

Visualization of the Absorption of Chemical Warfare Agents and Associated Simulants in Heterogeneous Coatings

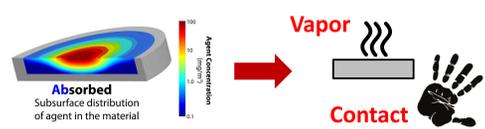
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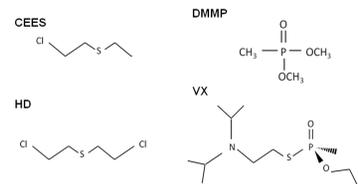
Introduction

Characterizing absorption of highly toxic chemicals into permeable materials is paramount for accurate hazard assessments. The design of decontamination approaches and mitigation of post-decontamination health risks relies on the ability to understand these mass transport processes. Of particular interest is the uptake of chemical warfare agents (CWA) and their simulants into multi-layer, polymeric coatings used on military assets.

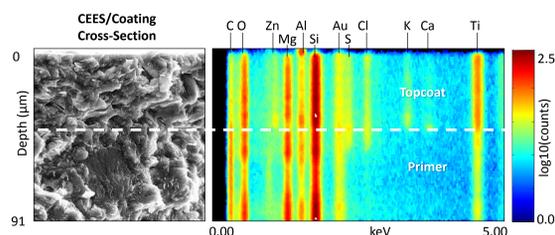
Contaminant Uptake



For this study, military relevant polyurethane and alkyd based paint coatings, in fully formulated and deconstructed states, were contaminated with bis(2-chloroethyl) sulfide (distilled mustard, blister agent HD) and *O*-ethyl *S*-[2-(diisopropylamino)ethyl] methylphosphonothioate (VX), an organophosphate nerve agent, as well as their respective simulants, 2-chloroethyl ethyl sulfide (CEES) and dimethyl methylphosphonate (DMMP), via liquid phase deposition.



By considering films prepared from single components of the fully formulated coatings, it is possible to resolve the relative impact of different components in the coatings that determine chemical permeation. Measurements of the materials cross-section were then performed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), which provide correlated morphology and elemental mapping data specific to each contaminant-material system.

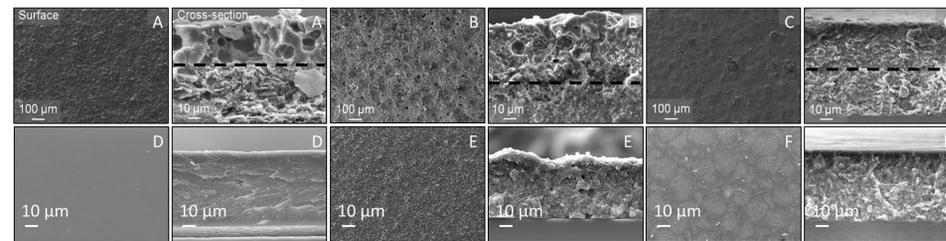


**** Throughout poster, the dashed line represents the delineation between topcoat and primer layers

Experimental Overview

Materials

- All coating materials were applied to Si(100) wafers to allow for facile cleaving of the coating and in turn provide a cross-sectional interface for SEM-EDS examination
- Samples represent full formulations of three different coatings including three deconstructed states of Coating B (see table below)
- Full formulations were sprayed directly onto substrates and deconstructed coatings were applied to the substrate with a drawdown method
- Coating B, a porous polyurethane formulation, was deconstructed down to its base components to understand the effect of specific components on mass transport
- SEM examination showed that the addition of the matting agent (Coating E) produced a microstructure similar to the full formulation (Coating B) but without the porosity



Coating	Notes
A	Full Formulation: Aliphatic, polyester polyurethane topcoat (50.5 ± 7.5 µm); Chromated primer (19 ± 4 µm)
B	Full Formulation: Polyurethane topcoat (50.5 ± 7.5 µm); White epoxy primer (37.5 ± 5 µm)
C	Full Formulation: Silicone alkyd topcoat (50.5 ± 7.5 µm); Zinc molybdate primer (85.75 ± 12.25 µm)
D	Deconstructed B: polyurethane base with defoamer, flow agent, and extra H ₂ O
E	Deconstructed B: polyurethane base with defoamer, flow agent, and M3 matting Agent
F	Deconstructed B: white epoxy primer

Experimental Setup

- Evex MiniSEM SX3000-FH
- Light element X-ray detector: Be UTW
- EDS resolution: 5 µm
- Charge reduction module (CRM) can reduce sample temperature to -52 °C
- SEM chamber and vacuum system are located inside a chemical fume hood allowing CWA work

Experimental Procedure

- Contamination**
 - Dose liquid phase contaminant
 - Residence times: 1, 5, and 30 min (under glass Petri)
 - Excess liquid is wicked away
- SEM Preparation**
 - Cleave sample and mount to holder
 - Au sputter coat, for conductivity
 - Introduce to SEM chamber and reduce sample temperature to -52 °C

Elemental Mapping

- Spectra are collected at each point in a 128 x 128 matrix, representing a 91 x 91 µm region of the cross-section
- Mapping residence time: 50 ms



First SEM capable of CWA work

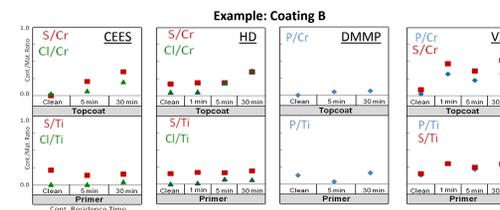
Data Analysis

- Spectra from each point of the elemental map are grouped by a specific region of interest: paint layer or depth
- Custom Matlab curve-fitting routine employed to remove noise/background signals and deconvolve overlapping peaks in EDS mapping spectra
- Fitted contaminant peaks are integrated to produce relative composition values and normalized by a material signal for sample comparison

Results and Conclusions

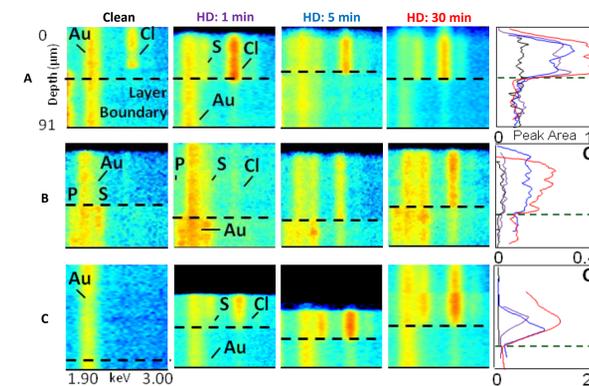
Simulant vs. Agent Uptake

- All topcoat layers exhibited a measurable increase in contaminant signals after exposure
- Simulant uptake did not always match agent uptake
- Lower resistivity to VX contamination over HD and DMMP indicates mass transport is affected by more than just contaminant molecular size in these systems



Contaminant Depth Profiling

- CWA elemental signature was mostly isolated to the topcoat layer
- Each coating exhibited notable differences in the uptake of HD vs. VX
- Depth profiles indicate polymeric chemistries influence contaminant penetration



Approximation of Diffusion Coefficients

- Depth profiles provide penetration depths for order of magnitude approximations of contaminant diffusion coefficients
- Contamination times included contamination (1, 5, 30 min) and preparation times (30 min) for a total of either 31, 35, or 60 min
- Calculated approximations correspond to diffusion coefficients for heterogeneous materials

Table of Diffusivity Approximations

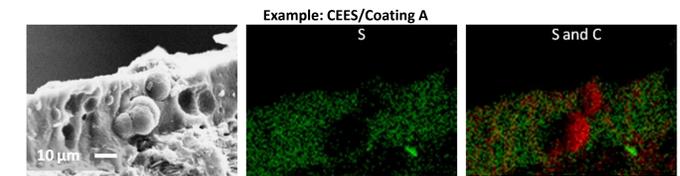
Coating	D _{HD} (m ² /s)		D _{VX} (m ² /s)	
	Topcoat	Primer	Topcoat	Primer
A	7 × 10 ⁻¹³	0*	7 × 10 ⁻¹³	1 × 10 ⁻¹²
B	4 × 10 ⁻¹³	3 × 10 ⁻¹³	1 × 10 ⁻¹²	6 × 10 ⁻¹³
C	3 × 10 ⁻¹³	0*	3 × 10 ⁻¹³	0*

* No penetration observed

$$D_{\text{cont}} \sim L^2/t_{\text{cont}} \quad L = \text{penetration depth} \\ t_{\text{cont}} = \text{contamination time}$$

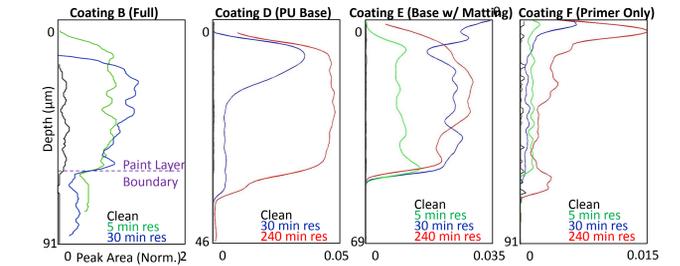
Spatially-Variied Mass Transport

- Elemental maps of contaminated Coatings A and C exhibited circular voids within the contaminant distribution that corresponded to specific paint components
- Behavior indicates a heterogeneous contamination system where different coating components exhibit different transport resistances for contaminant molecules



Full Formulation vs. Deconstructed Coating

- Deconstructed primer-only sample (Coating F) demonstrated high resistance to HD penetration as indicated by full formulation testing
- Addition of the matting agent to the polyurethane base changed mass transport behavior and matched what was observed in the full formulation



* Note only the fully formulated data set was normalized by a material signal the others were normalized by the substrate signal. Thus, magnitude of peak areas should not be directly compared.

Conclusions

- Polymeric and contaminant chemistries affected mass transport in coating layers
- CWAs and their simulants exhibited differing mass transport and chemical distributions in observed military coatings
- Certain particles within coating microstructure impeded contaminant transport
- Observed contamination systems exhibited spatially varying transport rates
- For deconstructed Coating B, the matting agent appeared to have the greatest effect on both microstructure and mass transport.

Next Steps:

- Continue examination of contaminated deconstructed coatings to understand how each major coating components influence contaminant molecular transport in coating systems
- Assess possible material reactivity with the contaminant itself

Acknowledgments

Research reported in this presentation was funded or supported by the Defense Threat Reduction Agency (CB3062)