Roles of surface wetting and bulk mass transport in the contamination of polyurethane-based coatings by distilled mustard blister agent, HD

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Abstract

- Development of decontamination processes for materials as well as permselective or hardened materials for enhanced hazard mitigation for use on military assets benefits significantly from a fundamental understanding of chemical ingress and retention mechanisms
- Upon liquid contaminant exposure to a material surface, a chemical can absorb via transport into bulk layers by multiple absorption routes including molecular diffusion and capillary flow, all of which are influenced by the liquid wetting behavior at the surface
- Decontamination burden and consequently the subsequent hazard is determined by the propensity for the material to retain the contaminant, both at the surface and in subsurface regions
- Work has focused on determining what physicochemical interactions influence material resistance to chemical contamination, specifically for chemical warfare agents interacting with polymeric materials
- Experimental work has been performed involving the deposition of liquid contaminants on polymeric coatings with various chemical composition and associated surface characteristics
- Multiple experimental tools were used to differentiate between total absorbed mass and liquid phase contaminants entrained in surface and near-surface capillary networks
- Results show that retained agent mass by a polymeric coating material is highly dependent on the agent-material pair and can be significantly influenced by both the texture of the surface exposed to the liquid agent as well as the specific polymer binder and supported solids in the bulk
- Understanding garnered from considering chemical retention will not only inform next generation decontamination approaches but also result in the design of new coatings formulations that are tuned for chemical resistance, reduced decontamination burden, and mitigated hazard for Warfighter personnel

Chemical Retention Factors

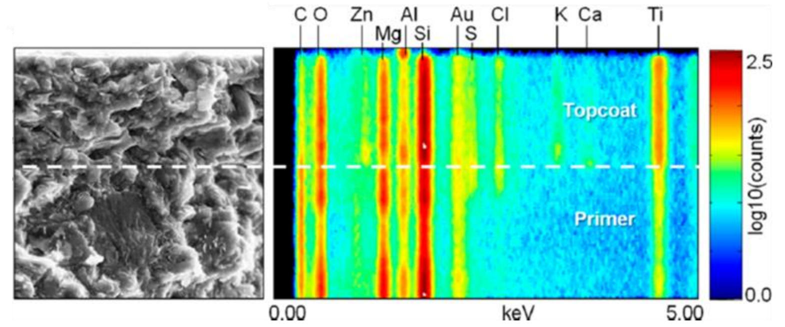
How do we identify mechanisms to understand and ultimately control for agent transport in coatings like paint?

Material characteristics can have a significant impact on the type of chemical transport as well as the degree of agent retention:

- Solids supported in polymer binder matrices, e.g., pigment particles, matting agents
- Microscale film defects from film curing or application
- Specific polymer binder chemical structure
- Physicochemical interactions between agents and coatings chemical and morphological structure
- Native agent chemical impurities present

Identification of rate limiting processes and relative magnitudes of impact on chemical retention enables formulation advancement

Chemical transport through bulk layers via molecular diffusion



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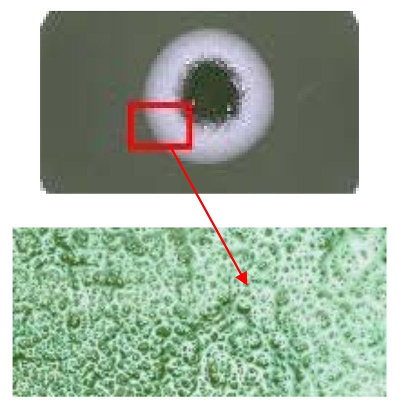
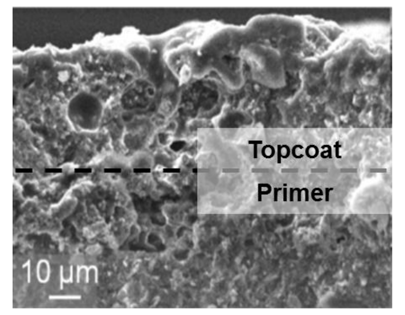
Liquid spread in surface capillary network



Fluid flow through bulk interstitial voids and surface defects



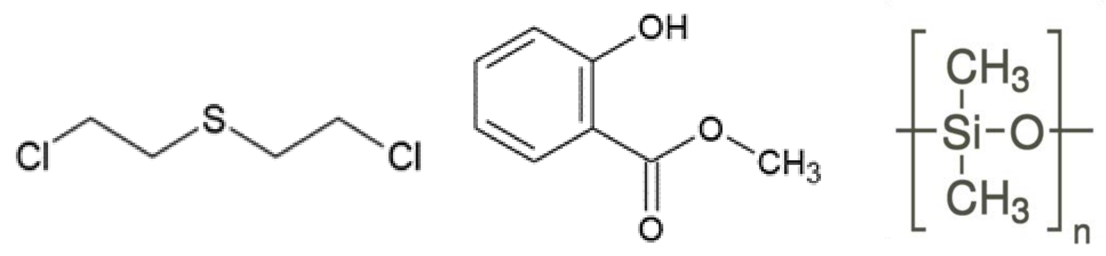
Materials and Methods

Chemicals and Materials

- Chemical Agent Standard Analytical Reference Material (CASARM) HD, methyl salicylate (MeS), and silicone oil; all chemicals deposited on to materials from liquid phase; liquid density, ρ (g/cm³), and kinematic viscosity, ν (cSt), listed as (ρ, ν)
- Materials: Low gloss, >50% by weight solids polyurethane (PU) paint (topcoat) with various pigmentation (black, tan, gray, green) in the form of free films or painted on metal substrates (<50 µm) with or without epoxy primer backing layer

Experimental Tools

- Chemical Agent Resistance Method (CARM) used for determining *overall* chemical retention, i.e., retained agent (RA) mass, for contaminated materials as a function of liquid phase exposure time to the contaminant via quantitative chromatographic analysis of solutions derived from liquid phase extraction of the contaminated material; measurement enables an assessment of total retained agent *regardless of where the agent is localized, e.g., surface, interfaces, bulk*
- Optical microscopy quantified the roughness for different materials types to demonstrate a relationship between surface morphology and chemical retention for specific chemicals
- Time-resolved attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy used to measure contaminant diffusivity and saturation concentration from breakthrough of liquid across the thickness of the coating thin films



Distilled mustard, HD: bis(2-chloroethyl) sulfide (1.27, 3.9)

HD simulant: methyl salicylate (MeS) (1.17, 2.2)

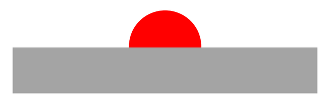
Silicone oil (liquid spreading simulant) (0.93, 10)

Painted metal substrate

Free film

CARM

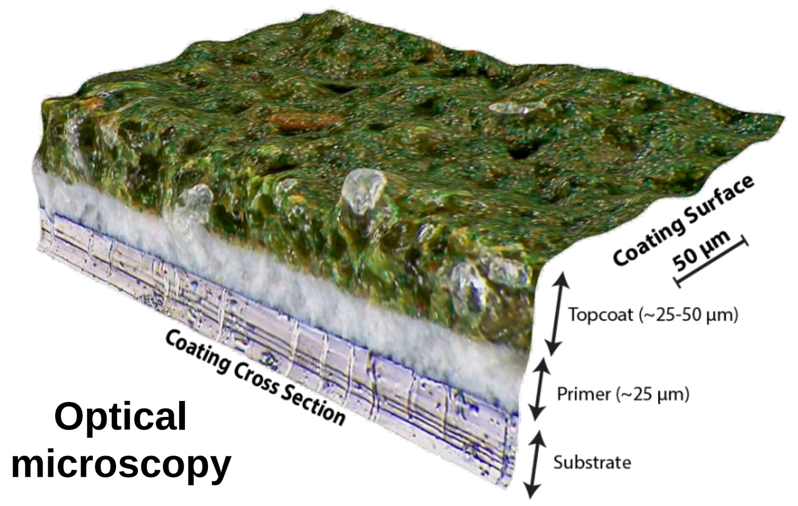
Deposit agent droplet



Allow droplet spread (contaminant age time) then rinse to remove surface bound liquid

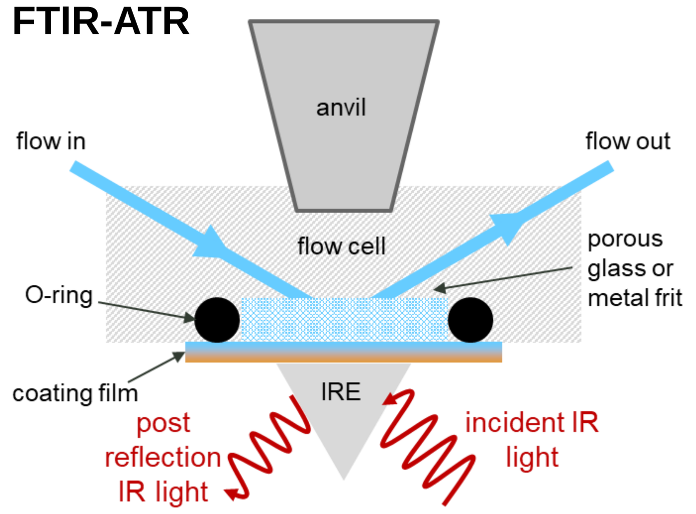
Immerse in soapy water (3 s) followed by water rinse

Remaining agent mass (RA) via analysis of solvent extraction of mass from material



Optical microscopy

FTIR-ATR



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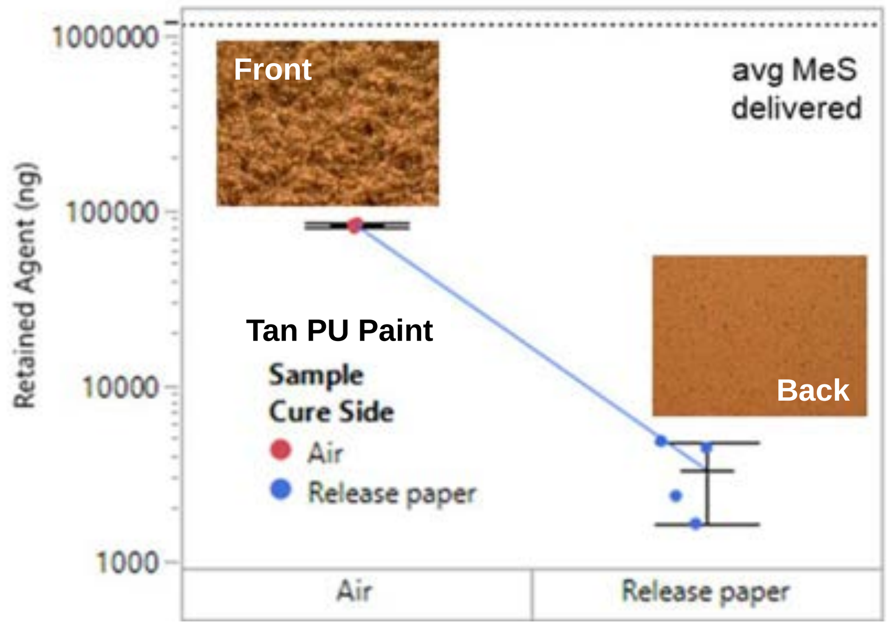
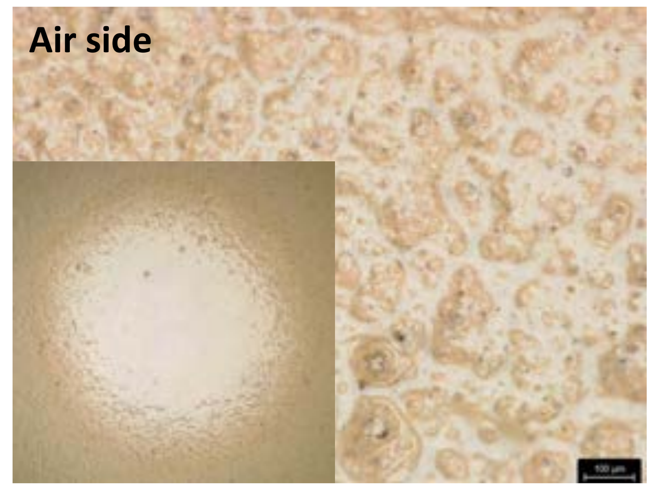
Polymer **180**, 121697 (2019)

Impact of Surface Morphology

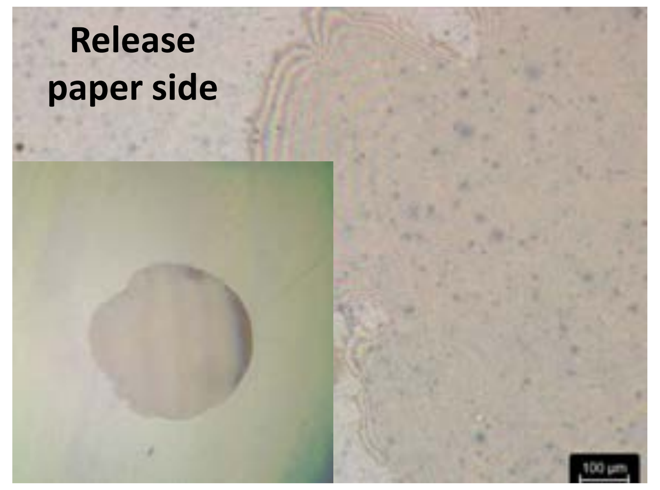
- Surface roughness has been shown to play a large role in chemical retention as a function of specific contaminants
- Necessary to account for impact of surface morphology on promoting surface and near surface retention, especially if the contaminants are not easily displaced by aqueous surface treatments
- Smoother paint coating films have tended to exhibit decreased chemical retention, possibly related to overall surface wetting but even more a function of the entrainment of liquid phase contaminants in the surface network
- Coatings have inherent roughness with variable wetting behavior for deposited liquid droplets, spreading of liquids on surfaces is an important consideration but its it is a surface phenomenon and will not fully explain retention due to diffusion into bulk layers



Bulk liquid entrained in rough surface texture-higher RA

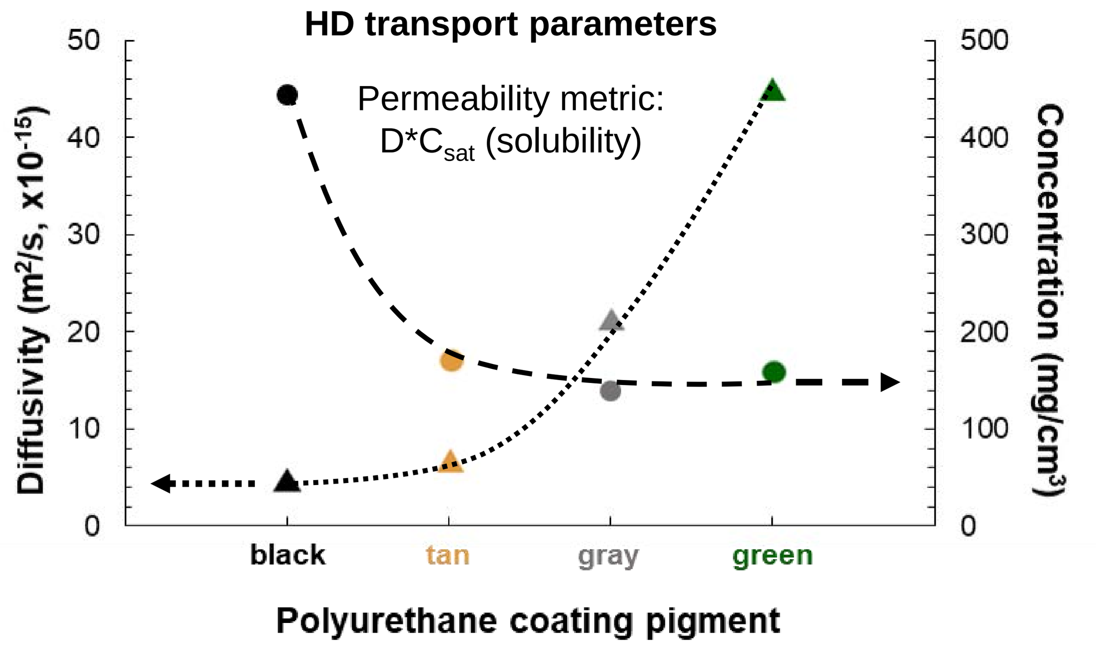


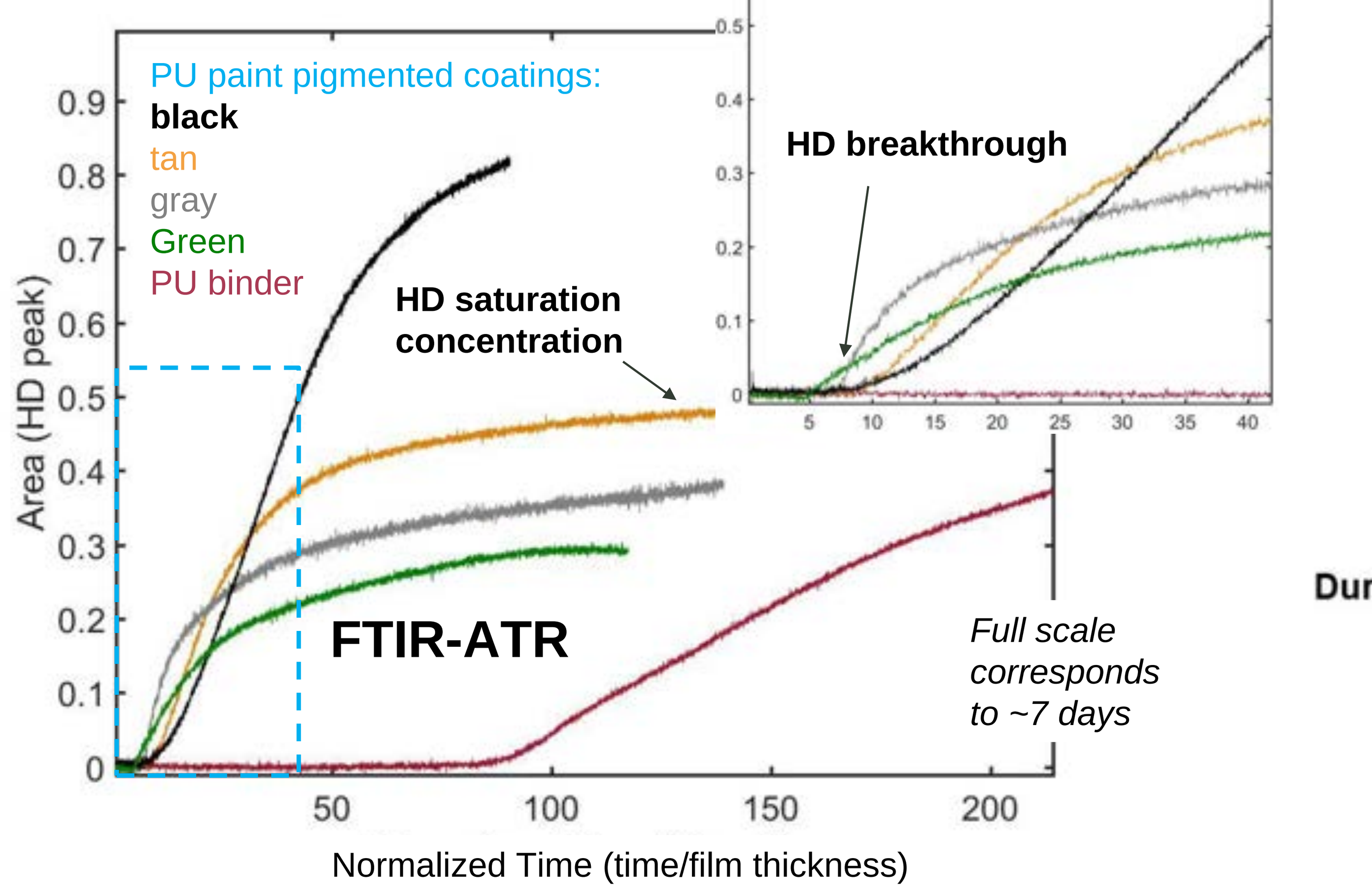
Bulk liquid remains on surface-lower RA

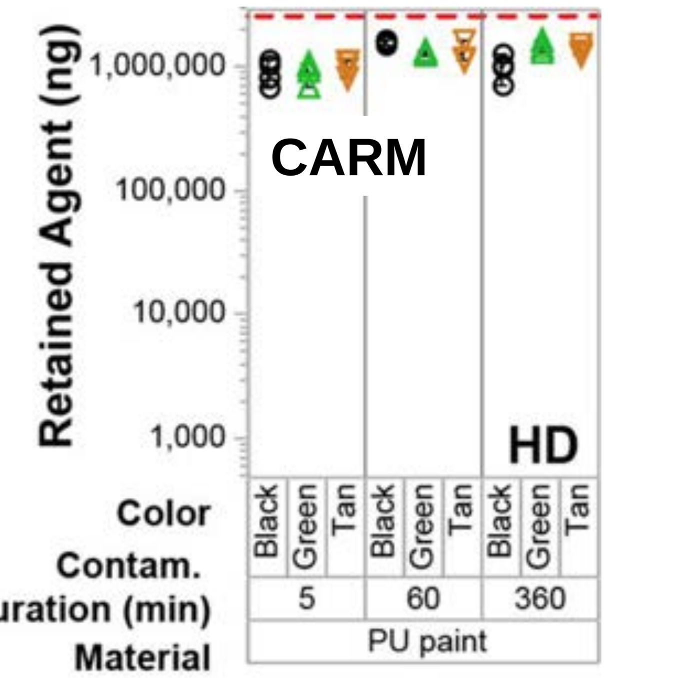


Impact of Pigmentation Solids in Coating Composition

- RA trends for coatings from the same class of PU paint varies as a function of polymer binders, and pigmentation (black, tan, gray, green) – **very similar paints can exhibit very different chemical resistance behavior**
- For the specific PU coating variant highlighted here, as a function of pigmentation, there is a variation observed in transport (diffusivity and saturation concentration) through paint films but not necessarily an associated variation in overall chemical retention
- Liquid HD breakthrough performed for PU paint films illustrates transport behavior that is dependent on specific coating composition
- Fitting uptake curves to appropriate diffusion models allows for quantification of variations in diffusivity and concentration as a function of film type







CARM shows fast retention
FTIR-ATR resolves pigment specific breakthrough

Conclusions

- Multiple, complementary experimental techniques were used to determine agent interactions with coatings materials including overall retention CARM as well as breakthrough dynamics (FTIR-ATR), which included utilizing coatings materials in the form of free films
- CARM provides overall retention of agent mass by a coating material but does not necessarily reflect where the contaminant is located (e.g., surface capillary network, bulk layers), which is critical information for coatings development with respect to enhancing chemical resistance
- Results show that retained agent mass by a polymeric coating material can be significantly influenced by both the texture of the surface exposed to the liquid agent as well as the specific polymer binder and supported solids in the bulk
- Understanding garnered from considering chemical retention will not only inform next generation decontamination approaches but also result in the design of new coatings formulations that are tuned for chemical resistance, reduced decontamination burden, and mitigated hazard

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