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14. ABSTRACT

Report developed under Topic #CBD13-101, contract W911NF-13-P-0010.
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100% Solids Polyurethane Sequestration Coating

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The purpose of this project is to develop a multifunctional coating that can be sprayed on a contaminated surface to sequester chemical agents, disclose the location of contamination, detoxify the agent, and be removable to enable further clean-up and recovery. Akita Innovations and FLIR Systems teamed to develop and test a two component, 100% solids coating that will absorb, sequester and detoxify chemical agent surrogates. Test results showed that the developed coating absorbed the chemical agent surrogate paraoxon at a surface loading of 10g/sqm and effectively sequestered the surrogate as there was no observed surrogate agent breakthrough at the surface of the coating at times up to 100 hours. The coating systems developed in this project will have potential application for the mitigation of the threat associated with chemical agent contaminated surfaces and for their remediation and decontamination.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

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TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

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(d) Manuscripts

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Number of Manuscripts:

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none

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Names of Post Doctorates

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Total Number:	

Names of Faculty Supported

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Names of personnel receiving PHDs

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Total Number:

Names of other research staff

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Total Number:	

Sub Contractors (DD882)

1 a. FLIR Systems, Agentase

1 b. 2240 William Pitt Way

Pittsburgh, PA PA 15238

Sub Contractor Numbers (c):

Patent Clause Number (d-1):

Patent Date (d-2):

Work Description (e): enzyme developmenttest and evaluation of coatings

Sub Contract Award Date (f-1): 5/29/13 12:00AM

Sub Contract Est Completion Date(f-2): 11/29/13 12:00AM

Inventions (DD882)

Scientific Progress

Technology Transfer

Akita
INNOVATIONS

267 Boston Road
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Final Technical Report

Contract #: W911NF-13-P-0010

Proposal #: 63958CHSB1

Project: 100% Solids Polyurethane Sequestration Coating

Contractor: Akita Innovations LLC
267 Boston Road, Suite 11
Billerica, MA 01862

Performance Period: 29 May, 2013 to 28 March, 2014

Contract Amount: $100,000

Amount of funds paid By DFAS to date: $83,371.44

Total amount Invoiced to date: $83,371.44

Number of Employees: 3

Number of Employees Placed on Contract This month: 2

Technical POC: Dr. Lawrence Hancock
617-448-1588
lawrence.hancock@akitainnovations.com

Submitted: April 10, 2014

Table of Contents

Executive Summary and Key Conclusions

Akita Innovations LLC and FLIR Agentase teamed in this project to develop a multifunctional coating that can be sprayed on a contaminated surface to sequester chemical agents, disclose the location of contamination, detoxify the agent, and be removable to enable further clean-up and recovery.

Key accomplishments of this project are:

- Two component, 100% solids thiol-ene coating formulations (Akita-01 and Akita-02) that possess rapid and controllable cure rates and which are suitable for spay application have been defined.
- The cohesive strength of Akita-01 and Akita-02 coatings allows the coatings to be peeled from polyethylene and glass substrates.
- Thiol-ene coating formulations are compatible with nanoparticle adsorbents and platelet shaped materials which can be used to modify absorption and permeation in the coatings.
- Thiol-ene coating formulations and cure chemistry are compatible with organophosphorous hydrolase (OPH) enzyme in that enzyme turnover of paraoxon chemical agent surrogate is retained in enzyme containing coatings.
- Both Akita-01 and Akita-02 formulations show excellent absorptivity of the chemical agent surrogates paraoxon, 2-chloroethylethylsulfide and diisopropylfluorophosphate.
- Tests of Akita-02 coatings with 10g/m^2 loading of paraoxon show no residual agent surrogate on an aluminum substrate nor any breakthrough of agent surrogate through the coating after 100 hours.
- Tests of Akita-02 coatings with 10g/m^2 loading of 2-chloroethylethylsulfide and diisopropylfluorophosphate show no residual agent surrogate on an aluminum substrate nor breakthrough of agent surrogate after 30 minutes.

Project Objectives

The Project Objectives of this Phase I effort were to:

- Develop and demonstrate a peelable sequestration coating material and application method capable of encasing, entraining and neutralizing chemical agent contamination on a surface, and to
- Define and execute an experimental plan to demonstrate sequestration coating performance with 3 chemical agent simulants.

Project Period

29, May 2013 through 28 March, 2014.

Project Tasks and Schedule

The Project Tasks, Milestones and work schedule are shown below.

PHASE I Project Schedule	Base Period						Option		
Month	1	2	3	4	5	6	7	8	9
(1) Define coating materials and application methods	🟥	🟥	🟥						
(2) Select absorbents and glass flake materials and demonstrate incorporation in the coating system		🟥	🟥	🟥					
(3) Define enzymes and mechanism for their incorporation in the coating system.	🟥	🟥	🟥						
(4) Select chemical hydrolytic materials and demonstrate incorporation of enzymes and chemical hydrolytic materials in the coating system		🟥	🟥	🟥					
(5) Define sequestration coating formulation and demonstrate performance with 3 chemical agent simulants			🟥	🟥	🟥	🟥			
(6) Option - Extend performance evaluation of sequestration coating.							🟥	🟥	🟥
(7) Option - Identify surety lab for live agent testing and develop test plan.								🟥	🟥
Major Events									
Kickoff Teleconference	🟥								
Define Seqeustration Coating Formulation for Test			🟥						
Report on Sequestration Coating and Performance						🟥			
Final Report and Phase 2 Plan									🟥

Major Events

Kickoff Teleconference

The project kickoff teleconference was conducted on June 18, 2013. Representing Akita Innovations were, Larry Hancock, Larry Takiff and Dick Minns. Representing ARO were Dr. Jennifer Becker and Ms. Wendy Mills. Representing DTRA were Dr. Charles Bass and Mr. Phillips.

Interim Progress Review

Akita Innovations participated in an Interim Progress Review with Dr. Jennifer Becker and Dr. Revell Phillips via teleconference on September 16, 2013.

Submission of Phase 2 Proposal

Akita Innovations prepared and submitted the Phase 2 proposal on October 31, 2013.

Research Performed and Results by Task

Task 1: Define Coating Materials and Application Methods.

<u>Summary of Task 1 Results</u>: Akita has completed its Phase 1 evaluation of coating materials and applications methods and identified certain thiol-ene formulations for coating development and metered-mixing airless spray systems for wide area application of coatings. Viscosity of pre-polymerized coating monomers and their cure rate are critical drivers for formulation development. Low viscosity is needed so that formulations can accommodate relatively high concentrations of high aspect ratio flake materials which are needed to improve barrier performance yet still be amenable to spray application. High cure rates are needed to ensure sequestration of chemical agents before they permeate through the freshly applied coating. Commercial availability, cost and low toxicity are also attractive attributes of thiol-ene systems.

Spray Application Systems

Early in our Phase I program we reviewed spray application systems in order to better define materials specifications for our two component, 100% solids coating formulation. Formulation viscosity and the particle size of additives in the formulation are critical for the development of a coating formulation for spray application. Most spray application systems are simply atomizers, with the main difference between them being how the liquid is transferred to the spray head. Transfer is often done by siphon, however this method is not compatible with high viscosity coating systems and is a poor choice for our development work. Alternatively, transfer may be done with a pressure-feed which is compatible with relatively viscous formulations. In pressure fed systems, the fluid is forced thru an orifice at the spray head either by pressurized air or by hydraulic pressure ('airless systems', see **Figure 1A**). The tip size of the spray head determines both the spray pattern and what range of fluid viscosities and particulate size can be used. For two-component coatings, there are two options: either pre-mixing the components and then immediately spraying the mixture with a single component sprayer ('hot-potting'); or 'metered-mixing' in which a sprayer with two reservoirs, two pumps and a proportioning pump are used and the two reactive components of the coating are mixed in the sprayer head. These units are more expensive but are used extensively for polyurethanes, epoxies, and high solids coatings. For the type of coatings investigated in this project, a metered-mixing airless spray system such as the Graco XP-70 is a good choice (**Figure 1B**). Similar units are sold by Binks, through their Devilviss subsidiary. One advantage of airless systems is that they do not require a large, separate air compressor, so they can be made fairly mobile.

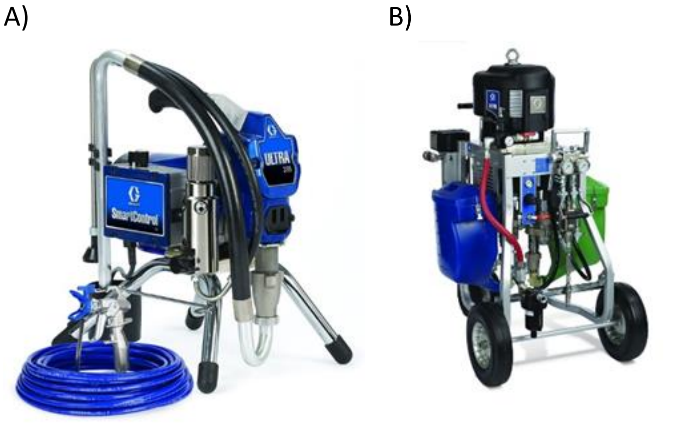
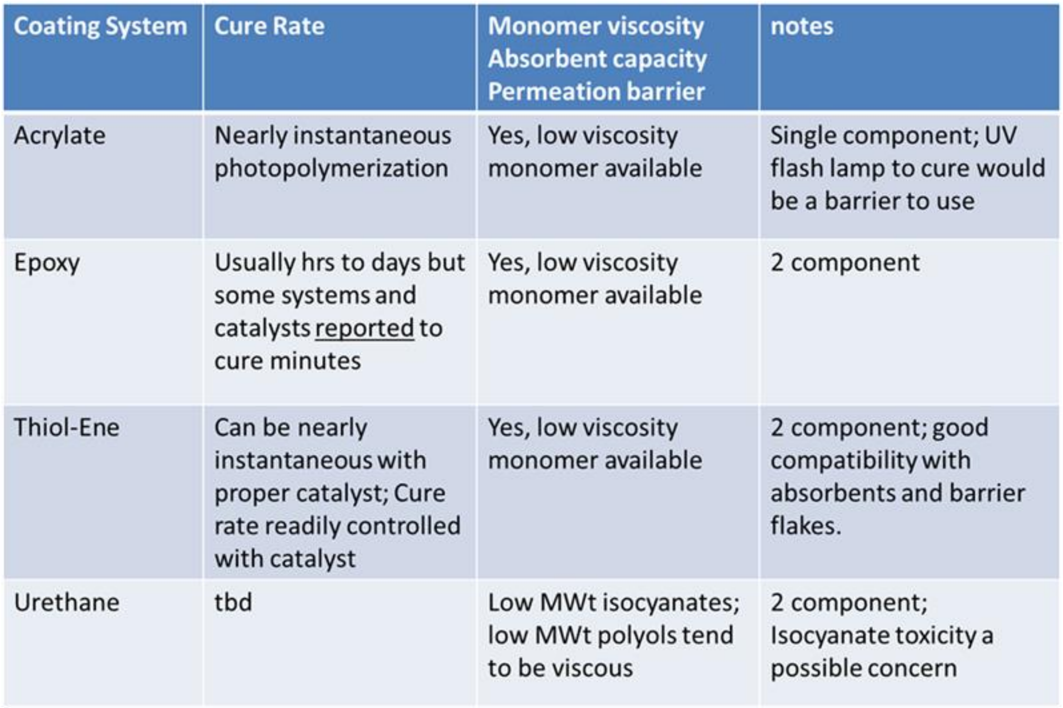


Figure 1: (A) Graco Ultra 395 single component airless sprayer, (B) Graco XP-70 Plural Component Sprayer

Coating Polymerization System

Early in the Phase I project we determined that it would be prudent to evaluate candidate polymerization systems more broadly than simply focusing exclusively on polyurethanes. The principal criteria used in our evaluation were the availability of low viscosity monomers and their cure rate. Low viscosity is needed so that the formulation can accommodate relatively high concentrations of high aspect ratio flake materials which are needed to improve barrier performance and other adsorbents and hydrolytic materials. High cure rates are needed to ensure sequestration of chemical agents before they permeate through the freshly applied coating. The review was also limited to 2 component, 100% solids material systems. Single component, spray application materials usually comprised of a solvated polymer or a polymer latex and a low viscosity solvent were ruled out as previous efforts suggested that migration and evaporation of the solvent aids in release of chemical agent into the air. Four material systems were reviewed and conclusions are summarized in **Table 1** and discussed below.

Table 1: Summary of coating material evaluation.



Coating System	Cure Rate	Monomer viscosity Absorbent capacity Permeation barrier	notes
Acrylate	Nearly instantaneous photopolymerization	Yes, low viscosity monomer available	Single component; UV flash lamp to cure would be a barrier to use
Epoxy	Usually hrs to days but some systems and catalysts reported to cure minutes	Yes, low viscosity monomer available	2 component
Thiol-Ene	Can be nearly instantaneous with proper catalyst; Cure rate readily controlled with catalyst	Yes, low viscosity monomer available	2 component; good compatibility with absorbents and barrier flakes.
Urethane	tbd	Low MWt isocyanates; low MWt polyols tend to be viscous	2 component; Isocyanate toxicity a possible concern

Photopolymerizable acrylate systems were considered as they can be polymerized nearly instantaneously and there are wide variety of low viscosity monomers available commercially. However these systems were ruled out as they would require coating application equipment to be outfitted with an UV illuminator to effect cure, which is not desirable.

Epoxy coating systems were also evaluated as a wide variety of monomers and coating systems are available commercially. Low viscosity monomers have been identified and early experiments showed these to be compatible with glass and aluminum flakes. However, the best achieved cure rates were on the order of hours, which is not acceptable for the present application.

Thiol-ene systems employ the base catalyzed Michael addition of thiols to activated double bonds such as acrylates as mentioned earlier. A good variety of a low viscosity difunctional, trifunctional and multifunctional thiol and acrylate monomers are commercially available at commodity pricing. We have demonstrated cure rates that are exceptionally rapid, minutes or less, using organic amines as catalysts. Furthermore we have demonstrated that the cure rate can be easily controlled through a combination of amine catalyst basicity and concentration. These characteristics make thiol-ene systems quite attractive.

Urethanes systems are also available commercially and low viscosity monomers are available. Reports indicate that very fast cure rates can be attained. However, volatile low molecular weight diisocyanates which would be used in such a system are quite toxic. The toxicity of these materials would create an additional burden at the point of application and also severely affect the handling, storage, transportation and training with a coating system comprised of these materials. For this reason we elected not to pursue urethane systems.

Description of Thiol-Ene Coating Formulation Selected for Development

Based on the Task 1 investigations described above, we chose to evaluate the absorption and permeation of chemical agent surrogates for various thiol-ene coating formulations. Thiol-ene polycondensation systems employ the addition of a thiol, R-SH, across a double or triple bond by either a free radical or an ionic mechanism, **Figure 2**. The reactions are efficient, high yielding, and tolerant of various solvents and functional groups. These characteristics make thiol-ene polycondensation chemistry ideal for a coating system which must tolerate the absorption of reactive chemical agents at relatively high loading.

Figure 2: Thiol-ene reaction, condensation of a thiol and an activated olefin.

Figure 3 shows the base components of two preliminary coating systems which were chosen for evaluation of absorption and permeation tests with various chemical agent surrogates. All formulation components are commercially available in bulk at commodity pricing. An important feature or this chemistry is that the polymerization cure rate is rapid and is easily controlled by the concentration and basicity of the amine catalyst (aminoethylpiperizine, AEP), **Table 2**. At high catalyst concentrations cure is nearly instantaneous. Lower concentrations provide slower cures that will allow for spray application and dissolution of the chemical agent contaminant into freshly applied coating.

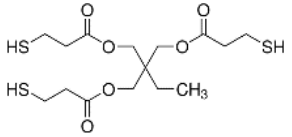
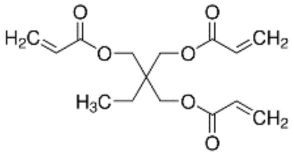
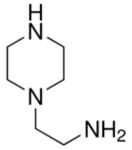
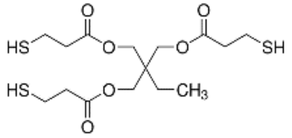
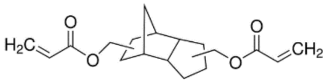
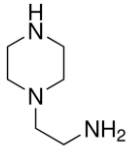
	Thiol	**Acrylate**	**Catalyst**
Akita-01	 TMPMP -Trimethylolpropane tris(mercaptopropionate)	 TMPTA - Trimethylolpropane triacrylate	 AEP – Amino ethylpiperizine
Akita-02	 TMPMP - Trimethylolpropane tris(mercaptopropionate)	 TCDDA - Tricyclo[5.2.1.0^{2,6}]decanedimethanol diacrylate	 AEP – Amino ethylpiperizine

Figure 3: Thiol-ene coating formulations selected for development.

Table 2: Cure rate as a function of catalyst for thiol-ene formulation Akita-01

Akita-01	Trithiol TMPMP	Triacrylate TMPTA	Catalyst AEP	Cure time
	1.00g	0.75g	5mg (0.3 wt%)	10 minutes - viscous liquid; 20 min – soft gel; 1 hr – clear elastomer
	1.01g	0.76g	12.3mg (0.7 wt%)	Viscous liquid in seconds; poured and pressed with a glass plate and cured to an elastomeric film in 12 min
	1.01g	0.77g	19.4mg (1.1 wt%)	10 to 30 seconds; exotherm, rapid gelation and cure to an elastomeric 'coin'

Laboratory evaluations also show that thiol-ene coatings have sufficient strength that they can be peeled or stripped from the substrate after they have been cured, **Figure 4**. At this point we have not concluded a complete study of the cohesive strength and adhesion of the chosen thiol-ene coatings. We have demonstrated that Akita-01 and Akita-02 formulations form elastomeric films with sufficient cohesive strength so that they can be peeled from a glass plate or polyethylene film. Cohesive strength of in this material system will be controlled by crosslink density and the molecular weight and chemical characteristics of the monomers. Crosslink density is controlled by fraction of multifunctional monomers. For example in formulation Akita-01 the selection of two tri-functional monomers yields a coating with a relatively high crosslink density. This provides good cohesive strength to the elastomeric coating even though the monomers themselves have a high degree of flexibility and would otherwise produce a relatively soft elastomer. Akita-02 uses a difunctional acrylate which reduces the crosslink density somewhat, however the relatively rigid tricyclodecane core of the acrylate adds strength to the elastomer. In fact, qualitatively the Akita-02 coatings were stronger than the Akita-01 coatings.

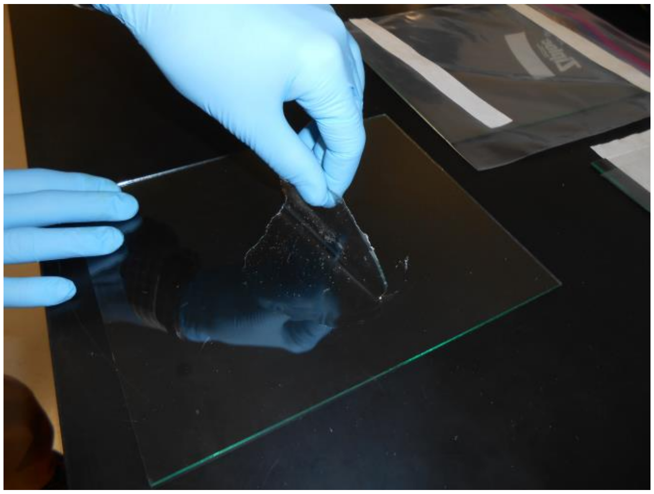


Figure 4: Thiol-ene coating Akita-02 being peeled from a glass plate.

An additional feature of the thiol-ene chemistry that we have studied is its compatibility with functional groups such as a combination of amines and alcohols that can chemically destroy chemical agents. For example, an effective decontamination formulation DS2 comprises an amine (diethylenetriamine, DETA, 70%), a primary alcohol (ethylene glycol monomethyl ether, EGME, 28%), and a basic accelerator (sodium hydroxide, NaOH, 2%). Since the alcoholysis of an agent such as sarin in the presence of an amine does not require NaOH, incorporation of amine and alcohol groups into our polymer films may be effective for decontamination. Amines are already present in our thiol-acrylate formulations to catalyze Michael addition polymerization, and tertiary amines in moderately high concentrations are compatible with acrylate esters as evidenced by the stability and commercial availability of 2-(dimethylamino) ethylacrylate. A particularly straightforward means of incorporating both amine and alcohol groups into acrylates is to mix diethanolamine (DEA) into a multifunctional acrylate such that sufficient acrylate groups remain for thiol-ene polymerization. The DEA adds to acrylate groups by Michael addition, thereby providing pendant arms that contain both tertiary amine groups and primary unhindered alcohol groups. Reaction of those alcohol groups with chemicals will both bind them to the polymer matrix and deactivate them. Alcoholysis of VX also avoids the formation of the toxic thionic acid species (EA 2192).

Absorption of chemical agent into the coatings both before and after cure of the coating is critical to performance of the coating system. Absorption after cure reflects the coating's ability to entrain and sequester chemical agent in the coating. Absorption before cure establishes the ability of the coating to cure in the presence of the chemical agent. In this work, dimethylmethylphosphonate (DMMP) was used as a surrogate to evaluate sorption of chemical agent into the coating system. This has been conducted in 2 ways; sorption of a DMMP droplet on a pre-formed coating and direct application of the coating mixture onto a beaded drop of liquid DMMP on a glass substrate. **Figure 5(A)** shows a photograph of a thiol-ene coating which had been spotted with a drop of DMMP with Nile Red dissolved in it for visualization. Gravimetric analysis of the coating sections showed that DMMP adsorption is relatively slow (hours to days) into the fully cured coating. Direct application of the coating formulation before it is fully cured onto the DMMP solution shows that DMMP readily dissolves in the formulation mixture yet does not inhibit curing of the mixture, **Figure 5(B)**. Once cured, the DMMP drop is incorporated into the coating material. From these results we conclude that the bulk of entrainment of the liquid agent is exceptionally efficient prior to final curing of the coating. This observation emphasizes how important it will be to control the cure rate of the coating and therefore the advantage that thiol-ene formulations have in that the cure rate can be easily controlled by the choice of catalyst and its concentration.

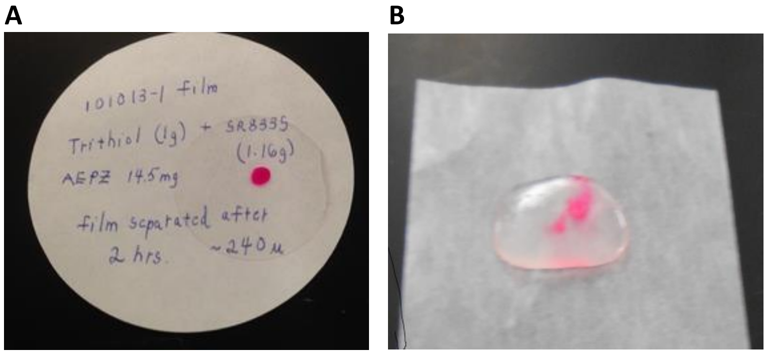


Figure 5: (A) Section of thiol-ene coating after sorption of DMMP/Nile Red droplet; (B) Thiol-ene mixture applied directly to DMMP/Nile Red droplet and then cured.

Task 2: Select Adsorbents and Glass Flake Materials and Demonstrate Incorporation in the Coating System

Summary of Task 2 Results: Within Task 2, Akita reviewed commercially available high aspect ratio, 2D flake materials and evaluated their compatibility with thiol-ene formulations and selected high surface area adsorbents for evaluation in coating formulations. High aspect ratio flake materials are to be used as additives in the coating system to decrease permeation of agents and thereby reduce the contact hazard and vapor hazard associated with the chemical agent contamination. Similarly adsorbents will be used to increase the capacity of the coating to adsorb agents.

Flake and Platelet –Shaped Permeation Barriers

In our Phase I project we demonstrated the compatibility of thiol-ene formulations with high aspect ratio glass flake and aluminum flake. High aspect ratio, 2D flake materials will be used as additives in the coating system to decrease permeation of agents and thereby eliminate contact hazard and vapor hazard at the surface of the coating. Metallic aluminum flake pigments which exhibit 'leafing'effects, **Figure 6,** are of particular interest. These materials are used as effect pigments in various commercial coating systems, particularly in the automotive industry. **Figure 7** shows a section of an aluminum flake loaded thiol-ene coating peeled off of a glass plate after cure.

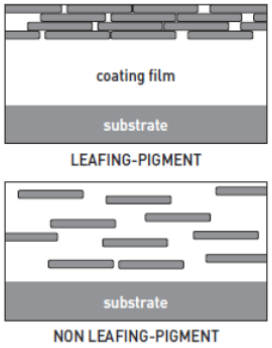


Figure 6: Leafing effect of metal flake pigments.

Figure 7: Thiol-ene coating incorporating aluminum flake

Adsorbents and Reactive Particles

Nanoparticulate $CaCO_3$ has also been identified as a chemically reactive material for the nucleophilic consumption of electrophilic chemical agents in particular phosphoryl fluoride agents since calcium reacts readily with fluoride to produce innocuous CaF_2. Calcium carbonate powder and flake are supplied commercially to the oil drilling industry. The incorporation of $CaCO_3$ nanoparticulate into thiol-ene coatings was demonstrated in our Phase I project.

Porous, nanoparticulate SiO_2 has also been identified and evaluated in coating systems. The effect of high capacity adsorbents on permeation through thin films is to delay breakthrough of permeant through the coating. It will however not decrease the equilibrium permeation rate through the coating. It is expected that delayed breakthrough through the coating will facilitate action of other hydrolytic enzymes and active nanoparticles to detoxify agents.

Task 3: Define Enzymes and Mechanism for their Incorporation in the Coating System

Summary of Task 3 Results: FLIR Agentase has identified Organophosphorus Acid Anhydrolase (OPAA) and Organophosphorous Hydrolase (OPH) for incorporation into the coating system. OPAA has been validated in our EBAD Decontaminant to be effective in catalytically destroying G-series nerve agents. Wild-type OPH has a less volatile substrate, paraoxon, which will be used as a physical simulant for breakthrough testing.

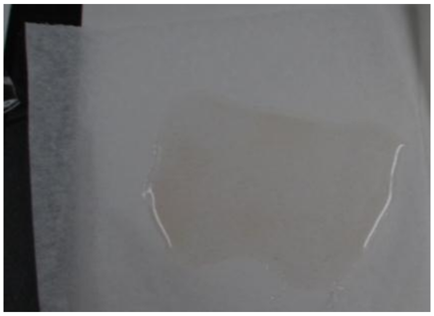


Figure 8: Cured thiol-ene coating incorporating OPH. Each coating section yielded 1.029 mg/mL of final OPH protein concentration

Organophosphorus Hydrolase (OPH) was incorporated directly into the thiol-ene coating formulation by direct addition after the formulation components were mixed to initiate cure. OPH was suspended in [50 mM] borate buffer pH 8.0. An aliquot of 2.68% (v/v) OPH was added to the coating formulation immediately after mixing of the formulation. The coating film was then spread utilizing a 50 mil drawdown applicator and allowed to cure for 2 hours and 30 minutes. **Figure 8** depicts results of OPH coating formulation. The thickness of the cured coating averaged 330 μm.

Task 4: Select chemical hydrolytic materials and demonstrate incorporation of enzymes and chemical hydrolytic materials in the coating system.

Summary of Task 4 Results: FLIR has identified a suitable enzyme system for incorporation into the coating and has provided the material as needed for formulation studies. Qualitative experiments show that enzyme can be dispersed in thiol-ene formulations and that the formulations cure into integral coatings.

A qualitative assessment of paraoxon turnover for validation of proof of concept was assessed by visualizing the evolution of p-nitrophenol in OPH containing Akita-02 thiol-ene coatings, **Figure 9**. Turnover of paraoxon by OPH yields p-nitrophenol (PNP) which is yellow in color. Intensity of the yellow color on exposure to paraoxon provides a qualitative assessment of enzyme reactivity. Since the films are to a large degree transparent, they represent an ideal media to visualize this catalytic mechanism. Briefly, three 10 g/m^2 droplets of neat paraoxon were spotted on an aluminum panel. Unlike previous experiments the paraoxon contained no oil red dye, which may obscure development of PNP. Three 5.0 cm^2 coating sections were immediately placed on top the paraoxon droplets. The coating compositions were as follows: a control thiol-ene coating containing no protein, a BSA thiol-ene coating containing, and an OPH thiol-ene

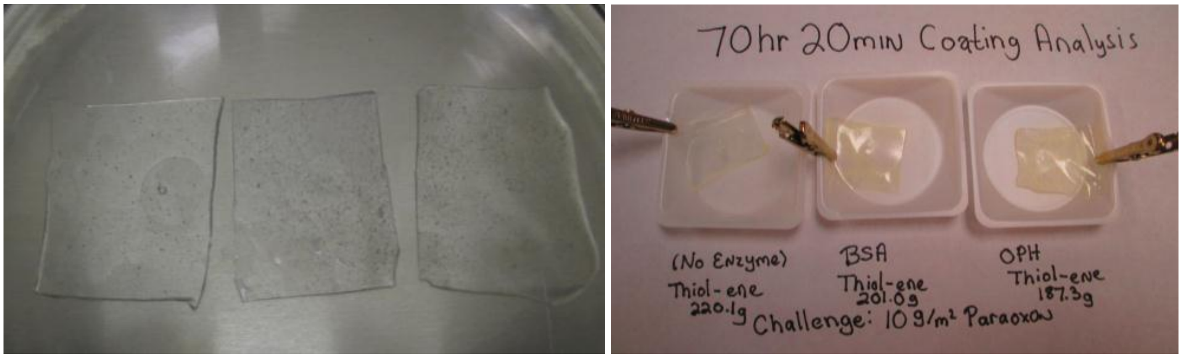


Figure 9: 10 g/m^2 Paraoxon Simulant Challenge. (A.) {Left} Control Thiol-ene coating, {Middle} BSA Thiol-ene coating, {Right} OPH Thiol-ene coating after addition onto Paraoxon droplet (B.) After a 70 hours and 20 minutes application dwell time, clear trends in PNP evolution are shown.

coating. The final protein content in each coating film segment was calculated to be 0.0016 mg for the BSA containing coating, and 0.0017 mg for the OPH containing coating. All coating formulations were Akita-02. Photographs in **Figure 9** show a clear trend of evolution of PNP due to catalytic hydrolysis for both the BSA and OPH samples as compared to the control sample. It should be noted that BSA contains mild esterase activity, much lower than paraoxon, but measurable, which hydrolyzes paraoxon into PNP, producing a yellow color. The OPH-containing sample demonstrates the deepest yellow coloration, indicating that enzymatic activity is well-maintained.

A more quantitative assessment of paraoxon turnover was determined by the development of a benchtop enzymatic assay for the OPH containing coating. Utilizing a UV/Vis spectrophotometer at λ405 nm, absorbance measurements were ascertained at 30 second intervals for 10 minutes. The coating sample sections (Akita-02) initially measured at 5.0 cm^2 were dissected into multiple pieces and kept under constant stirring to maximize diffusion. All reactors were 5.0 mL and containing pH 9.0 CHES buffer [100mM] and paraoxon [0.04 mM]. The reactors tested were as follows: 100 µL native OPH in Borate Buffer [50 mM], 100 µL Borate Buffer [50 mM], 5.0 cm^2 thiol-ene coating section containing no OPH, 5.0 cm^2 OPH thiol-ene coating section. **Figure 10** displays results of the enzymatic activity assay showing that OPH activity is retained in the thiol-ene coatings.

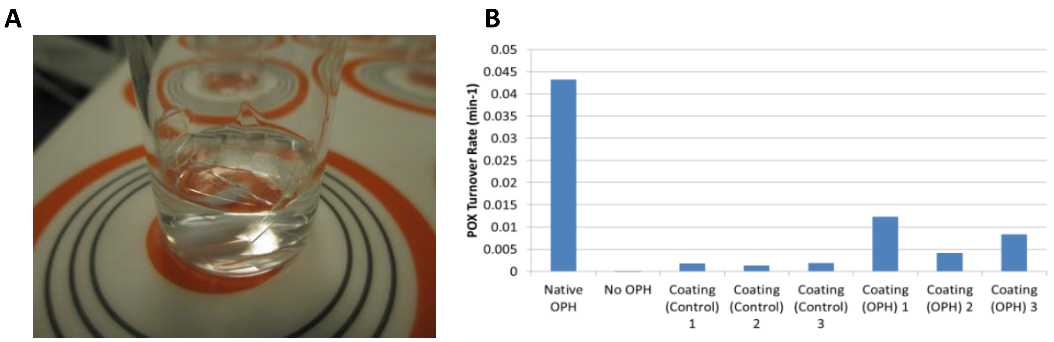


Figure 10: OPH Activity Assay Development **A** - Control Coating reactor containing buffer, control Akita-02 coating, and paraoxon under constant stirring. **B -** Paraoxon turnover rates of various components assayed. OPH containing Akita-02 thiol-ene coating clearly has retained hydrolytic activity as compared to the control which contained no OPH

Task 5: Define sequestration coating formulation and demonstrate performance with 3 chemical agent simulants.

Summary of Task 5 Results: Within Task 5 Akita Innovations and FLIR Agentase demonstrated the performance of 2 thiol-ene coating formulations with 3 chemical agent surrogates.
In earlier months we demonstrated:

- Tests of Akita-02 coatings with 10g/m^2 loading of paraoxon show no residual agent surrogate on an aluminum substrate nor any breakthrough of agent surrogate through the coating after 100 hours.

- Tests of Akita-02 coatings with 10g/m^2 loading of 2-chloroethylethylsulfide and diisopropylfluorophosphate show no residual agent surrogate on an aluminum substrate nor breakthrough of agent surrogate after 30 minutes.

In earlier Tasks we identified two component thiol-ene coating systems with relatively low viscosities and controllable cure rates that make them well suited for the development of 100% solids formulations for spray application. Furthermore, preliminary coating formulations have shown that they can absorb chemical agent surrogates and that they are compatible with various particulate and platelet additives which will be used to aid absorption and detoxification of chemical agents and to prevent breakthrough of the agent to the surface of the coating. The coatings are also sufficiently durable such that they can be peeled or stripped from the substrate on which they were coated. Within this Task, more detailed studies of the absorption and permeation of 3 chemical agent surrogates were conducted.

<u>Evaluation of Thiol-Ene Coating Absorption and Permeation with 3 Chemical Agent Surrogates</u>

Working with FLIR Agentase, we conducted an evaluation of the absorption and permeation of 3 chemical agent surrogates, 2-chloroethylphenylsulfide (2-CEPS), diisopropylphosphate (DFP), and paraoxon. The basic experimental design is shown schematically in **Figure 11**. The surrogate agent is placed on a substrate and a section of coating is then placed over it. A contact sampler (filter paper) is placed over the coating sample and then an impermeable piece of foil and a contact weight is placed on top. Replicate samples are periodically disassembled, extracted and analyzed by GC/MS to determine the mass of surrogate agent which migrates from the substrate surface into the coating and potentially through the coating to the contact sampler at its outer surface.

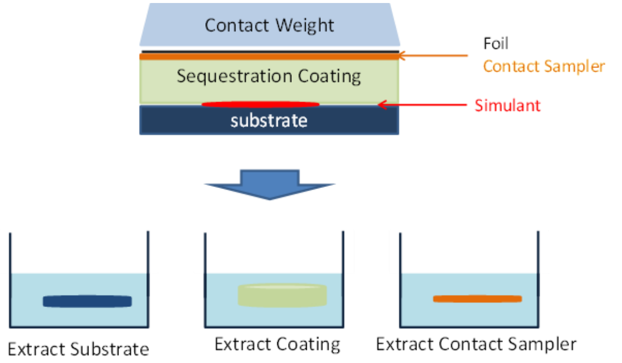


Figure 11: Contact sampling experimental test for evaluation of the absorption and permeation of chemical agent surrogates in sequestration coatings.

Figure 12 summarizes results for coating samples of the Akita-01 coating formulation. In these tests a 10 g/m^2 loading of the surrogate agent paraoxon was placed on an aluminum substrate. A section of pre-cured thiol-ene coating (Akita-01 formulation) was then placed over the agent and the contact sampler and weight placed on top of that. The assembly was taken apart and the surrogate recovered by extraction of the substrate, the coating and the contact sampler as described above at three timepoints; 5 min, 30 min and 4 hr. GC/MS analysis of the various extracts yielded 2 important conclusions. First, there is <u>no measurable breakthrough</u> of surrogate through the coating sample through the full course of the 4 hour experiment. (The recorded measure of paraoxon in each of the breakthrough samples is an artifact of the calibration curve as shown for the dichloromethane (DCM) control.) Second, entrainment of the agent surrogate from the aluminum substrate into the coating progresses steadily through the full course of the 4 hr experiment as the fraction of the recovered by extraction from the coating increases steadily through the course of the experiment, while residual surrogate recovered from the substrate decreases.

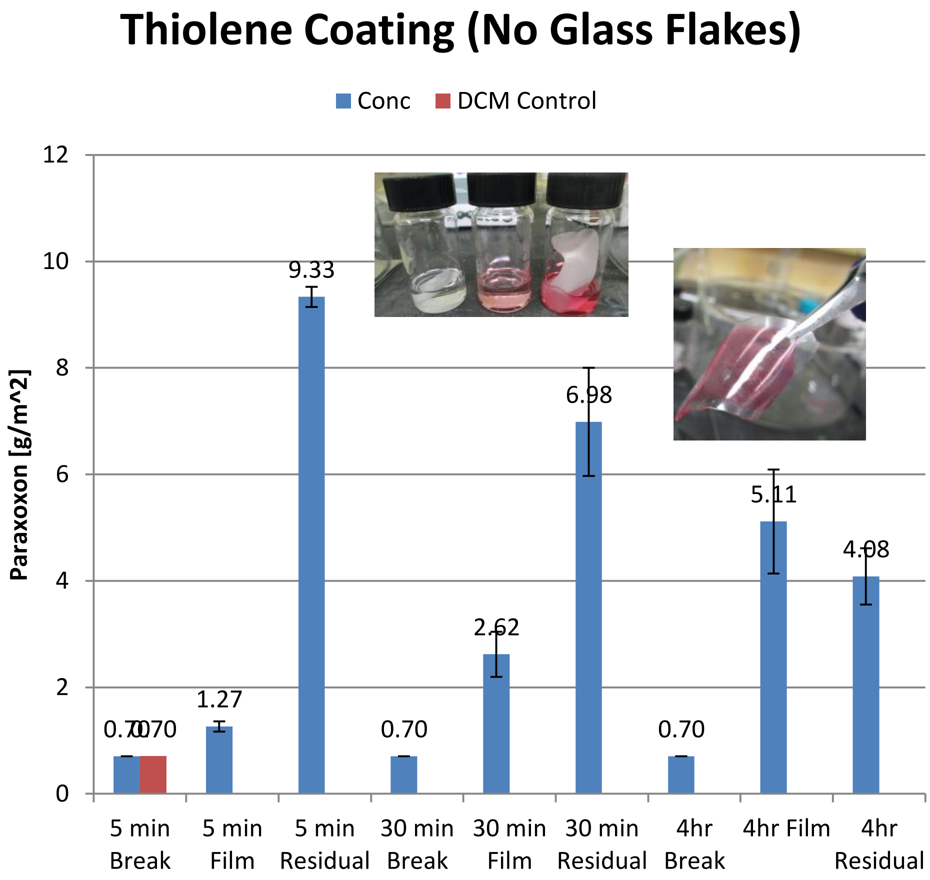


Figure 12: Test results of Akita-01 coatings for absorption and permeation of paraoxon. Paraoxon is dyed red for visualization and substrate loading is 10 g/m^2 in the tests. Inset photos show an example of extractions for a given sample and show the absorbed paraoxon in the Akita-01 coating.

Studies to define the effect of various coating additives were also conducted with paraoxon as the chemical agent surrogate. **Figure 13** shows results from a series of coatings (Akita-01) which are loaded with $CaCO_3$ nanoparticles (20nm), SiO_2 nanoparticles (20nm), and aluminum flakes. Again paraoxon surrogate was applied at 10g/m^2 to an aluminum substrate. For each tested coating, there was significant absorption of agent surrogate (paraoxon) after 30 minute but no observed breakthrough. Absorption ranged from 50% for the pure polymer coating to 90% for coatings loaded with Aluminum flake.

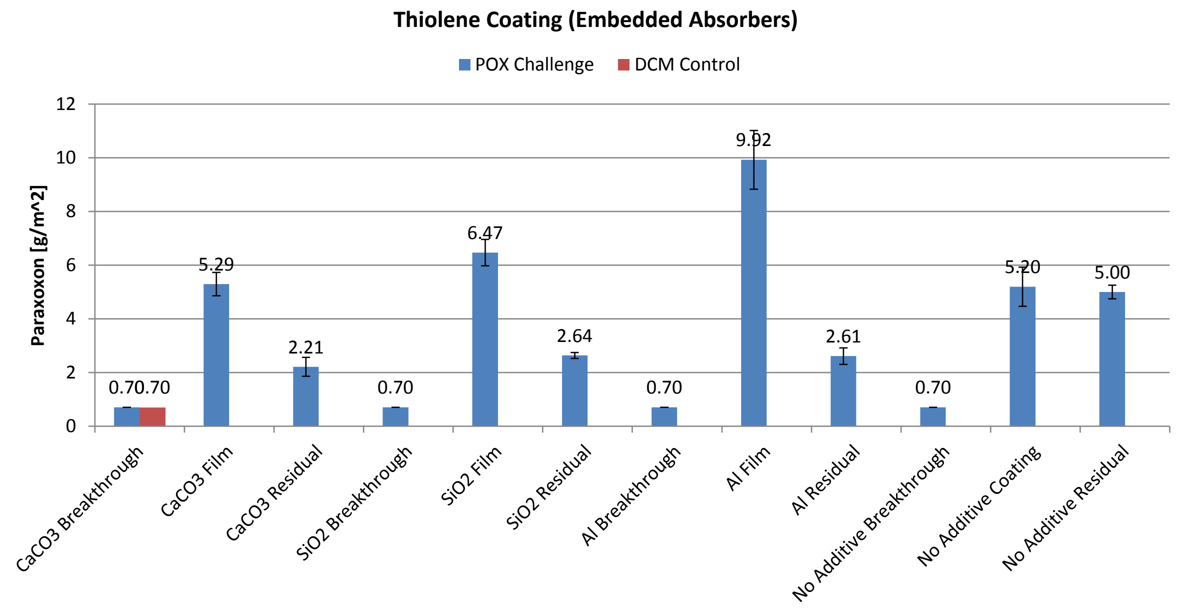


Figure 13: Test results of Akita-01 coatings loaded with varying additives; form left to right, 2 wt% $CaCO_3$ (20nm particles), 2 wt% SiO_2 (20nm particles), 1 wt% aluminum flake, and control coating. Paraoxon substrate loading 10 g/m^2. All samples were obtained at 30 min.

Further investigations evaluated the absorption and permeation of chemical agent surrogates for thiol-ene coating formulation Akita-02 (shown above in **Figure 3)**. In these expanded studies Akita and FLIR Agetnase evaluated the absorption and sequestration of 3 chemical agent surrogates; 2-chloroethylphenylsulfide (2-CEPS), diisopropylphosphate (DFP), and paraoxon at time periods of up to 100 hours.

Figure 14 presents results obtained for paraoxon using an identical test protocol to that previously described with the exception that the dwell time was increased from 30 minutes to 100 hours. When tests are extended to 100 hours, the chemical agent paraoxon is recovered principally from the thiol-ene coating, both extraction of the contact sampler at the surface of the coating and the residual obtained from the substrate showed no recovered paraoxon. Therefore, even with the dwell time extended to 100 hours, there was no breakthrough of chemical agent surrogate through the coating. In addition, since there was no residual agent recovered from the substrate, the coatings showed effective entrainment of the agent from the substrate into the coating. The recovery of paraoxon from the coatings varied from 60% to 80% suggesting that there were some losses due to evaporation of decomposition of the surrogate over the duration of the experiment.

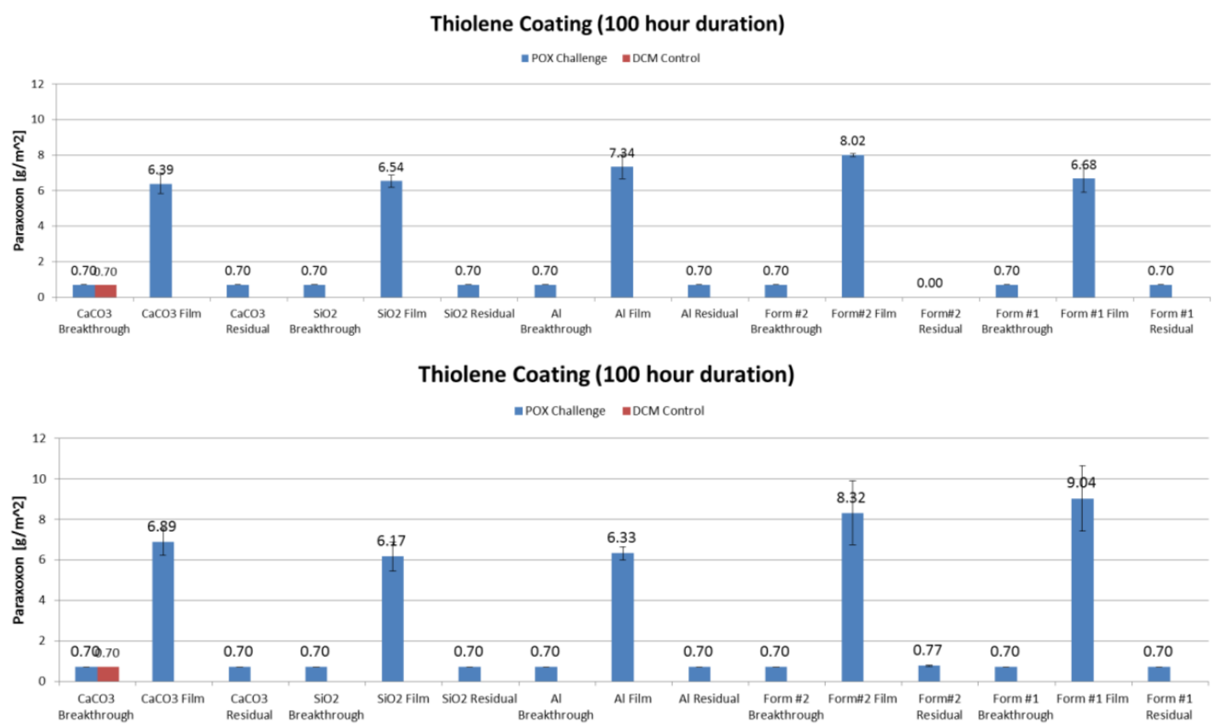


Figure 14: 100 hour Dwell Time Analysis of Akita-02 thiol-ene Coating samples with simulant paraoxon.

Two additional simulants were screened for absorption into the thiol-ene coating and breakthrough, diisopropyl fluorophosphates (DFP) and 2-chloroethylphenylsulfide (2-CEPS). Diisopropyl fluorophosphate (DFP) is an organophosphate based simulant with a vapor pressure of 0.579 mmHg at 20°C. Protocol for analysis of this simulant followed identical procedures as paraoxon. Briefly, neat DFP was stained with 1% (w/v) Oil Red EGN to improve simulant visualization and a 10 g/m^2 spot was applied to the aluminum panel. The thiol-ene coating was placed over the simulant, the breakthrough paper placed on top of the coating, and finally a second aluminum panel. This sandwich was then loaded with a 220g weight for a dwell time of 30 minutes. Subsequent extraction was conducted into dichloromethane (DCM) containing the internal standard tributyl phosphate (TBP). **Figure 15** displays extraction results. A significant fraction of DFP (>70%) was not recovered as either residual on the panel, absorbed in the coating or as breakthrough in the contact paper. This may be either due to volatilization loss of the DFP simulant or direct reaction of DFP with residual thiol or amine functional groups in the coating. Of the DFP which was recovered, 2/3 of the simulant that is found absorbed within the thiol-ene coating matrix and again no significant breakthrough is observed.

The last simulant screened was the half-mustard blister simulant 2-chloroethylphenylsulfide (2-CEPS). 10 g/m^2 neat 2-CEPS was tested with a 30 minute dwell time and 220 g load. After the dwell time, the simulant was extracted into 5.0 mL of dichloromethane with dissolved thioanisole (THA) as an internal standard; results are shown in **Figure 16**. It appears that all the simulant recovered is absorbed within the coating film with none being recovered from the aluminum panel or breakthrough. Again the thiol-ene coating shows good affinity for 2-CEPS as with the other simulants. Controls (not shown) with no thiol-ene coating were extracted with similar recovery of around 70% after 30 minute dwell time. Unrecovered simulant may be due to either evaporation or decomposition of surrogate through reaction with residual thiol or amine in the coating.

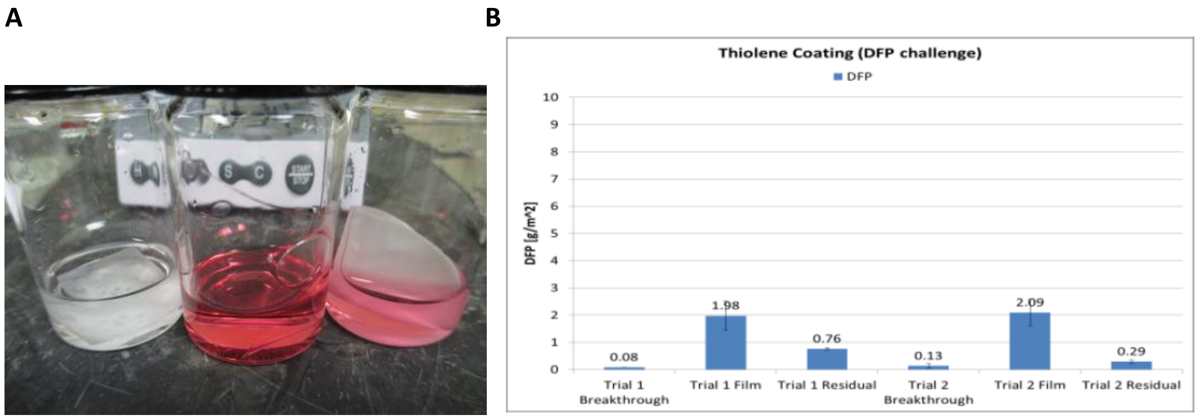


Figure 15: A - Thiol-ene Coating DFP Simulant Extraction (Left Vial) Breakthrough phase, (Middle Vial) Coating Film, (Right Vial) Residual Fraction. **B –** Recovered DFP simulant as breakthrough, absorbed in film and residual.

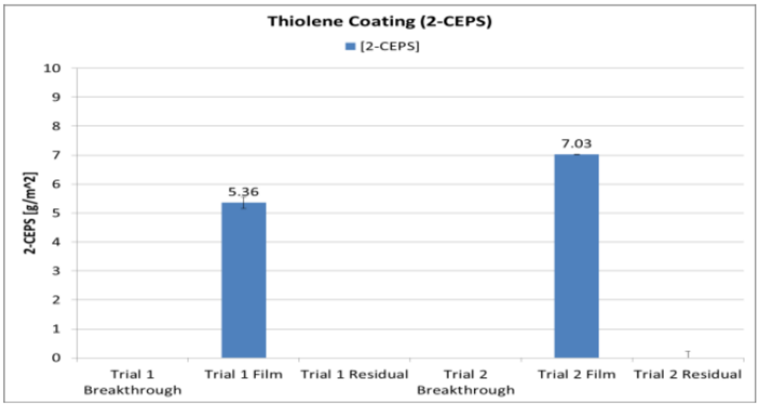


Figure 16: Thiol-ene coating with simulant 2-CEPS.

Task 6: Option – Extend performance evaluation of sequestration coating.
Status: Option not executed.

Task 7: Option - Identify surety lab for live agent testing and develop test plan.
Status: Option not executed.

Potential Applications

Product

Our initial product will be a sequestration coating with indicating and decontamination properties for a range of chemical threats, which can be rapidly deployed and used with portable sprayers to respond to chemical agent incidents either indoors or outdoors. A single sequestration coating will be able to be used for any of multiple agents. The coating material will be a two-part composition with a shelf life of at least two years, and once sprayed on a contaminated surface will cure within minutes to form an impermeable coating that will absorb and sequester the chemical agent. Once the material is cured and the air around the site has been exchanged, personnel will be able to enter the contaminated area with minimal or no protective clothing and equipment, to complete the remediation of the area by peeling away the coating and disposing of it. Our initial product will be tested against chemical agent threats such as GB (sarin), HD (sulfur mustard), and VX, and will include both generic detoxification agents as well specific detoxification agents (enzymatic systems). Subsequent products will be designed (with different enzymes, and additional neutralizing agents) to more broadly address commercial hazardous chemical spills. These subsequent products will be marketed to both U.S. government and commercial/industrial customers.

Markets

The market for chemical hazard decontamination is dominated by military and civil defense users, but also includes other government operators of critical infrastructure, airlines and airport operators and air cargo operators, shipping and port managers, mass transit managers, and chemical plant operators and operators of industrial plants which use hazardous chemicals. The market for ECBN (explosive, chemical, biological, & nuclear) decontamination technology is currently estimated at $10.1B in 2012 with a 13.7% compound annual growth rate (CAGR) forecast thru 2019. Decontamination by chemical processes is estimated at $3.8B with a 13.4% CAGR, as shown in **Figure 17**. This market is segregated by usage as shown in **Table 3**, and by region in **Table 4**.

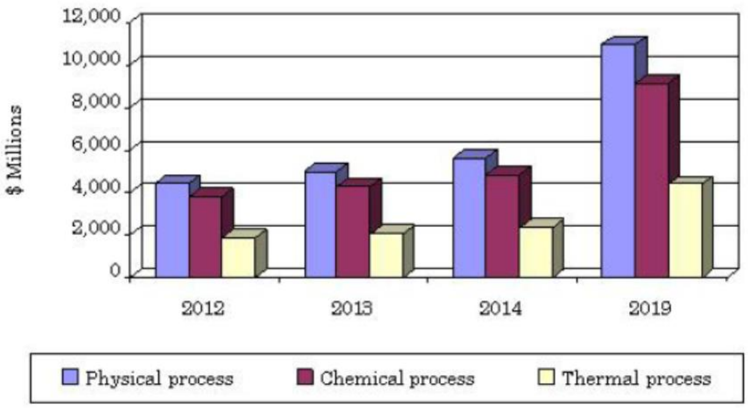


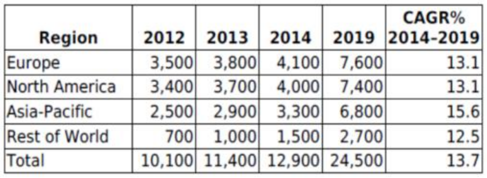
Figure 17: Global market for ECBN contamination equipment, 2012 – 2019. Source, BCC Research

Decontamination equipment includes decon kits, mobile decon systems, shelters, showers, and accessories. Many decontaminants are liquids, fogs, or foams, which require time-consuming clean-up. Some are reactive gasses, but these may not be effective for nerve agents and other chemical hazards. Our sequestration/decontamination coating will be easy to apply and as a 100% solids coating, will require no heat or light to cure and no clean-up or removal of solvents. Once the coating has cured and the enzymatic or hydrolytic decontamination of the agent has taken place, the then-nontoxic coating can be removed by simply stripping it from the substrate and disposing of it as ordinary trash (though disposal as hazardous waste is another option). A check of the substrate for any residual contamination (for example, by the FLIR Disclosure spray or a similar product) would likely be performed to verify that the surfaces are safe.

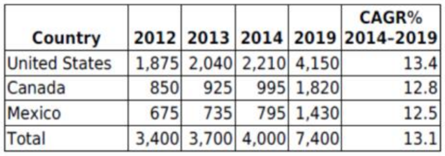
Table 3: Global market for ECBN decontamination equipment by type, 2012 – 2019. From BCC Research

Application	2012	2013	2014	2019	CAGR% 2014-2019
Infrastructure decontamination	4,540	5,120	5,790	11,200	14.1
Equipment decontamination	3,090	3,490	3,950	7,450	13.5
Personnel decontamination	2,470	2,790	3,160	5,850	13.1
Total	10,100	11,400	12,900	24,500	13.7

Table 4: Regional segmentation of ECBN hazard decontamination. From BCC Research



Region	2012	2013	2014	2019	CAGR% 2014-2019
Europe	3,500	3,800	4,100	7,600	13.1
North America	3,400	3,700	4,000	7,400	13.1
Asia-Pacific	2,500	2,900	3,300	6,800	15.6
Rest of World	700	1,000	1,500	2,700	12.5
Total	10,100	11,400	12,900	24,500	13.7



Country	2012	2013	2014	2019	CAGR% 2014-2019
United States	1,875	2,040	2,210	4,150	13.4
Canada	850	925	995	1,820	12.8
Mexico	675	735	795	1,430	12.5
Total	3,400	3,700	4,000	7,400	13.1

The technology we develop for this project will also be applicable to other types of coatings besides chemical hazard sequestration coatings. Coatings are used extensively to protect wood, glass, metal, and other materials from environmental hazards, and the technology we develop in this project (minus the neutralization enzymes) may find use in some of these applications. In particular, there is rapid growth in high-solids and emerging coating technologies, as these avoid the solvents and need for drying of the most common solvent and waterborne coatings. High solids coatings were a $15B market worldwide in 2011, growing at a 5.7% CAGR. North America accounts for about 25% of that market. Major U.S. companies involved in the coatings market include PPG Industries ($10.9B coating revenue in 2011), Sherwin Williams ($6.6B), Du Pont Performance Coatings ($4.3B), Valspar ($3.7B), and RPM ($2.5B).