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ORIGINAL PAPER

N-halamine biocidal coatings

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Abstract Novel *N*-halamine siloxane and epoxide coatings are described. The coatings can be rendered biocidal by exposure to dilute bleach. Once the bound chlorine is lost from the coatings, it can be regenerated by further exposure to dilute bleach. Synthetic schemes and biocidal efficacy data are presented. The stabilities of the bound chlorine on the surfaces are also addressed. Substrates employed include sand, textiles, and paint. Potential uses for the technology are discussed.

Keywords Biocides · Biocidal polymers · Biocidal coatings · *N*-halamines · Disinfectants

Introduction

Work in these laboratories for two decades has focused on the development of novel biocidal *N*-halamine derivatives [23, 24]. Water-soluble cyclic *N*-halamine derivatives such as 1,3-dihalo-5,5-dimethylhydantoin and halogenated isocyanurates (e.g., trichlor and dichlor) have been employed as biocides for industrial and recreational water uses for many years, but the water-soluble *N*-halamine compounds produced in these laboratories (oxazolidinones and imidazolidinones) are superior because of their long-term stabilities in aqueous solution and in dry storage. This exceptional stability is a result of their chemical structures; all have electron-donating alkyl groups substituted on the heterocyclic rings adjacent to the oxidative N–Cl or N–Br moieties which hinder the release of "free halogen" into aqueous solution. The combined *N*-halamines thus serve as the contact biocides.

Although combined *N*-halamine monomers generally require longer contact times at a given halogen concentration than does "free halogen" to inactivate pathogens, it has been demonstrated in these laboratories that it is possible to concentrate *N*-halamine moieties on insoluble polymers, thus producing a substantial reservoir of combined halogen for enhanced disinfection purposes. Furthermore, the functionalized *N*-halamine polymers are superior in overall performance (taking into account biocidal efficacy, stability at varying pH and in the presence of organic receptors, rechargeability, lack of toxicity, and cost) to other biocidal polymers which have been developed over the years, some of which are in the commercial sector, such as halogenated poly-styrene-divinylbenzenesulfonamides [7, 8], polymeric phosphonium materials [10], and polymeric quaternary ammonium compounds [9, 11].

Several commercial polymers have been functionalized with *N*-halamine moieties rendering them biocidal upon surface contact with pathogens. These include cellulose [19, 20], nylon [12, 20], PET [13, 20], Kraton rubber [6], and various surface coatings [4]. But to date, the most important *N*-halamine polymers developed,

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because of their potential for economical disinfection of potable water, thus improving world health, are the N-halogenated poly-styrenehydantoins [14–18]. These products were originally in the form of granular solids which were insoluble in water, but they could be chlorinated or brominated by adding free chlorine or bromine, respectively. The final products were amorphous solids, which were insoluble in water and could be packed into glass columns which functioned as cartridge filters. It was observed that the filters inactivated numerous species of bacteria, fungi, and even rotavirus in only seconds of contact time in flowing water [14–18]. Also, it was observed that the columns did not leach out organic decomposition products into the water [16], and that the free chlorine and bromine concentrations leached into the flowing water were less than 0.1 mg/L and less than 2.0 mg/L, respectively. Furthermore, once the halogen supply was exhausted through various loss processes, it could be replenished on the polymers by simply exposing them to flowing aqueous free halogen (e.g., sodium hypochlorite bleach for the chlorinated derivative). The chlorinated polymer will be useful for potable water disinfection applications throughout the world, and the brominated polymer should work well in disinfecting recreational water sources. The products have been produced in the form of porous beads to enhance flow properties [2, 3].

Recently, it was shown that the technology developed in these laboratories could be extended to the preparation of biocidal polyurethane coatings through functionalization of a reactive diol with a hydantoin moiety which could then be copolymerized with commercial polyols and isocyanates to form a polyurethane. An application of free halogen (e.g., with household bleach) rendered the coating biocidal [22]. In a recent International Conference on Hygienic Coatings and Surfaces in Orlando the topic of biocidal *N*-halamine siloxane coatings was introduced [21]. In the current work we show how the technology can further be extended to the preparation of biocidal siloxane and epoxide coatings (see structures in Fig. 1). Such siloxane coatings have been employed in the past utilizing biocidal quaternary ammonium salt derivatives [5], but the *N*-halamine functionality provides superior biocidal efficacy.

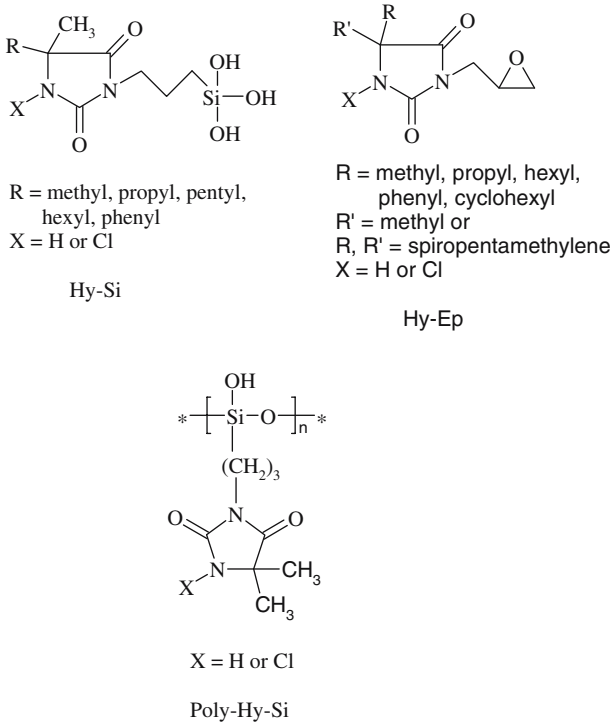

Fig. 1 Structures of monomers and polymers employed in this work

Materials and methods

Preparation of siloxane monomers and polymers

Trialkoxysilylpropylhydantoin derivatives (Hy-Si in Fig. 1) were prepared according to a procedure similar to that outlined in US Patent 4,412,078 [1] and discussed at the Orlando Conference [21]. First, the appropriate 5,5-dialkylhydantoin was prepared by reaction of ammonium carbonate, potassium cyanide, and the necessary dialkyl ketone (Aldrich Chemical Company, Milwaukee, WI) in a 2.0:1.0:0.67 molar ratio in a water/ethanol (1:1 by volume) solvent mixture at 50–60°C for 4–10 h. The crude products were isolated by exposure to dilute HCl and filtration; purification was effected by recrystallization from water/ethanol. Products were confirmed by ^{1}H NMR; yields ranged from 88 to 99% by weight. Then the potassium salts of the dialkylhydantoins were prepared by mixing the dialkylhydantoins with equimolar quantities of KOH in ethanol and heating at reflux for about 5 min. The salts were isolated by removal of the solvent under vacuum. After drying overnight at 50°C, the salts were dissolved in dimethyl formamide (DMF) at 60°C. An equimolar solution of 3-chloropropyltriethoxysilane (Aldrich Chemical Company, Milwaukee, WI) in DMF was then added dropwise at 100°C, and the resulting mixture was held at 100°C for 4–8 h. The KCl produced in the reaction was removed by filtration, and the DMF was removed at reduced pressure. Purification was effected by dissolving the resulting oil or solid in ethyl acetate, shaking with water, and removing the ethyl acetate by evaporation. The structures of the 3-triethoxysilylpropyl-5-alkyl-5-methylhydantoin derivatives were confirmed by ^{1}H NMR; yields ranged from 85 to 95% by weight. The derivatives could be chlorinated

before or after a coating procedure using a 10% solution of sodium hypochlorite bleach buffered to pH 7.

Polymers of the trialkoxysilylpropylhydantoin derivatives (Poly-Hy-Si in Fig. 1) discussed above could be prepared by either reacting the potassium salt of the hydantoin derivative with poly(3-chloropropylsilane) prepared as described previously [21], or by direct polymerization of the monomers discussed above in dilute HCl at elevated temperature [21]. The polymers could be chlorinated before or after a coating procedure using a 10% solution of sodium hypochlorite bleach buffered to pH 7.

Preparation of hydantoinyl epoxides

The hydantoinyl epoxide derivatives (Hy-Ep in Fig. 1) were prepared by reacting the sodium salts of the appropriate hydantoins with equimolar concentrations of commercial epichlorohydrin (Aldrich Chemical Company, Milwaukee, WI) at ambient temperature for 6–10 h in aqueous solution. The 5,5-dialkylhydantoin derivatives were synthesized by the procedure noted above. The sodium salts were produced by simply mixing dilute NaOH with the hydantoins at ambient temperature. In fact, in this case the reaction of the alkali base with the hydantoin derivatives, and subsequently with the epichlorohydrin, was accomplished in one pot. Following the reaction, water was removed by evacuation, and the desired product was dissolved in acetone. Then the sodium chloride produced in the reaction was removed by filtration, and the acetone was removed by evacuation. The spiropentamethylene derivative was produced as a white solid; the other dialkyl derivatives were recovered as oils. Further purification was not deemed necessary. The structures of the hydantoinyl epoxide derivatives were confirmed by ^{1}H NMR.

Coating surfaces

Solutions of the precursor siloxane monomers or polymers (in 1:1 ethanol/water by volume) at concentrations ranging from 2 to 10 weight percent were either sprayed onto the various surfaces or employed in soaking baths to coat the materials. The treated surfaces were cured at temperatures ranging from ambient to 145°C for various time periods dependent upon the nature of the material. In the case of liquid paint, the 5,5-dimethylhydantoinylsiloxane derivative (monomeric and polymeric forms) was simply mixed into a commercial floor enamel at weight percent ranging from 2.5 to 5.0%. The monomer was dissolved in water which was miscible with the paint; for the polymer, an ethanol/water (1:1 by volume) solution was used. The paint was then brushed onto wood coupons and was allowed to dry in air at ambient temperature for 24 h before chlorination.

Solutions of the precursor hydantoinyl epoxide derivatives were prepared for use in coating onto cotton. The same molar concentration (0.26) of each derivative was dissolved in a 1:1 by weight solution of acetone and water. Swatches of cotton were soaked in each solution for 15 min and then cured at 95°C for 1 h and then further at 145°C for 20 min. Then the swatches were soaked in a 0.5% detergent solution for 15 min, rinsed several times with water, and dried in air at 70°C. In the case of polyester fabric (PET), the swatches were generally first treated with dilute NaOH at temperatures ranging from ambient to 100°C for time periods of 5–60 min. After rinsing thoroughly with water, the swatches were soaked in an aqueous bath containing 9% by weight of the 5,5-dimethylhydantoinyl epoxide derivative at ambient temperature for 30 min. The swatches were then squeezed on a padding machine and dried at 60°C for 60 min and cured at temperature ranging from 75 to 175°C for time ranging from 5 to 120 min.

Chlorinating treated surfaces

The treated surfaces were rendered biocidal by either spraying them with or soaking them in 5–10% aqueous solutions of household bleach (sodium hypochlorite). After rinsing with distilled, deionized water, and drying in air at 25–50°C, samples of the materials were analyzed for oxidative chlorine coverage using an iodometric/thiosulfate titration procedure. In some cases this was repeated over an extended time period to evaluate the stability of the chlorinated surfaces.

Biocidal efficacy testing

Treated surfaces were challenged with *Staphylococcus aureus* (ATCC 6538) and/or *Escherichia coli* O157:H7 (ATCC 43895) bacterial suspensions in pH 7 phosphate buffer solution. The surfaces were quenched with 0.02 N sodium thiosulfate solution at various contact times. Serial dilutions of the solutions contacting the surfaces were plated on tryptic soy agar, incubated for 48 h at 37°C, and colony counts were made to determine the presence or absence of viable bacteria.

Results and discussion

Siloxane monomers and polymers

Several types of experiments were performed for the siloxanes. In one experiment the monomer 3-triethoxy-

silylpropyl-5,5-dimethylhydantoin was polymerized on sand particles to produce an adhered film which upon chlorination with 10% bleach (to produce a weight percent of 0.28 Cl^+) became biocidal. The biocidal sand (26.0 g) was packed into a 25.0 cm glass column with inside diameter of 1.0 cm to a length of 18.0 cm; the empty-bed volume was 6.42 mL. Then 50 mL portions of distilled water containing either *S. aureus* (about 3×10^6 CFU) or *E. coli* O157:H7 (about 3×10^7 CFU) were repeatedly pumped through the column at a flow rate of 1.5 mL/s. Periodically small aliquots were removed for plating and colony enumeration. Identical control columns containing uncoated sand and unchlorinated coated sand were also challenged with the bacteria. The results are shown in Table 1 for the two pathogens. From the data in the table it is evident that the biocidal sand caused complete inactivation of *S. aureus* and *E. coli* O157:H7 in less than or equal to 1 and 5 min, respectively. It was also shown that after 50 L of distilled water was flowed through an identical column of chlorinated sand, there was only a loss from 0.28 to 0.25% of titratable Cl^+, and 0.27% could then be recovered by rechlorination. Thus, the siloxane coating was not appreciably hydrolyzed off of the sand under the conditions of the experiment. Such biocidal sand may be useful in some water treatment applications.

For the experiments involving the addition of the monomer and polymer of 3-triethoxysilylpropyl-5, 5-dimethylhydantoin to a commercial floor enamel, the stabilities of the bound chlorine over a 60 day period are shown in Table 2. One can see from Table 2 that the chlorine loading does decline over a 60 day period for both the monomer and polymer additives, the polymer stabilizing the chlorine somewhat better. It should be noted that prior work in these laboratories has demonstrated that a Cl^+ loading of 1×10^{16} atom/cm^2 on a surface utilizing an *N*-chloramine is sufficient to provide biocidal activity [21, 22]. The chlorine loading could be partially restored upon rechlorination after 60 days, e.g., for the 5.0% monomer sample a rechlorination yielded 1.09×10^{17} atom/cm^2. However, we have observed a decline in chlorination potential with time if the hydantoinylsiloxane compounds are allowed to remain in the original wet paint. It is recommended that the compounds be added immediately before use of the paint.

Table 1 Biocidal efficacy of coated sand against *S. aureus* and *E. coli* O157:H7

Sample in column filter	Contact time (min)	Log reduction *S. aureus*[a]	Log reduction *E. coli* O157:H7[a]
Sand control[b]	0		
	1	1.906	0.146
	5	2.599	0.208
	10	2.860	0.208
	15	2.943	0.483
Sand control[c]	0		
	1	0.824	0.198
	5	1.814	0.198
	10	2.135	0.247
	15	2.363	0.495
Chlorinated sand[d]	0		
	1	6.491	2.956
	5	6.491	7.447
	10	6.491	7.447
	15	6.491	7.447

[a] Errors in log reductions were less than 10%

[b] Untreated sand control (see text)

[c] Sand treated with unchlorinated polymer (see Fig. 1 and text)

[d] Sand treated with unchlorinated polymer and then chlorinated to form the biocidal sand (see Fig. 1 and text)

Several studies have been conducted on the various dialkyl derivatives of the hydantoinylsiloxanes (see Fig. 1) on cotton. To achieve a complete inactivation of *E. coli* O157:H7 (>5.7 logs), the dimethyl derivative containing 0.49% Cl^+ required a contact time of at least 60 min; however, the hexyl methyl and methyl phenyl derivatives containing high Cl^+ loadings of 1.4 and 1.1%, respectively, both inactivated this bacterium (7.4 logs) in less than 15 min, the shortest contact time tested. The superior performance of the hexyl methyl and methyl phenyl derivatives can be attributed to higher chlorine loadings on the cotton surface and increased lipophilicity of the hydantoinyl functional group with the bacterial cells. A stability study of the chlorinated derivatives coated on cotton was also performed; typical results are indicated in Table 3. One notes from Table 3 that the starting concentration of Cl^+ is lowest for the dimethyl derivative

Table 2 Stability of bound chlorine in a commercial paint

Sample type and loading	Cl^+ content immediately after chlorination of dried surface in atom/cm^2	Cl^+ content 60 d after chlorination of dried surface in atom/cm^2
2.5% monomer on painted wood	0.57×10^{17}	0.12×10^{17}
5.0% monomer on painted wood	1.49×10^{17}	0.81×10^{17}
2.5% polymer on painted wood	0.60×10^{17}	0.33×10^{17}
5.0% polymer on painted wood	1.90×10^{17}	1.38×10^{17}

The error range for these values as determined by iodometric/thiosulfate titration was 5–10%

Table 3 Stability of bound chlorine on hydantoinylsiloxyl-derivatized cotton (% Cl^+ remaining)

Day	Dimethyl	Methyl phenyl	Heptyl methyl	Diphenyl
0	0.53	0.90	0.83	0.83
7	0.53	0.89	0.82	0.82
14	0.53	0.87	0.81	0.81
21	0.52	0.88	0.82	0.82
28	0.52	0.87	0.82	0.82
35	0.51	0.85	0.81	0.80
57	0.52	0.85	0.81	0.79
120	0.51	0.83	0.80	0.74

These values determined by iodometric/thiosulfate titration have an accuracy of ± 0.02

probably indicating that it bonds least strongly to the surface of the cotton, although an electronic effect can not be excluded since heptyl and phenyl are better electron donors than methyl, which could serve to strengthen the N–Cl bond. The shelf lives of all of the derivatives were very good. The relative stabilities during repeated standard washing tests (AATCC test method 61-1986) were also evaluated. The results are presented in Table 4. All of the derivatized cotton samples would remain biocidal after 50 washes; loadings of 0.05% Cl^+ have been shown to provide antibacterial activity. The dimethyl polymeric derivative remains bonded to the surface of cotton better than does the monomeric derivative during the severe washing process. Initial loadings are greatest for the higher alkyl derivatives. We conclude that the chlorinated hydantoinylsiloxyl derivatives have potential for use to render cotton biocidal.

Hydantoinyl epoxide derivatives

As for the dialkylhydantoinylsiloxanes, dialkylhydantoinylepoxides (see structures in Fig. 1) bound to cotton loaded different weight percents of chlorine dependent upon the derivative. The results are shown in Table 5. These results are not easily rationalized. Several factors may be operable here including electronic and steric effects. The alkyl groups are all electron-donating substituents, which should stabilize the N–Cl bonds; this effect should increase roughly with the number of carbon atoms in the alkyl group. Increased size of the alkyl groups should hinder the approach of water molecules in a hydrolysis process to remove the Cl^+ and to cause hydrolysis of the epoxide from the cellulose. Both arguments can rationalize why the dimethyl derivative either loads the least amount of chlorine and/or bonds the least firmly to the cotton. Also, the methyl phenyl derivative might be expected to cause less steric hinderance than does the spirocyclohexyl derivative since the benzene ring is planar, while the cyclohexane ring is shaped like a chair in its lowest-energy conformation. In any case, it is apparent that the capacity of the dialkylhydantoinylepoxide derivatives bound to cotton to bind chlorine varies with the nature of the alkyl group, a fact, which might be useful in tuning a particular structural group for a particular application. Stability studies for the various derivatives are underway.

The 5,5-dimethylhydantoinylepoxide adds to polyester fibers through disruption of a portion of the ester linkages, a process, which is accelerated in the presence of dilute NaOH. The results of washing tests (AATCC test method 61-1986) on the derivatized PET fibers are shown in Table 6. It is evident that pretreatment of the PET with dilute NaOH does enhance the loading of the epoxyhydantoin derivative on the material as evidenced by the increased loading of Cl^+. Furthermore, although the washing process causes the dissociation of bound chlorine from the PET, it can almost entirely be replenished by exposure to dilute bleach. In a practical use pattern, one should add dilute bleach into each wash cycle, which should serve to maintain biocidal activity for the lifetime of the PET material. Finally, identical samples to those listed in Table 6 which had been pretreated with dilute NaOH were exposed to

Table 4 Stability toward washing of bound chlorine on hydantoinylsiloxyl-derivatized cotton (% Cl^+ remaining)

Washing cycles	Dimethyl monomer	Dimethyl polymer	Methyl propyl	Hexyl methyl
0	0.61	0.40	0.85	0.90
5	0.42	0.25	0.56	0.83
10	0.41	0.20	0.42	0.62
25	Nd[a]	Nd[a]	0.13	0.46
50	0.10	0.13	0.14	0.22

These values determined by iodometric/thiosulfate titration have an accuracy of ± 0.02

[a] No determination

Table 5 Initial chlorine loadings on dialkylhydantoinylepoxides coated on cotton from baths containing equimolar concentrations of the epoxide derivatives

Dialkylhydantoinylepoxide derivative	Initial weight percent of Cl^+
Dimethyl	0.14
Methyl propyl	0.19
Hexyl methyl	0.96
Methyl phenyl	0.29
Spirocyclohexyl	0.16

These values determined by iodometric/thiosulfate titration have an accuracy of ± 0.02

Table 6 Stability toward washing of bound chlorine on hydantoinylepoxy-derivatized polyester (% Cl^+ remaining)

Washing Cycles	Pretreat in % Cl^+ left	Water[a] after recharge	Pretreat in % Cl^+ left	NaOH[b] after recharge	Pretreat in % Cl^+ left	NaOH[c] after recharge
0	0.12		0.19		0.21	
5	0.01	0.09	0.01	0.16	0.01	0.17
10	0.00	0.09	0.01	0.15	0.01	0.17
25	0.00	0.09	0.00	0.15	0.00	0.17
50	0.00	0.07	0.00	0.14	0.00	0.16

These values determined by iodometric/thiosulfate titration have an accuracy of 2–3%

[a] The PET was pretreated with a 10% solution of 5,5-dimethylhydantoinylepoxide in water for 30 min

[b] The PET was pretreated with a 10% solution of 5,5-dimethylhydantoinylepoxide in a 1% solution of NaOH for 30 min

[c] The PET was first soaked in a 1.0 N solution of NaOH at 60 °C for 60 min and then pretreated with a 10% solution of 5,5-dimethylhydantoinylepoxide in a 1% solution of NaOH for 30 min

ambient air for 90 days. The losses of Cl^+ (in weight %) for the two types of samples were 0.19–0.11, and 0.21–0.12 over the 90 day period.

Conclusions

Preparation procedures and some test data for some biocidal siloxane and some hydantoinylepoxide coatings have been presented. It can be concluded that *N*-halamine siloxane monomers and polymers and *N*-halamine hydantoinylepoxide derivatives can be very useful in constructing biocidal surface coatings. This has been demonstrated herein for sand, cotton, polyester, and paint. Numerous potential applications can be envisualized.

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