations Referencing F08637-02-C-7020 and FA8650-07-1-5908

Publications

- 1) J. Lin, C. Winkelmann, S.D. Worley, J. Kim, C. I. Wei, U. Cho, R.M. Broughton, J.I. Santiago, and J. F. Williams, "Biocidal Polyester," J. Appl. Polym. Sci., 85, 177 (2002).
- 2) Y. Chen, S. D. Worley, J. Kim, C-I. Wei, T-Y. Chen, J. I. Santiago, J. F. Williams, and G. Sun, "Biocidal Polystyrenehydantoin Beads for Disinfection of Water," Ind.Eng. Chem. Res., 42, 280 (2003).
- 3) S. D. Worley, F. Li, R. Wu, J. Kim, C-I. Wei, J. F. Williams, J. R. Owens, J. D. Wander, A. M. Bargmeyer, and M. E. Shirtliff, "A Novel *N*-Halamine Monomer for Preparing Biocidal Coatings," Surf. Coat. Intern. Part B Coat. Trans., 86, B4, 273(2003)(invited paper).
- 4) Y. Chen, S. D. Worley, J. Kim, C. I. Wei, T. Y. Chen, J. Suess, H. Kawai, and J. F. Williams, "Biocidal Polystyrene Beads. II. Control of Chlorine Loading," Ind. Eng.Chem. Res., 42, 5715 (2003).
- 5) Y. Chen, S. D. Worley, T. S. Huang, J. Weese, J. Kim, C-I. Wei, and J. F. Williams, "Biocidal Polystyrene Beads. III. Comparison of *N*-halamine and Quat Functional Groups," J. Appl. Polym. Sci., 92, 363 (2004).
- 6) Y. Chen, S. D. Worley, T. S. Huang, J. Weese, J. Kim, C-I. Wei, and J. F. Williams, "Biocidal Polystyrene Beads. IV. Functionalized Methylated Polystyrene," J. Appl. Polym. Sci., 92, 368 (2004).
- 7) S. D. Worley, Y. Chen, J-W. Wang, R. Wu, U. Cho, R. M. Broughton, J. Kim, C-I. Wei, J. F. Williams, J. Chen, and Y. Li, "Novel *N*-Halamine Siloxane Monomers and Polymers for Preparing Biocidal Coatings," Surf. Coat. Intern. Part B: Coat. Trans., 88, 93 (2005) (invited paper).
- 8) J. Liang, R. Wu, T. S. Huang, "Polymerization of a Hydantoinylsiloxane on Particles of Silicon Dioxide to Produce a Biocidal Sand," J. Appl.Polym. Sci., 97, 1161 (2005).
- 9) J. Liang, R. Wu, J-W. Wang, K. Barnes, S. D. Worley, U. Cho, J. Lee, R. M. Broughton, and T. S. Huang, "*N*-Halamine Biocidal Coatings," J. Ind. Microbiol, &Biotechnol, 34, 157 (2007) (invited paper).
- 10) J.Liang, Y. Chen, K. Barnes, R. Wu, S. D. Worley, and T-S. Huang, "*N*-Halamine/Quat Siloxane Copolymers for Use in Biocidal Coatings," Biomaterials, 27, 2495 (2006).
- 11) J. Liang, J. R. Owens, T. S. Huang, and S. D. Worley, "Biocidal Hydantoinylsiloxane Polymers. IV. *N*-Halamine Siloxane-Functionalized SilicaGel," J. Appl. Polym. Sci., 101, 3448 (2006).
- 12) A. Akdag, S. Okur, M. L. McKee, and S. D. Worley, "The Stabilities of N-Cl Bonds in Biocidal Materials," J. Chem. Theory Comput., 2, 879 (2006).

- 13) A. Akdag, M. L. McKee, and S. D. Worley, "Mechanism of Formation of Biocidal Imidazolidin-4-one Derivatives: An *ab initio* DFT Study," J. Phys. Chem. A, *110*, 7621 (2006).
- 14) A. Akdag, T. Webb, and S. D. Worley, "Oxidation of Thiols to Disulfides with Monochloro Poly(styrenehydantoin) Beads," Tett. Lett., *47*, 3509 (2006).
- 15) K. Barnes, J. Liang, R. Wu, S. D. Worley, J. Lee, R. M. Broughton, and T. S. Huang, "Synthesis and Antimicrobial Applications of 5,5'- ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)hydantoin]," Biomaterials, *27*, 4825 (2006).
- 16) J. Lee, R. M. Broughton, A. Akdag, S. D. Worley, and T. S. Huang, "Antimicrobial Fibers via a Dyeing Process: Synthesis and Application of an S-Triazine-based Novel *N*-Halamine Biocide," Fibers and Polymers, *8*, 148 (2007).
- 17) L. Kou, J. Liang, S. D. Worley, J. Lee, R. M. Broughton, and T. S. Huang, "Antimicrobial Cellulose: Preparation and Application of 5-methyl-5-aminomethylhydantoin," Res. J. Tex. Apparel, *10*, 44 (2006).
- 18) J. Lee, R. M. Broughton, J. Liang, S. D. Worley, and T. S. Huang, "Antimicrobial Acrylic Fiber," Res. J. Tex. Apparel, *10*, 61 (2006).
- 19) A. Akdag, J. Liang, and S. D. Worley, "Oxidation of Organic Sulfides by *N*-Halamine Compounds," Phosphorous, Sulfur, and Silicon, *182*, 1525 (2007).
- 20) J. Liang, K. Barnes, A. Akdag, S. D. Worley, J. Lee, R. M. Broughton, and T. S. Huang, "An Improved Antimicrobial Siloxane," Ind. Eng. Chem. Res., *46*, 1861 (2007).
- 21) J. Lee, R. M. Broughton, A. Akdag, S. D. Worley, and T. S. Huang, "Antimicrobial Fibers Coated via Polycarboxylic Acid Durable Press Finishing," Textile Res. J., *77*(8), 604 (2007).
- 22) K. Barnes, J. Liang, S. D. Worley, J. Lee, R. M. Broughton, and T. S. Huang, "Modification of Silica Gel, Cellulose, and Polyurethane with a Sterically Hindered *N*-Halamine Moiety to Produce Antimicrobial Activity," J. Appl. Polym. Sci., *105*(4), 2306 (2007).
- 23) A. Akdag, S. D. Worley, O. Acevedo, and M. L. McKee, "Mechanism of 5,5-dimethylhydantoin Chlorination: A Computational Study of the Formation of a Biocide," J. Chem. Theory Comput., *3*(6), 2282 (2007).
- 24) A. Akdag, H. B. Kocer, S. D. Worley, R. M. Broughton, T. R. Webb, and T. H. Bray, "Why Does Kevlar Decompose, While Nomex Does Not When Treated with Aqueous Chlorine Solutions?," J. Phys. Chem. B, *111*, 5581 (2007).
- 25) J. Lee, X. Ren, R. M. Broughton, J. Liang, S. D. Worley, and T. S. Huang, "Electro-spun Antimicrobial Acrylic Fiber," J. Korean Soc. Dyes and Fin., *19*, 44 (2007).
- 26) J. Liang, Y. Chen, X. Ren, R. Wu, K. Barnes, S. D. Worley, R. M. Broughton, U. Cho, H. Kocer, and T. S. Huang, "Fabric Treated with Antimicrobial *N*-Halamine Epoxides," Ind. Eng. Chem. Res., *46*(20), 6425 (2007).

- 27) X. Ren, L. Kou, H. B. Kocer, C. Zhu, S. D. Worley, R. M. Broughton, and T. S. Huang, "Antimicrobial Coating of an *N*-Halamine Biocidal Monomer on CottonFibers," Coll. & Surf. A: Physiochem. Eng. Aspects, *317*, 711 (2008).
- 28) X. Ren, L. Kou, J. Liang, S. D. Worley, Y. M. Tzou, and T. S. Huang, "Antimicrobial Efficacy and Light Stability of *N*-Halamine Siloxanes Bound to Cotton," Cellulose, *15*, 593 (2008).
- 29) J. Lee, R. M. Broughton, S. D. Worley, and T. S. Huang, "Antimicrobial Polymeric Materials; Cellulose and *m*-Aramid Composite Fibers," J. Eng. Fibers & Fabrics,*2*(4), 25 (2007).
- 30) X. Ren, H. Kocer, L. Kou, S. D. Worley, R. Broughton, Y. M. Tzou, and T. S.Huang, "Antimicrobial Polyester," J. Appl. Polym. Sci., *109*, 2756 (2008).
- 31) X. Ren, A. Akdag, C. Zhu, L. Kou, S. D. Worley, and T. S. Huang, "Electrospun Polyacrylonitrile Nanofibrous Biomaterials," J. Biomed. Mater. Res. Part A, *91A*(2), 385 (2009).
- 32) X. Ren, L. Kou, H. B. Kocer, S. D. Worley, R. M. Broughton, Y. M. Tzou, and T. S. Huang, "Antimicrobial Modification of Polyester by Admicellar Polymerization," J. Biomed. Res. Part B, Appl. Biomat., *89B*(2), 475 (2009).
- 33) H. B. Kocer, A. Akdag, X. Ren, R. M. Broughton, S. D. Worley, and T. S. Huang, "The Effect of Alkyl Derivatization on Several Properties of *N*-Halamine Antimicrobial Coatings," Ind. Eng. Chem. Res., *47*, 7558 (2008).
- 34) X. Ren, H. B. Kocer, S. D. Worley, R. M. Broughton, and T. S. Huang, "Rechargeable Biocidal Cellulose: Synthesis and Application of 3-(2,3- dihydroxypropyl)-5,5-dimethylimidazolidine-2,4-dione," Carbohydrate Polym.,*75*(4), 683 (2009).
- 35) X. Ren, C. Zhu, H. B. Kocer, l. Kou, S. D. Worley, R. M. Broughton, and T. S. Huang, "Acyclic *N*-Halamine Polymeric Biocidal Films," J. Bioact. Compat.Polym., *25*(4), 392 (2010).
- 36) L. Kou, J. Liang, X. Ren, H. B. Kocer, S. D. Worley. Y-M. Tzou, and T. S. Huang, "Synthesis of a Water Soluble Siloxane Copolymer and Its Application for Antimicrobial Coatings," Ind. Eng. Chem. Res., *48*, 6521 (2009).
- 37) X. Ren, H. B. Kocer, S. D. Worley, R. M. Broughton, and T. S. Huang, "*N*-Halamine-coated Cotton for Antimicrobial and Detoxification Applications," Carbohydrate Polym., *78*, 220 (2009).
- 38) .L. Kou, J. Liang, X. Ren, H. B. Kocer, S. D. Worley, R. M. Broughton, and T. S. Huang, "Novel *N*-Halamine Silanes," Coll. & Surf. A: Physiochem. Eng. Aspects,*345*, 88 (2009).
- 39) H. B. Kocer, S. D. Worley, R. M. Broughton, O. Acevedo, and T. S. Huang, "Effect of Phenyl Derivatization on the Stabilities of Antimicrobial Chlorohydantoin Derivatives," Ind. Eng. Chem. Res., *49*(22), 11188 (2010).
- 40) H. B. Kocer, A. Akdag, S. D. Worley, O. Acevedo. R. M. Broughton, and Y. Wu, "Mechanism of Photolytic Decomposition of *N*-Halamine Antimicrobial Siloxane Coatings," ACS Appl. Mat. Interf., *2*(8), 2456 (2010).

- 41) .I. Cerkez, H. Kocer, S. D. Worley, R. M. Broughton, and T. S. Huang, "*N*- Halamine Biocidal Coatings via a Layer-by-Layer Assembly Technique," *Langmuir*, 27(7), 4091 (2011).
- 42) H. B. Kocer, S. D. Worley, R. M. Broughton, and T. S. Huang, "A Novel *N*- Halamine Acrylamide Monomer and Its Copolymers for Antimicrobial Coatings," *Reac. & Func. Polym.*, 71, 561 (2011).
- 43) H. B. Kocer, I. Cerkez, S. D. Worley, R. M. Broughton, and T. S. Huang, "Polymeric Antimicrobial *N*-Halamine Epoxides," *ACS Appl. Mat. Interf.*, 3, 2845 (2011)(invited manuscript for a special issue on Biocidal Materials and Interfaces).
- 44) H. B. Kocer, I. Cerkez, S. D. Worley, R. M. Broughton, and T. S. Huang, "Cellulose, Starch, Hals. Composite Fibers Extruded from an Ionic Liquid," *Carbohydrate Polym.*, 86, 922 (2011).
- 45) H. B. Kocer, I. Cerkez, S. D. Worley, R. M. Broughton, and T. S. Huang, "*N*-Halamine Copolymers for Use in Antimicrobial Paints," *ACS Appl. Mat. Interf.*, 3, 3189 (2011).
- 46) I. Cerkez, H. B. Kocer, S. D. Worley, R. M. Broughton, and T. S. Huang, "Multifunctional Cotton Fabric: Antimicrobial and Durable Press," *J. Appl. Polym. Sci.*, 124(5), 4230 (2012).
- 47) X. Ren, H. B. Kocer, S. D. Worley, R. M. Broughton, and T. S. Huang, "Biocidal Nanofibers via Electrospinning," *J. Appl. Polym. Sci.*, 127(4), 3192 (2013).
- 48) I. Cerkez, H. B. Kocer, S. D. Worley, R. M. Broughton, and T. S. Huang, "Epoxide Tethering of Polymeric *N*-Halamine Moieties," *Cellulose*, 19, 959 (2012).
- 49) I. Cerkez, H. B. Kocer, S. D. Worley. R. M. Broughton, and T. S. Huang, "*N*-Halamine Copolymers for Biocidal Coatings," *Reac. Func. Polym.*, 72, 673(2012).
- 50) B. W. McCann, H. Song, H. B. Kocer, I. Cerkez, O. Acevedo, and S. D. Worley, "Inter- and Intramolecular Mechanisms for Chlorine Rearrangements in Trimethyl-substituted Hydantoins," *J. Phys. Chem. A*, 116, 7245 (2012).
- 51) O. Yildiz, I. Cerkez, H. B. Kocer, S. D. Worley, R. M. Broughton, and T. S. Huang, "*N*-(Hydroxymethyl)acrylamide as a Multifunctional Finish to Cotton and a Tether for Grafting Methacrylamide for Biocidal Coatings," *J. Appl. Polym. Sci.*, in press.
- 52) .I. Cerkez, S. D. Worley, R. M. Broughton, and T. S. Huang, "Antimicrobial Coatings for Polyester and Polyester/Cotton Blends," *Prog. Org. Coat.*, under review.
- 53) .I. Cerkez, S. D. Worley, R. M. Broughton, and T. S. Huang, "Rechargeable Antimicrobial Coatings for Poly(lactic acid)," *Polymer*, 54, 536 (2013).
- 54) .H. B. Kocer, "Residual Disinfection with *N*-Halamine Based Antimicrobial Paints," *Prog. Org. Coat.*, 74, 100 (2012).
- 55) .I. Cerkez, "Rapid Disinfection by *N*-halamine Polyelectrolytes," *J. Bioact. Compat. Polym.*, in press.

Patents

- 56) S. D. Worley and Y. Chen, Biocidal Polystyrene Hydantoin Particles, U. S. Patent, 6,852,312, Feb. 8, 2005.
- 57) S. D. Worley, Y. Chen, J. Wang, R. Wu, and Y. Li, *N*-Halamine Siloxanes for Use in Biocidal Coatings and Materials, U. S. Patent, 6,969,769 B2, Nov. 29, 2005.
- 58) S. D. Worley, Y. Chen, J. Liang, R. Wu, K. Barnes, R. M. Broughton, U. Cho, and J. Lee, Biocidal Siloxane Coating Material Containing *N*-Halogenated Amine and Amide Functional Groups, U. S. Patent, 7,335,373 B2, Feb. 26, 2008.
- 59) S. D. Worley, J. Liang, Y. Chen, R. M. Broughton, J. W. Wang, R. Wu, U. Cho, J. Lee, and K. Barnes, Biocidal *N*-Halamine Epoxides, U.S. Patent, filed Mar. 10, 2006.
- 60) R. M. Broughton, H. B. Kocer, S. D. Worley, and A. Maddox, Disinfecting and Detoxifying *meta*-Aramid Particles, U.S. Patent, filed Sep. 3, 2010.
- 61) S. D. Worley, R. M. Broughton, H. B. Kocer, and I. Cerkez, Novel *N*-Halamine Acrylamide Monomers and Copolymers thereof for Biocidal Coatings, U.S. Patent, Filed Oct. 11, 2011.

Presentations

- 62) S. D. Worley, Y. Li, R. Wu, and C.-I. Wei, "A Novel *N*-Halamine Monomer for Preparing Biocidal Polyurethane Coatings," International Meeting on Hygienic Coatings, Paint Research Association, Brussels, Belgium, July 2002.
- 63) S. D. Worley, J. Lin, C. Winkelmann, Y. Chen, J. Wang, R. Wu, R. M. Broughton, U. Cho, C. I. Wei, J. Kim, J. F. Williams, and J. Chen, "Biocidal Coatings for Natural and Synthetic Fibers," Cell. Abs. 77, 225th National ACS Meeting, New Orleans, La, Mar. 2003.
- 64) U. Cho, R. M. Broughton, and S. D. Worley, "Use of Halamines to Produce Biocidal Surfaces," Cell. Abs. 92, 225th National ACS Meeting, New Orleans, La, Mar. 2003.
- 65) Y. Chen, S. D. Worley, J. Kim, C. Wei, and J. F. Williams, "Control of Chlorine Loading in Biocidal Poly(styrenehydantoin) Beads," Environ. Chem. Abs. 201, 226th National ACS Meeting, New York, NY, Sep. 2003.
- 66) Y. Chen, S. D. Worley, J. Kim, C. Wei, and J. F. Williams, "Control of Chlorine Loading in Biocidal Poly(styrenehydantoin) Beads," Sci. Mix Session, 226th National ACS Meeting, New York, NY, Sep. 2003.
- 67) S. D. Worley, Y. Chen, J. Wang, R. Wu, J. F. Williams, J. Chen, and Y. Li, "Novel *N*-Halamine Siloxane Monomers and Polymers for Preparing Biocidal Coatings," International Meeting on Hygienic Coatings, Paint Research Association, Orlando, FL, Jan. 2004.
- 68) S. D. Worley, "Rechargeable Halogen – Binding Polymers: Composition, Synthesis, and Recharge," Amer. Soc. Trop. Med. And Hyg., 53rd Ann. Meet., Miami, FL, Nov. 2004. S. D. Worley, J. Liang, R. Wu, U. Cho, and R. M. Broughton, "*N*-Halamine

Biocidal Coatings,” International Meeting on Hygienic Coatings, Paint Research Association, Paris, FR, Mar. 2005.

- 69) S. D. Worley, J. Liang, R. Wu, J-W. Wang, K. Barnes, U. Cho, J. Lee, R. M. Broughton, and T. S. Huang, “*N*-Halamine Biocidal Coatings,” Soc. Ind. Microbiol, Biofilms 2005 Symp., Arlington, VA, Apr. 2005.
- 70) J. Liang, T-S. Huang, and S. D. Worley, “Coating Poly(5,5-dimethylhydantoinylpropylsiloxane) on Silica Gel to Prepare Biocidal Silica Gel,” Ind. Eng. Chem. Abs. 52 at the 230th National ACS Meeting, Washington DC, August 2005.
- 71) S. D. Worley, J. Liang, R. M. Broughton, and T. Huang, “*N*-Halamine Biocidal Coatings,” Pacifichem 2005 meeting in Honolulu, Hawaii, Abs. 560, Dec. 2005.
- 72) R. M. Broughton, U. Cho, J. Lee, J. Liang, and S. D. Worley, “Preparation of New Antimicrobial Materials Using Halamines,” Pacifichem 2005 meeting in Honolulu, Hawaii, Abs. 623, Dec. 2005.
- 73) A. Akdag, M. L. McKee, and S. D. Worley, “Thermodynamics and Kinetics of Monohalogenation of 2,2,5,5-Tetramethylimidazolidin-4-one: A Theoretical Study,” Org. Abs. 122 at the 231st National ACS Meeting in Atlanta, GA, Mar. 2006.
- 74) A. Akdag, T. R. Webb, and S. D. Worley, “Oxidation of Thiols with Polystyrenehydantoin (PSH) Monochloro and Dichloro Beads,” Org. Abs. 367 at the 231st National ACS Meeting in Atlanta, GA, Mar. 2006.
- 75) K. Barnes, J. Liang, S. D. Worley, J. Lee, R. M. Broughton, and T. S. Huang, “Synthesis and Applications of 5,5'-ethylenebis[5-methyl-3-(3-triethoxysilylpropyl)imidazolidin-2,4-dione] for Durable and Regenerable Antimicrobial Surfaces,” Ind. Eng. Chem. Abs. 50 at the 231st National ACS Meeting in Atlanta, GA, Mar. 2006.
- 76) J. Liang, K. Barnes, Y. Chen, S. D. Worley, J. Lee, R. M. Broughton, and T. S. Huang, “New Rechargeable Biocidal *N*-halamine Siloxanes,” Ind. Eng. Chem. Abs. 48 at the 231st National ACS Meeting in Atlanta, GA, Mar. 2006.
- 77) J. Liang, T. S. Huang, and S. D. Worley, “Coating New *N*-halamine Siloxanes on Silica Gel to Prepare Biocidal Silica Gels,” Ind. Eng. Chem. Abs. 49 at the 231st National ACS Meeting in Atlanta, GA, Mar. 2006.
- 78) J. Lee, R. M. Broughton, S. D. Worley, T. S. Huang, and X. Fan, “Mixed Solution of Cellulose and m-Aramid Polymers,” Cell. Abs. 9 at the 232nd National ACS Meeting in San Francisco, CA, Sep. 2006.
- 79) S. D. Worley, J. Liang, K. Barnes, J. Lee, R. M. Broughton, and T. S. Huang, “New *N*-Halamine Antimicrobial Coatings for Textiles,” Cell. Abs. 135 at the 233rd National ACS Meeting in Chicago, IL, March 2007.
- 80) C. Zhu, A. Akdag, J. Liang, S. D. Worley, and T. S. Huang, “Synthesis and Applications of a Novel Biocidal polymer,” Cell. Abs. 61 at the 233rd National ACS Meeting in Chicago, IL, March 2007.

- 81) L. Kou, J. Liang, A. Akdag, , S. D. Worley, H. B. Kocer, R. M. Broughton, and T. S. Huang, "Synthesis and Application of a New Antimicrobial *N*-Halamine Siloxane," Cell. Abs. 69 at the 233rd National ACS Meeting in Chicago, IL, March 2007.
- 82) S. D. Worley, A. Akdag, J. Liang, L. Kuo, C. Zhu, and X. Ren, "Novel Antimicrobial Polymeric Coatings," Coll. Abs. 459 at the 224th National ACS Meeting in Boston, MA, Aug. 2007.
- 83) X. Ren, S. D. Worley, L. Kuo, C. Zhu, H. B. Kocer, R. M. Broughton, H. Kocer, and T. S. Huang, "*N*-Halamine Disinfectant Coatings," Coll. Abs. 462 at the 224th National ACS Meeting in Boston, MA, Aug. 2007.
- 84) S. D. Worley, J. Liang, A. Akdag, X. Ren, L. Kuo, C. Zhu, K. Barnes. R. M. Broughton, and T. S. Huang, "Novel Polymerization of a[n] *N*-Halamine Biocidal Monomer on the Surface of Cotton Fibers," Coll. Abs. 180 at the 224th National ACS Meeting in Boston, MA, Aug. 2007.
- 85) X. Ren, S. D. Worley, C. Zhu, L. Kuo, A. Akdag, H. B. Kocer, R. M. Broughton, and T. S. Huang, "*N*-Halamine Coating of Cotton with the Crosslinking Agent BTCA," Cell. Abs. 121 at the 225th National ACS Meeting in New Orleans, LA, Apr. 2008.
- 86) X. Ren, S. D. Worley, L. Kuo, H. B. Kocer, C. Zhu, R. M. Broughton, and T. S. Huang, "Antimicrobial Polyester," Cell. Abs. 116 at the 225th National ACS Meeting in New Orleans, LA, Apr. 2008.
- 87) L. Kou, A. Akdag, X. Ren, L. Kou, S. D. Worley, and T. S. Huang, "Biocidal Polyurethane Coating," I&EC. Abs. 85 (also in the SCI MIX) at the 225th National ACS Meeting in New Orleans, LA, Apr. 2008.
- 88) C. Zhu, A. Akdag, X. Ren, L. Kou, S. D. Worley, and T. S. Huang, "Synthesis and Application of a Novel Biocidal Polymer," I&EC. Abs. 86 (also in the SCI MIX) at the 225th National ACS Meeting in New Orleans, LA, Apr. 2008.
- 89) X. Ren, S. D. Worley, L. Kou, A. Akdag, C. Zhu, and T. S. Huang, "Nanosized Antimicrobial Polyacrylonitrile Fiber," I&EC. Abs. 87 (also in the SCI MIX) at the 225th National ACS Meeting in New Orleans, LA, Apr. 2008.
- 90) S. D. Worley, L. Kou, and X. Ren, "Synthesis and Testing of an Improved Antimicrobial Siloxane Copolymer," Cell Abs. 139 at the 237th National ACS Meeting in Salt Lake City, Mar. 2009.
- 91) H. B. Kocer, R. M. Broughton, S. D. Worley, and E. S. Klinc-Balci, "Cellulose Starch/HALS Composite Fibers for Biocidal Applications," Cell Abs. 210 at the 239th National ACS Meeting in San Francisco, March 2010.
- 92) S. D. Worley, "Effect of Phenyl Derivatization on *N*-Halamine Antimicrobial Siloxane Coatings," Sustainable Textiles and Medical Protection Conference, University of California Davis, June 2010 (invited presentation).
- 93) H. B. Kocer, S. D. Worley, R. M. Broughton, and T. S. Huang, "Effect of Phenyl Derivatization on Several Properties of *N*-Halamine Antimicrobial Siloxane Coatings," PMSE Abs. 369 at the 240th National ACS Meeting in Boston, Aug. 2010.

- 94) H. B. Kocer, A. Akdag, S. D. Worley, R. M. Broughton, and Y. Wu, "Mechanism of Decomposition of Antimicrobial *N*-Halamine Siloxane Coatings," PMSE Abs. 368 at the 240th National ACS Meeting in Boston, Aug. 2010.
- 95) S. D. Worley, H. B. kocer, R. M. Broughton, and T. S. Huang, "*N*-Halamine Acrylamide Copolymers and Their Use for Rendering Surfaces and Paints Antimicrobial," POLY Abs. 187 at the 242nd National ACS Meeting in Denver, Aug. 2011, invited presentation.
- 96) I. Cerkez, H. B. Kocer, S. D. Worley, R. M. Broughton, and T. S. Huang, "Polymeric *N*-Halamine Epoxides," IE&C Abs. 50 at the 242nd National ACS Meeting in Denver, Aug. 2011, invited presentation.
- 97) I. Cerkez, H. B. Kocer, S. D. Worley, R. M. Broughton, and T. S. Huang, "Multifunctional Cotton Fabric: Antimicrobial and Durable Press Finish," IE&C Abs. 85 at the 242nd National ACS Meeting in Denver, Aug. 2011, also in Sci. Mix.
- 98) S. D. Worley, I. Cerkez, H. B. Kocer, R. M. Broughton, and T. S. Huang, "Epoxide Tethering of Antimicrobial Polymeric *N*-Halamine Moieties to Cellulose," Cell Abs147 at the 243rd National ACS Meeting in San Diego, Mar. 2012, invited presentation.
- 99) S. D. Worley, H. B. Kocer, I. Cerkez, R. M. Broughton, and T. S. Huang, "Antimicrobial Materials for Coatings and Latex Paints," Coll Abs 666 at the 243rd National ACS Meeting in San Diego, Mar. 2012, invited presentation.
- 100) I. Cerkez, S. D. Worley, and R. M. Broughton, "Antimicrobial Finishing of Polyester and Cotton Fabrics," Fiber Society Meeting, Nov. 2012.

LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS

AFRL	Air Force Research Laboratory
AIBN	azobis(isobutyronitrile)
aq	aqueous
BA-1	3-triethoxysilylpropyl-5,5-dimethylhydantoin
cell	cellulose (cotton)
CM	commercial monomer, 3-chloro-2-hydroxypropyl methacrylate
cm	centimeters
cm ⁻¹	wavenumbers
d	days
equiv	equivalents
FTIR	Fourier-transform infrared spectrometry
g	grams
GM	glycidyl methacrylate
h	hours
$h\nu$	photons
L	liters
MHz	megahertz
mL	milliliters
mM	millimolar
min	minutes
N	normality
NMR	nuclear magnetic resonance spectrometry
s	seconds
SEM	scanning electron microscopy
UV	ultraviolet
UVA	lowest-energy UV light
μL	microliters