



N-CHLORAMIDE MODIFIED NOMEX[®] AS A REGENERABLE SELF-DECONTAMINATING MATERIAL FOR PROTECTION AGAINST CHEMICAL WARFARE AGENTS

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14. ABSTRACT

Recent interest in the treatment of textiles for chemical and biological agent defense has led to the creation of materials that contain N-chloramide moieties. These materials have demonstrated efficacy against weaponizable bacteria, mustard, and VX, as well as possessing antimicrobial properties against nuisance organisms that cause conditions such as athlete's foot or molds. Here, N-chloramides have been attached to Nomex intended for use as self-decontaminating regenerable military textiles. The materials were assayed for content of active oxidizing agent, and tested for efficacy against 2-chloroethyl ethyl sulfide and Demeton-S, simulants for mustard and VX, respectively. The decomposition products for each reaction were identified as well as reaction pathways to form each by-product as correlated to analogous products of mustard and VX. Furthermore, the rate constant for the neutralization of each simulant on the reactive material was calculated from data collected by GC-MS and ATR-FTIR real-time studies.

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N-chloramide modified Nomex[®] as a regenerable self-decontaminating material for protection against chemical warfare agents

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Abstract Recent interest in the treatment of textiles for chemical and biological agent defense has led to the creation of materials that contain *N*-chloramide moieties. These materials have demonstrated efficacy against weaponizable bacteria, mustard, and VX, as well as possessing antimicrobial properties against nuisance organisms that cause conditions such as athlete's foot or molds. Here, *N*-chloramides have been attached to Nomex[®] intended for use as self-decontaminating regenerable military textiles. The materials were assayed for content of active oxidizing agent, and tested for efficacy against 2-chloroethyl ethyl sulfide and Demeton-S, simulants for mustard and VX, respectively. The decomposition products for each reaction were identified as well as reaction pathways to form each by-product as correlated to analogous products of mustard and VX. Furthermore, the rate constant for the neutralization of each simulant on the reactive material was calculated from data collected by GC-MS and ATR-FTIR real-time studies.

Introduction

Chemical warfare can be traced back to the Peloponnesian War (431–404 BC) when Spartans used arsenical smoke in an effort to choke their adversaries. Perhaps the most notable record of chemical warfare agent (CWA) use was the campaign led by Fritz Haber of Germany, wherein chlorine, phosgene, and mustard gas were used against the Allies on Europe's western front on numerous occasions during World War I [1]. Since that time, nations have sought practical ways to decontaminate mustard agents and similar vesicants. With the appearance of nerve agents, in particular the persistent V-series agents, the need for decontamination strategies became more pressing.

Ideally, a decontaminating agent should act fast, produce by-products of low toxicity, exhibit relatively low toxicity, and perform in all weather conditions. During World War II, the United States began to investigate using chloramide-containing solutions to decontaminate mustard agents [2, 3]. A more recent development is the use of *N*-chloramide hydantoins as "self-decontaminating" components that are integral to such militarily relevant materials as tents, paints, and uniforms. Hydantoin chloramides are nontoxic, regenerable, and are easily attached to polymer substrates via a siloxane or silazane linkage [4, 5]. Chloramides effectively decontaminate thioethers, e.g., sulfur mustards [6, 7]; however, the reaction of phosphonothiolates, including the nerve agent *S*-2-diisopropylaminoethyl *O*-ethyl methylphosphonothioate (VX), with chloramides have not been adequately characterized [7].

In this work, poly(*m*-phenylenediamine isophthalamide) (Nomex[®], Fig. 1) was derivatized with 1-chloro-5,5-dimethyl 3-(triethoxysilylpropyl)hydantoin, and the mechanism and rate of reactivity of this material with the CWA simulants 2-chloroethyl ethyl sulfide (2-CEES) and *S*-2-

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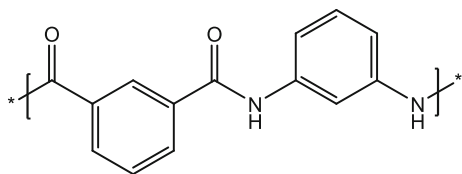


Fig. 1 Molecular structure of a single subunit of Nomex[®]

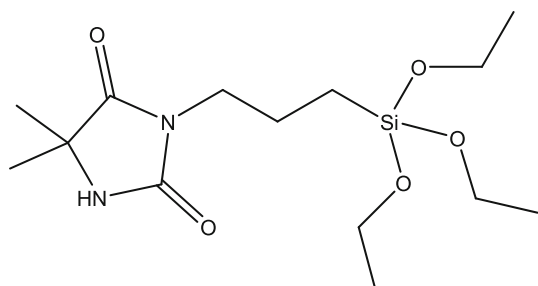


Fig. 2 Molecular structure of the hydantoin derivative, BA-1

ethylthioethyl *O,O*-dimethyl phosphorothioate (Demeton-S) were characterized.

The reactive component attached to the Nomex[®] liner is a chlorinated analog of 5,5-dimethyl-3-(triethoxysilylpropyl)hydantoin (BA-1), (Vanson–HaloSource) (Fig. 2). This compound can be covalently bound to a layer of Nomex[®], cellulose, or nylon via siloxane or silazane linkages with the loss of ethanol. Nomex[®] was chosen for this project because of its flame-resistant polyaramide structure, ease of treatment, and its small contribution to the net weight of a composite material [8, 9]. The treated materials offer several benefits, namely a readily available, polymer-bound oxidant that is capable of decontaminating select chemical and biological threats, and that is biocidal to nuisance organisms such as fungi and molds [6, 10–12].

The materials tested were composite laminates consisting of a nominally impermeable polyurethane shell glued to a Nomex[®] liner. Once the liner or scrim was treated with BA-1, the materials were treated with a 0.6% solution of sodium hypochlorite for 30 min to chlorinate the hydantoin amide group, as shown in Fig. 3.

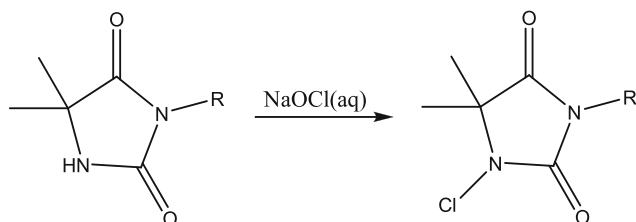


Fig. 3 Chlorination of BA-1 derivatives by hypochlorite $R = -\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{O-substrate})_3$

Decontamination pathways

The simple chemical structure of mustard gas (HD) is bis(2-chloroethyl) sulfide; however, intermolecular nucleophilic displacement of a chloride ion can lead to the formation of an ion pair with a cyclic sulfonium cation (Fig. 4). This episulfonium cation is a powerful vesicant due to its ability to alkylate proteins and nucleotides, preferentially at N-7 of guanine and N-1 of adenine [13]. Because of the Chemical Weapons Convention of 1993, only a limited number of locations are allowed to conduct research using banned chemical agents such as HD. These restrictions necessitate the use of simulants that mimic the chemical and/or physical properties of the actual CWAs. The compound 2-CEES is often used as a simulant for HD due to similarities in structure, chemistry, and physical properties [14].

N-chloramides such as BA-1 are effective decontaminants of both HD and 2-CEES primarily because oxidation terminates at the sulfoxide. Many other oxidants have been used successfully; however, they typically will oxidize the thioether to the sulfone or other more harmful fragmented products [15, 16]. In the presence of water, hypochlorite/hypochlorous acid can form from the N–Cl bond of a chloramide. The equilibrium between hypochlorite and hypochlorous acid is dependent upon pH, with neutral to acidic pHs driving the formation of hypochlorous acid and more basic systems driving the formation of hypochlorite. Both species of the conjugate acid–base pair are capable of oxidizing mustards to a sulfoxide (Fig. 5). The oxidation potentials for the two species are not great enough to produce the sulfone, which is almost as toxic as the original material [6].

N-chloramides have been shown to be highly effective against Demeton-S, a simulant for the CWA VX. Both VX and Demeton-S have a low vapor pressure, and both contain an oxidizable, electron-rich heteroatom. Degradation of VX by oxidation is a feasible and efficient process [17–19].

Demeton-S has been shown to degrade via oxidation of the thioether moiety into sulfoxides and sulfones [20]. An additional oxidation product predicted from the reaction of Demeton-S with the chloramide fabric is the vinyl phosphorothioate derived from Demeton-S. This reaction would correlate extremely well with the neutralization of VX by oxidation [18, 19]. The pathway for the oxidation of VX as well as the predicted mechanism for Demeton-S is shown in Fig. 6 below. It is important to note that the toxic hydrolysis product of VX, EA 2192, or its analog for Demeton-S is not formed by this method of decontamination [21].

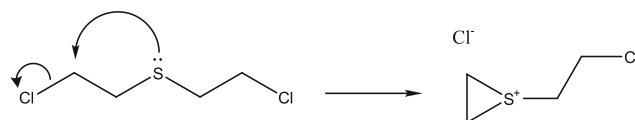
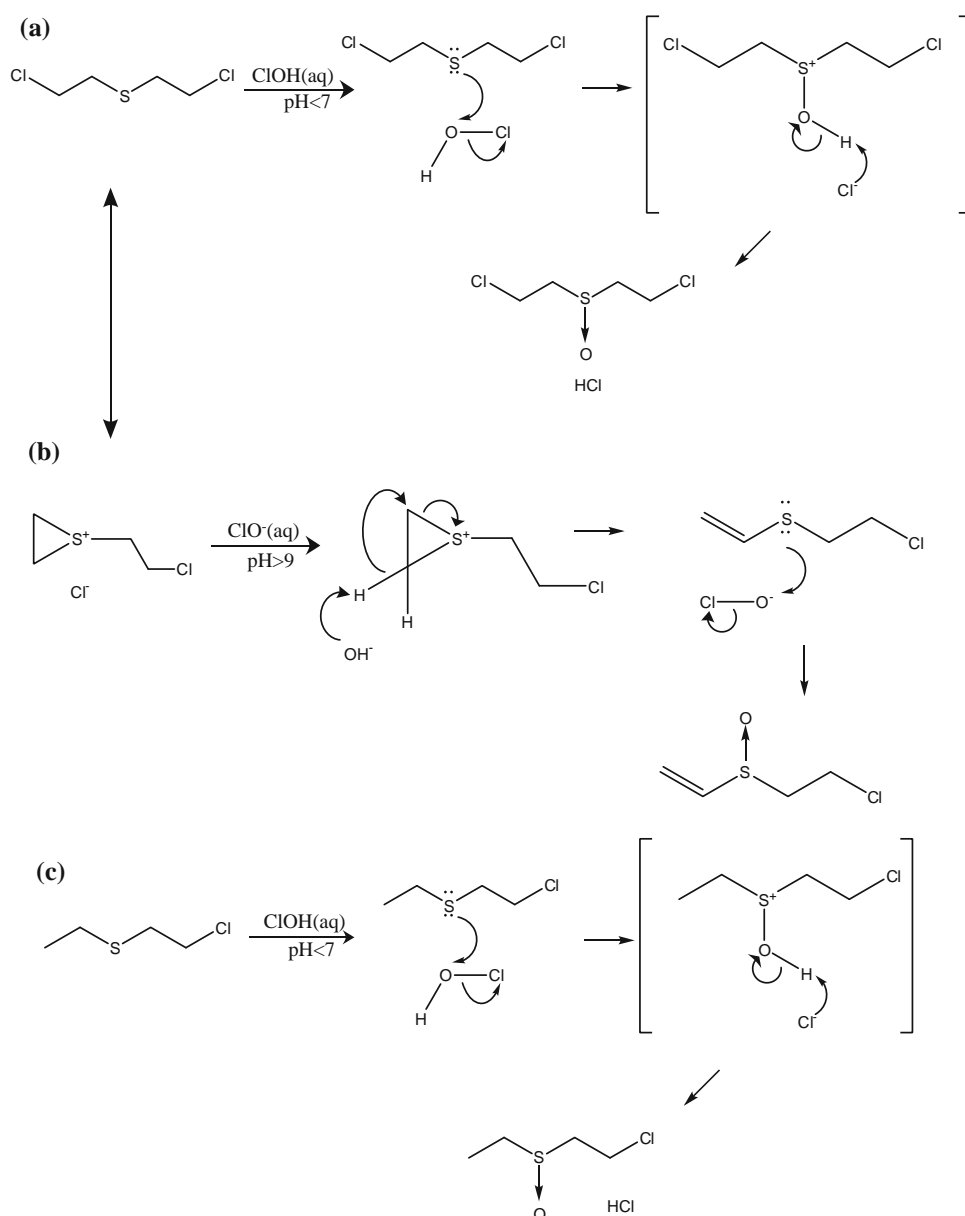


Fig. 4 Formation of an episulfonium cation from HD

Fig. 5 Decontamination pathways for (a) HD, (b) HD in episulfonium form, and (c) 2-CEES after exposure to *N*-chloramides. Formation of the episulfonium cation by intermolecular displacement of HD is illustrated in Fig. 4. Equilibrium shift of the hypochlorous acid/hypochlorite conjugate acid–base pair is dependent upon pH. This mechanism coincides with one proposed by Yang, Baker, and Ward [17]



Treatment procedure

Nomex[®] was treated with BA-1 via microwave-promoted addition of siloxanes to the polymer substrate. The treatment solution was composed of a 3:1:1 (v/v) mixture of acetone, BA-1, and deionized water. Nomex[®] sheets were saturated with the reaction solution, and then irradiated with microwaves in a standard 2.45-GHz microwave oven at 50% power for three intervals of 30 s separated by intervals of roughly 30 s.

The BA-1 treated Nomex[®] was chlorinated by exposing the treated material to an aqueous solution of 0.6% NaOCl for 30 min. The sheets were then rinsed thoroughly with deionized water and dried overnight at room temperature.

Experimental procedures

The reactivity of the treated Nomex[®] to 2-CEES was investigated using the test apparatus depicted in Fig. 7. The test cell is composed of a stainless steel cylinder ($h = 38$ mm, $d = 89$ mm) formed by the attachment of two conflat flanges using six 57-mm hex bolts. The center of the cylinder is open allowing a coupon of fabric ($i_d = 38$ mm, $o_d = 54$ mm) to be secured between the upper (channel 1) and lower (channel 2) halves of the cell. A Teflon[®] injection valve is side mounted on a 60° facing along the outside of the upper flange to allow the coupon to be treated with CWA simulants. Gas flow through each half of the cell is routed through 12-mm holes bored across the cell's diameter (illustrated below).

Fig. 6 A pathway for the degradation of VX by hypochlorous acid oxidation is shown to the left (a). The predicted reaction for Demeton-S is shown on the right (b). The nitroxyl intermediate in (a) and the sulfoxide intermediate in (b) are unstable, and undergo rearrangement and subsequent reactions [22]

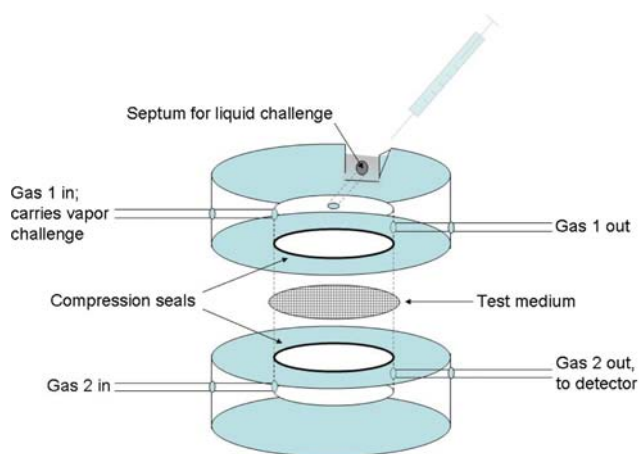
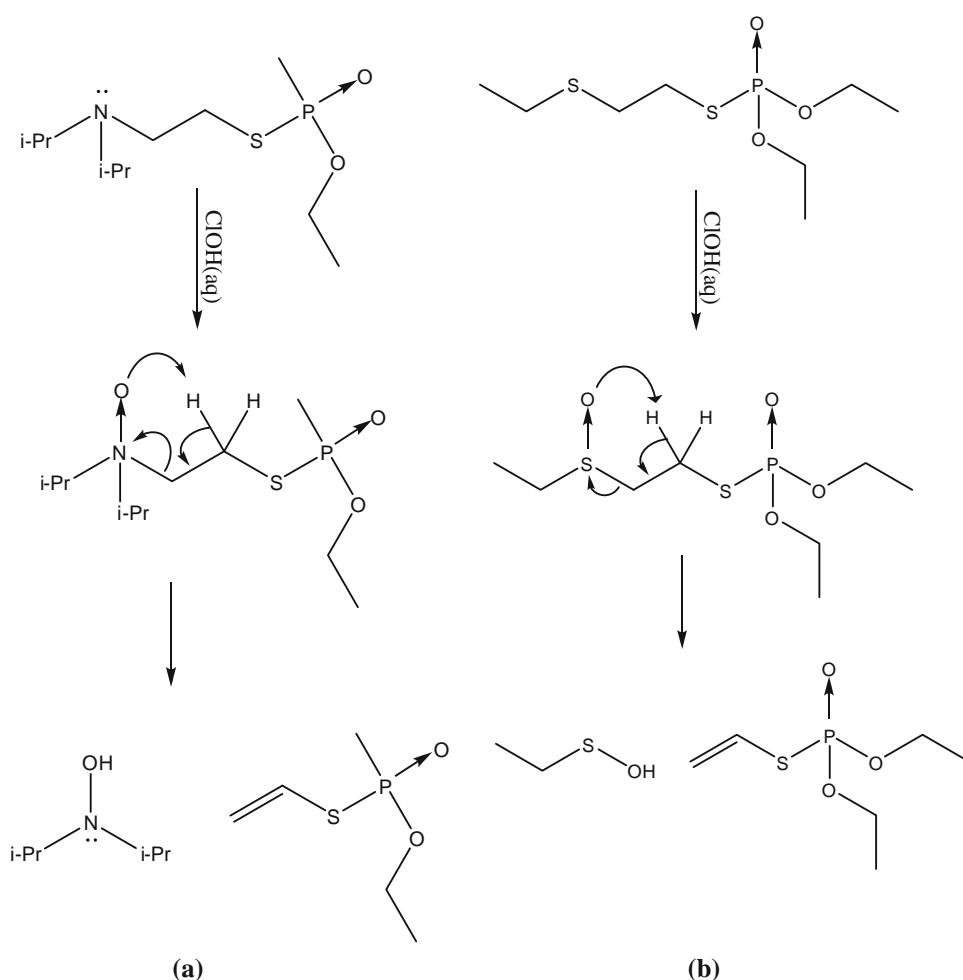


Fig. 7 Diagram of chemical challenge test cell; the Gas 1 inlet was not used to introduce vapor challenges in these experiments

A relative humidity (RH) generator used in conjunction with two mass flow controllers regulates the amount of moisture inside the test cell. The test apparatus, pressure transducer, and RH generator are contained in an insulated polystyrene container to maintain an adiabatic system.

A circulating chiller regulates the internal temperature of the system at 25 °C. Flow rate, RH, and temperature are controllable in gas flows through the upper and lower halves of the test cell.

Vesicant challenges consisted of 25 μL of a 45-g/L solution of 2-CEES in acetonitrile, delivered onto 11.0 cm^2 of the materials (1.0 g/m^2) via the injection port in the upper chamber. This produced a random droplet pattern; however, the solvent quickly absorbed into the fabric, dispersing the simulant across the material. The concentration of simulant inside the test cell was measured by GC-MS of the channel 1 effluent trapped in acetonitrile (~ 0 °C). Channel 2 measurements were not taken for these experiments since the goal here was to determine reactivity of surfaces and not permeability.

Analyses were carried out on a Thermo Finnigan Trace DSQ GC-MS. Aliquots of 0.5 μL were injected into a programmed temperature vaporization injection port run in split mode at 250 °C. Analytes were separated on an HP-5ms 30 m \times 0.25 mm \times 0.25 μm column. The temperature program consisted of a 4-min isotherm at 40 °C, a 20 °C/min ramp to 270 °C, and a 2-min isotherm at

270 °C. A solvent delay of 7 min was implemented because the analytes of interest all eluted after 9 min. The MS was operated in scan mode with a scan rate of 1,807 [m/z]/s at 5 scans/s. 2-CEES was quantified at m/z 124 and $t_R = 9.40$ min, with characteristic ions at m/z 126 and 75. Experimental conditions for the test apparatus were set to 25 °C and 90% RH. Recoveries of 2-CEES were calculated against a four-point linear calibration from 0.8 to 22 mg/L ($R^2 = 0.998$).

Samples of the Nomex[®] composite were challenged with 1.0 g/m² of Demeton-S dissolved in either acetonitrile or ethyl ether. Due to insufficient vapor pressure, data for Demeton-S was not collected from the test cell. Instead the reactions were carried out in petri dishes inside a drying oven. After a preset reaction time had elapsed, the sample was immersed in 10 mL of acetonitrile to extract any unreacted Demeton-S and any products that might have formed. Once extracted, an aliquot of the solvent was analyzed by GC-MS using the method described above.

To better understand the kinetics of Demeton-S decontamination, a real-time study of the material was performed using a Nicolet 6700 FTIR spectrometer. Spectra were obtained on a multi-bounce ZnSe Attenuated Total Reflectance (ATR) accessory with a liquid-nitrogen-cooled mercury–cadmium telluride detector. A 1.0-g/m² challenge of Demeton-S in ethyl ether was applied to a swatch of fabric. IR spectra of the challenged material were obtained every 1.7 s for 20 min beginning at the challenge application. The solvent was used to ensure homogenous application of Demeton-S across the sample surface. The ether carrier solvent evaporated on contact with the substrate, and no trace of it was found in the IR spectra.

Results and discussion

2-CEES

Controls for the reaction cell were conducted on aluminum foil due to its low reactivity to the challenge agent, its impermeability, and its inability to absorb the challenge agent. Two control experiments produced an average 2-CEES recovery of 83.6%. Furthermore, 78.0% or more of the original challenge was recovered after 15 min. Considering loss of material through adhesion to the syringe, control material, and test cell, the 16.4% average loss of the simulant is reasonable for mass balance.

Material controls were conducted on the Nomex[®] liner, which was neither hydantoin treated nor chlorinated. These tests were conducted for 150 min each, with sampling intervals at 15, 30, 45, 60, 90, and 150 min. Fabrics were initially cut to 54 mm in diameter to fit into the grooves of the two flanges. The exposed area of the fabrics measured

38 mm in diameter. This was the area that was able to be contacted by droplets sprayed from the syringe tip, and was the basis for the dimensions used to calculate the challenge. Mass spectra were taken for aliquots from each time interval, and analyzed for the presence of 2-CEES and its two main oxidation products, 2-chloroethyl ethyl sulfoxide and 2-chloroethyl ethyl sulfone. The control material averaged a 60.6% recovery for three fabrics, with challenge agent concentrations reaching baseline values within 45 min of the challenge application. A single test conducted to 260 min showed no variation in the baseline concentration of 2-CEES over this time interval, and no oxidation products were detected.

Tests of the BA-1-treated, chlorinated material were conducted over the same time intervals as aforementioned. The average recovery for the challenge on the treated material was a mere 17%, most of which was recovered in the first 15 min. Table 1 summarizes the results from the three treatments tested.

As expected, the hydantoin-treated, chlorinated fabrics outperformed the untreated controls. Significant reduction in simulant concentration was observed after just 15 min, with samples reaching a baseline concentration after 30 min. There was a 23% difference in recoveries between the aluminum foil control and the untreated textile control, which can be attributed to liquid absorption by the fabric and intermolecular forces between 2-CEES and Nomex[®].

Mass spectra of the trapped headspace from the 2-CEES reactions revealed no traces of the suspected oxidation products. To verify the presence of these, the challenged fabrics were extracted for 2 h in 25 mL of acetonitrile. Analysis of the extracts yielded 2-CEES and 2-chloroethyl ethyl sulfoxide. The sulfone oxidation product was not detected. It was concluded that the polarity of the sulfur–oxygen dative bond must be interacting with the Nomex[®]; thus, the material has a high affinity for the oxidation product. The concentration of the sulfoxide could not be quantitatively ascertained due to the lack of a pure reagent for standardization. The presence of the sulfoxide on the fabric is reasonable to explain the 43.6% difference (60.6–17.0%) of 2-CEES from the chlorinated material to the untreated, unchlorinated control.

Table 1 Summary of 1.0-g/m² 2-CEES challenge against *N*-chloramide treated Nomex[®] and control materials at 90% RH and 25 °C

Material	Average 2-CEES percent recovery for a 1.0-g/m ² challenge (%)
Aluminum foil	83.6
Untreated unchlorinated Nomex [®]	60.6
Hydantoin-treated chlorinated Nomex [®]	17.0

A follow-up study was conducted to measure reaction stoichiometry of the chloramide with 2-CEES. The BA-1-treated, chlorinated Nomex[®] was tested in triplicate against challenges of 0.5, 1.0, and 1.5 g/m². To minimize unwanted diffusive effects caused by capillary action and to increase the percent recovery, the test materials were trimmed to the exact inner diameter of the test cell (38 mm). The stoichiometric challenges were averaged, and plotted as a function of concentration. The plot confirms linearity of the varying challenges with a coefficient of determination of 0.986. The fabrics were tested at the target level of 1.0 g/m², and then at ratios of 1:2 and 3:2, giving additional challenges of 0.5 and 1.5 g/m², respectively (Fig. 8). The initial data indicate that the chloramides oxidized 2-CEES at a 1:1 mol ratio; however, further testing needs to be conducted to determine how this trend evolves as the chlorinated material approaches exhaustion.

The data set used to determine the stoichiometric relationship between 2-CEES and the *N*-chloramides was also used in a kinetic analysis for the rate of decay of 2-CEES (Fig. 9). Experimental results revealed the reaction to be first-order overall and first order in the chloramide, validated by the linearity of a plot of ln[2-CEES] versus time. The rate law for the chloramide reaction with 2-CEES is given by the expression $v = k[\text{NCl}]$ where [NCl] represents the molar concentration of the chloramide, k is the rate constant at 25 °C in reciprocal seconds, and v is the rate of reaction in mol L⁻¹ s⁻¹.

Demeton-S

Extraction of the BA-1-treated, unchlorinated control sample yielded 85% recovery of the Demeton-S challenge, with no observable products of oxidation or hydrolysis. Extraction of the BA-1-treated, chlorinated test samples yielded significant amounts of *S*-(2-ethylsulfinyl)ethyl

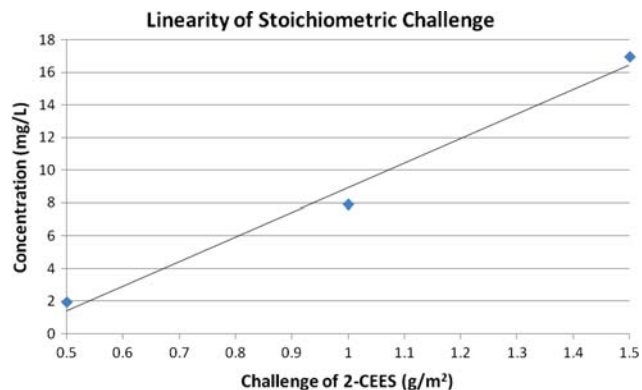


Fig. 8 Demonstration of linearity of the stoichiometric challenge; $R^2 = 0.986$

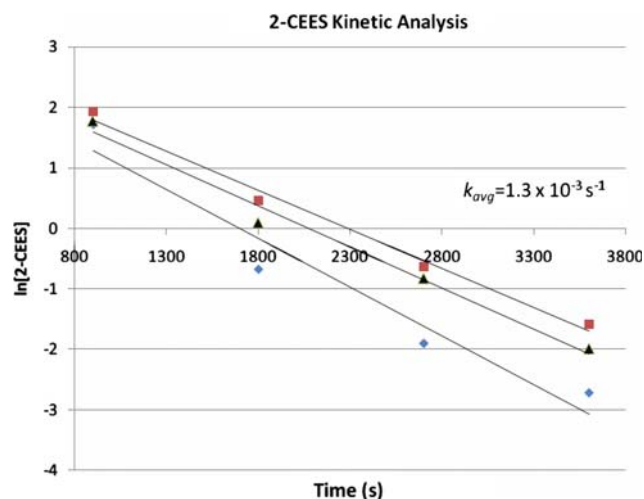


Fig. 9 Analysis of the decay rates of 2-CEES. The natural logarithm of the simulant concentration is plotted against time giving a linear plot, which is indicative of first-order kinetics

O,O-diethyl phosphorothioate, a common oxidative decomposition product from Demeton-S. The average loss of Demeton-S for these samples was >90%, and in several cases, neutralization of up to 98% of a 1.0-g/m² challenge of Demeton-S was observed at room temperature after as little as 30 min (Table 2). The oxidative breakdown product of the simulant was also observed in the extracted aliquot analyzed by GC-MS. The ion at m/z 196 and subsequent fragments clearly identify the vinyl thioester (Fig. 6b).

From the data in Table 2, it is clear that the degradation of Demeton-S occurred well within 30 min of contact with the chloramides. No significant difference in the performance of the reactive material was observed at a higher temperature (35 °C). Allowing longer times for deactivation of Demeton-S also had no observable effect, suggesting that degradation of the simulant occurs rapidly once introduced. Due to inherent delays of analysis by GC-MS, the FTIR method for Demeton-S breakdown was

Table 2 Summary of the average percent reduction of a 1.0-g/m² Demeton-S challenge on laminate as determined by GC-MS

Experimental conditions	Reduction of challenge on unchlorinated Nomex [®] (%)	Reduction of challenge on BA-1 treated chlorinated Nomex [®] (%)
30 min, 22 °C	1.0	98.1
60 min, 22 °C	24.1	97.8
120 min, 22 °C	10.4	97.9
30 min, 35 °C	17.4	74.2
60 min, 35 °C	19.7	98.3
120 min, 35 °C	27.4	86.0

developed. The GC-MS data confirmed that the amount of chlorine on the fabrics is sufficient to neutralize the 1.0-g/m² challenge.

As can be seen from the FTIR spectra of Demeton-S (Figs. 10 and 11), the vinyl oxidation product begins to form within 1 min of the challenge application. The 90% reduction in Demeton-S observed by GC-MS cannot yet be directly correlated with formation of the vinyl product. The decrease in the IR peak at 3,600 cm⁻¹ (Fig. 11) may be an indication that the proposed sulfoxide intermediate

(Fig. 6b) is undergoing subsequent reactions. Because the transition state of the VX analog should be the more stable of the two intermediates, this has no relevance to actual agent decontamination. The continued growth of the peaks at 1,010 and 1,220 cm⁻¹ suggests that further oxidation may be taking place.

Sample FTIR spectra of Demeton-S on the reactive material, and its conversion into the vinyl oxidation product are shown below. Establishment of the C=C stretching peak near 1,630 cm⁻¹ is crucial to identifying the

Fig. 10 FTIR spectra of Demeton-S on *N*-chloramide treated Nomex[®] during the first minute of reaction. The blue spectrum was obtained immediately after the challenge was deposited onto the test material ($t = 0.026$ min), the purple spectrum at 0.291 min, and the red spectrum at 1.007 min

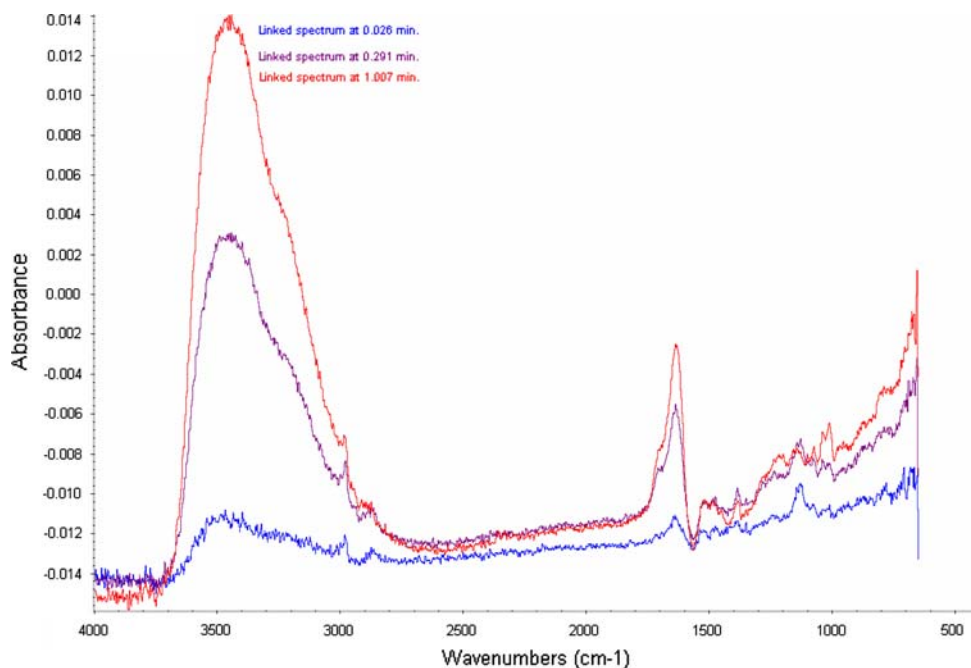


Fig. 11 FTIR spectra of Demeton-S challenge on *N*-chloramide treated Nomex[®]. The blue spectrum was obtained at 5.0 min, the purple spectrum at 10.0 min, and the red spectrum at 20.0 min

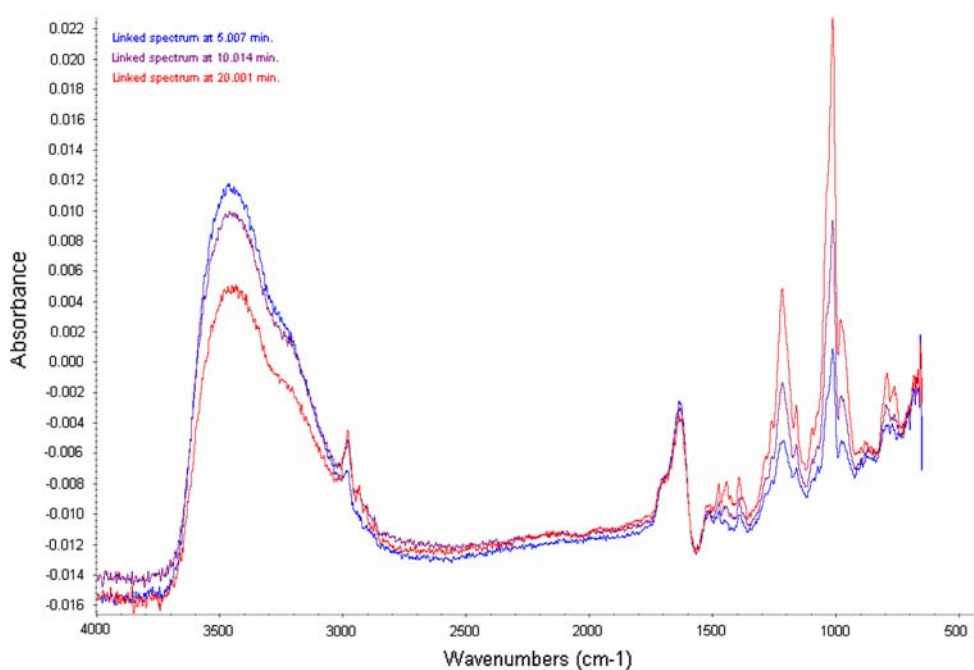


Table 3 Characteristic peaks in the IR spectrum of the Demeton-S vinyl oxidation product

Wavenumber range (cm ⁻¹)	Vibration
3,600–3,300	Other alcohol/thiol product
3,050–2,900	H ₂ C–CH ₃ stretch
1,635–1,625	C=C stretch
1,220–1,215	C–O stretch
1,030–1,010	Phosphate stretch

breakdown product. Table 3 summarizes the characteristic peaks of these spectra.

Little to no change in IR absorbance was observed in the BA-1-treated, unchlorinated control samples, as shown in the Gram–Schmidt plot below (Fig. 12). BA-1-treated, chlorinated samples showed significant changes in IR absorbance. The Gram–Schmidt plot for the chlorinated fabrics indicates that the greatest absorbance change occurs within the first minute of the challenge application (Fig. 13).

Due to the speed of the reaction, kinetic data were taken from the FTIR experiments since that method was more conducive to acquisition in real time than GC-MS. Experimental results revealed the reaction with Demeton-S to be first-order overall, confirmed by linearity of the natural logarithm of the vinyl thioester product's

concentration versus time (Fig. 14). The rate constant for this reaction was roughly the same as that of the rate constant for the neutralization of 2-CEES, which was somewhat unexpected since much of the Demeton-S was consumed within the first minutes of the reaction.

Correlation to Chlorine Content

All simulant testing was carried out on untreated Nomex[®], BA-1-treated, unchlorinated Nomex[®], and BA-1-treated, chlorinated Nomex[®] in triplicate. The untreated and the treated, chlorinated samples were assayed for chlorine content by iodometric back titration [10, 11]. Treated, unchlorinated materials were not titrated. Table 4 below summarizes titration data for these samples.

The BA-1-treated, chlorinated samples from this set of titrations contained an average of 10.2 mmol Cl/m² corresponding to a concentration of approximately 4370 ppm of chlorine. Samples tested against 2-CEES and then extracted in acetonitrile were also titrated to quantify the remaining chloramide concentration. After the complete destruction of 1.0 g/m² of 2-CEES, the treated, chlorinated materials still contained an average of 3.3 mmol Cl/m². This signifies that the 2-CEES was completely consumed in the reaction without exhausting the total chlorine contained within the sample, and suggests a favorable stoichiometry for the material's intended purpose.

Fig. 12 Gram–Schmidt plot of 1.0-g/m² Demeton-S on unchlorinated, BA-1 treated Nomex[®]

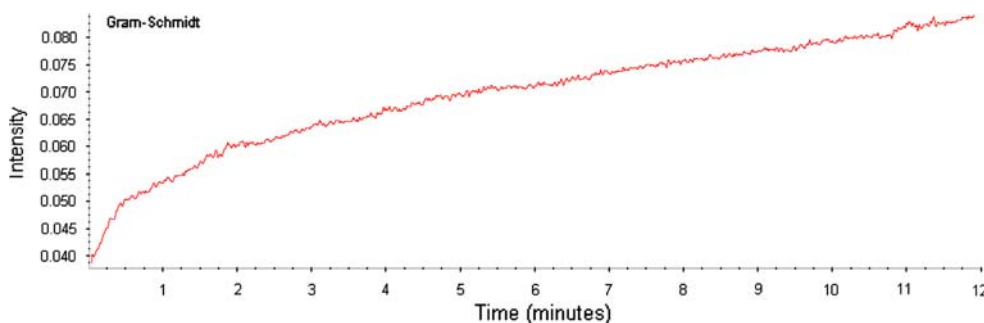
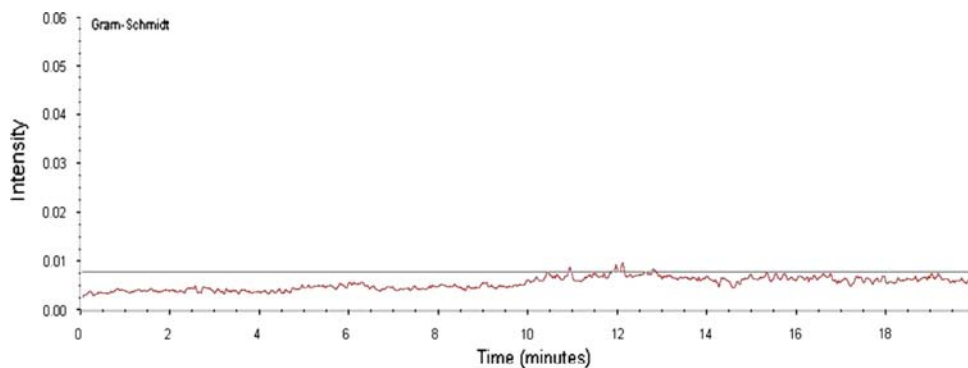


Fig. 13 Gram–Schmidt plot of Demeton-S on BA-1 treated, chlorinated Nomex[®] reveals a significant absorbance increase during the first minutes after application. The changes in the IR spectra confirm

the presence of the vinyl oxidation product detected by GC-MS, and yield information about the kinetic regime for the formation of this by-product

Fig. 14 Rate of formation of vinyl thioester from Demeton-S at 20 °C

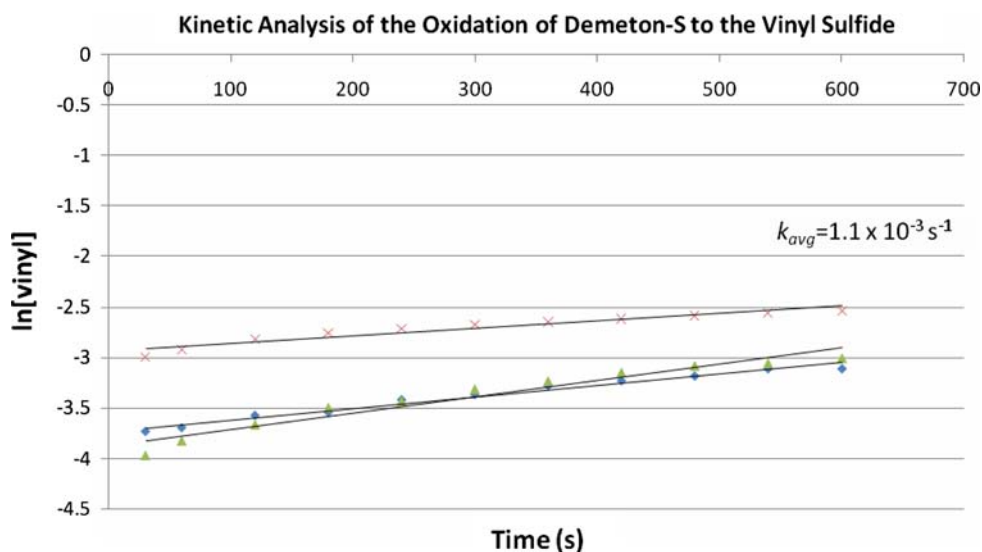


Table 4 Chlorine content of laminates before and after exposure to 1.0-g/m² 2-CEES

Sample type	Before reaction with 2-CEES (mmol Cl/m ²)	After reaction with 2-CEES (mmol Cl/m ²)
BA-1 treated chlorinated	12.0	3.2
BA-1 treated chlorinated	8.3	3.4
Untreated	0.0	0.0, 0.1

Sun and Sun were able to show that Nomex[®] itself can be chlorinated by hypochlorite while conserving the polymer's functional properties. In addition the chlorinated Nomex[®] demonstrated efficacy against both Gram-positive and Gram-negative strains of bacteria [8]. In order to dispel any doubts about the usefulness of BA-1 as a chlorine scavenger, a chlorination study was carried out by chlorinating both Nomex[®] and BA-1 treated Nomex[®]. The results of the study can be seen in Table 5. The data reveal that the attachment of BA-1 prior to chlorination dramatically increases the material's capacity for chlorine compared to that of Nomex[®] alone.

Table 5 Chlorine content of Nomex[®] with and without BA-1

Sample type	Average mmol Cl/m ² material	Average ppm Cl
Chlorinated Nomex [®]	0.2	100
BA-1 treated chlorinated Nomex [®]	7.5	3200

Data in this table was taken from a separate study, and does not directly pertain to CWA simulant testing reported in this communication

Conclusions

To evaluate *N*-chloramide-treated Nomex[®] for performance against chemical weapons, the material was tested against 2-CEES and Demeton-S. A G-agent simulant was not selected because chloramides are known to be completely ineffective against these compounds, and since G-agents are nonpersistent the need for decontamination is not as critical. Reactions with 2-CEES were carried out in a temperature- and RH-controlled reaction cell. The cell was held at ~25 °C and 90% RH. Within 30 min, the materials neutralized 2-CEES via the formation of the sulfoxide. The toxic sulfone product was not detected.

A stoichiometric challenge was conducted to determine the ratio at which the chloramide reacts with 2-CEES. The ratio was found to be 1:1; however, this information is of secondary importance to that of the challenge versus the chlorine load. For a 1.0-g/m² challenge, an average concentration of 10.2 mmol Cl/m² was sufficient to neutralize the HD simulant and still leave ~3.3 mmol Cl/m². The stoichiometric data set was also used to determine the rate constant of the reaction at $T = 25$ °C ($k_{avg} = 1.3 \times 10^{-3} \text{ s}^{-1}$).

Testing the treated Nomex[®] against Demeton-S showed equally impressive results. Originally 90% of a 1.0-g/m² challenge was degraded in the first minutes after exposure to the chloramide-treated fabric. The materials tested most recently revealed an average rate constant of $1.1 \times 10^{-3} \text{ s}^{-1}$ at $T = 20$ °C. The primary oxidation product is not the extremely toxic EA 2192 analog, but a vinyl product formed from oxidation of the terminal thioether sulfur and subsequent rearrangement. The vinyl product formed still possesses certain structural requirements of nerve agents; however, its toxicity is unknown. The product is expected to be less persistent and also less

stable in the body. While it is undoubtedly less toxic than Demeton-S itself, further studies need to be conducted to determine if this derivative presents any hazards to humans.

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