Surface Modification to Improve Chemical Resistance of Coatings

Wesley Gordon[1], Gregory Peterson [1], Erin Durke[1], Matthew Shue[1]

[1]Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD

Abstract

Coatings are required to demonstrate chemical resistance in order to protect material, vehicles, and personnel. Plasma enhanced chemical vapor deposition (PECVD) of perfluorinated compounds has been used for years to improve resistance of fabrics and materials to water and other chemicals. Here we report the application of a PECVD method that not only induces hydrophobicity to a real world coating, but dramatically improves the resistance of the coating to the spreading and absorption of the chemical warfare agents, HD and VX. These results suggest that surface modification strategies may be effective in improving chemical resistivity, without changing the bulk properties, or requiring a significant reformulation effort.

Background

Decontamination of chemical warfare agents (CWAs) remains a challenge. Coatings and paints must also meet several other specifications such as spectral signature, durability, and robustness under field conditions. Meeting these multiple specifications can be extremely challenging, dramatically increasing the cost and time required in order to successfully reformulate a paint system to meet new demands.

We propose that a possible alternative to reformulation is to develop surface treatments or coatings for military paint systems. Certain characteristics of the paint such as water repellency or chemical resistance can be improved by simply altering the surface rather than reformulating the entire paint, which may result in reduction in time and funds spent on development of new paints.

Results collected in our laboratory demonstrate this concept on commercially available coatings. A polyurethane coating was treated in a vacuum plasma chamber with a feed gas of perfluorocarbon compounds (e.g. C_2F_6). This plasma modifies the surface in two manners: 1) fluorinating the surface, and 2) modifying surface morphology through etching. These two modifications, when combined, result in improvement of the coating's resistance to the spread and absorption of CWAs.

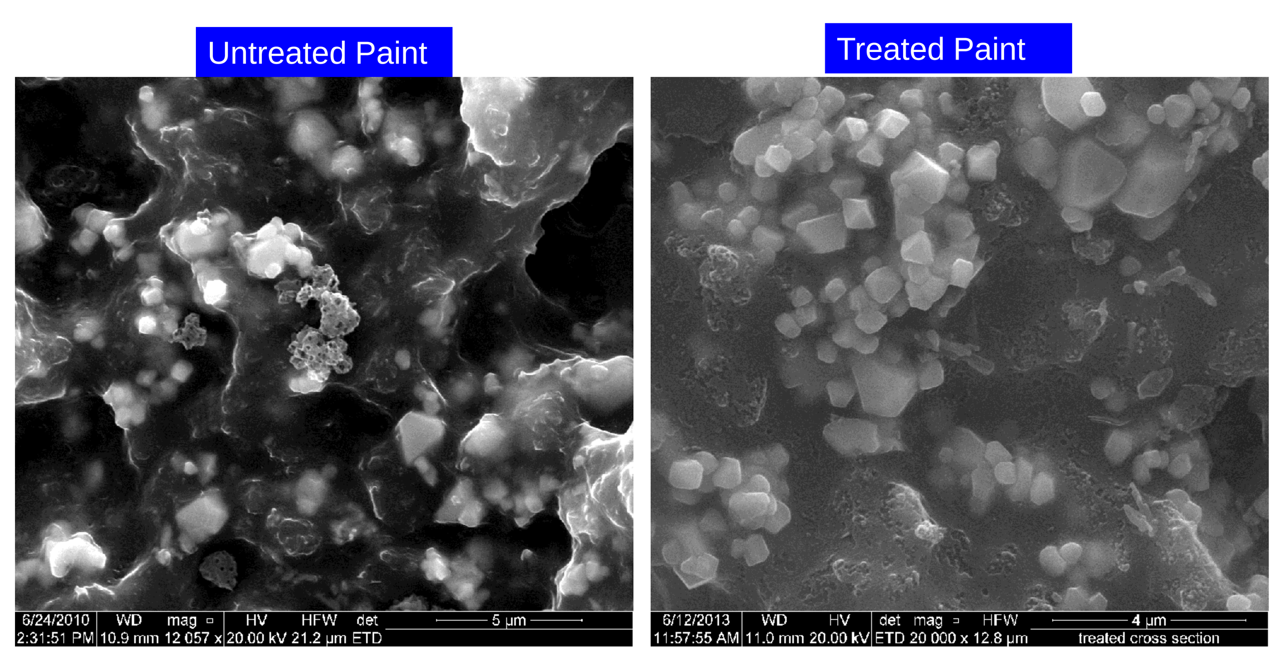
Approved for Public Release

Materials and Methods

Polyurethane coatings were sprayed per manufacturer suggestions at a commercial paint shop on 1x1" or 2" diameter type 304 stainless steel substrates. Coatings were cured for 7 days by the vendor prior to packaging, to minimize contamination. All coatings studied had been stored in a climate controlled environment for at least a year to ensure complete cure.

Clean coated surfaces were placed as-is in the 2L chamber of a Thierry Corporation Femto Version 6 vacuum plasma chamber. After evacuation to 0.3 mbar, perfluorinated alkane precursor was admitted into the chamber at a flow rate of 5 mL/min. The plasma generator was operated at a power of 50 W for 30 min.

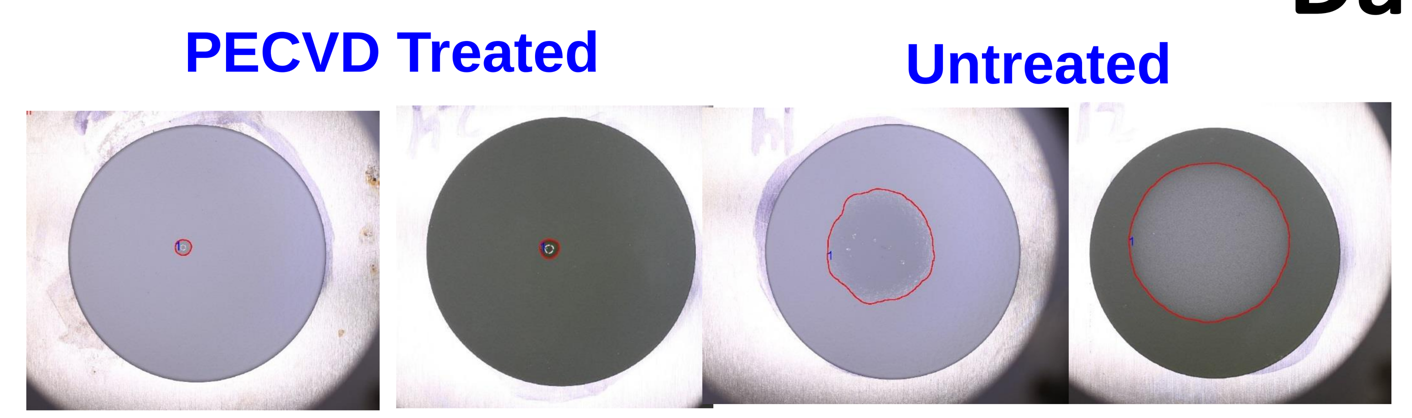
Picture of Plasma Furnace



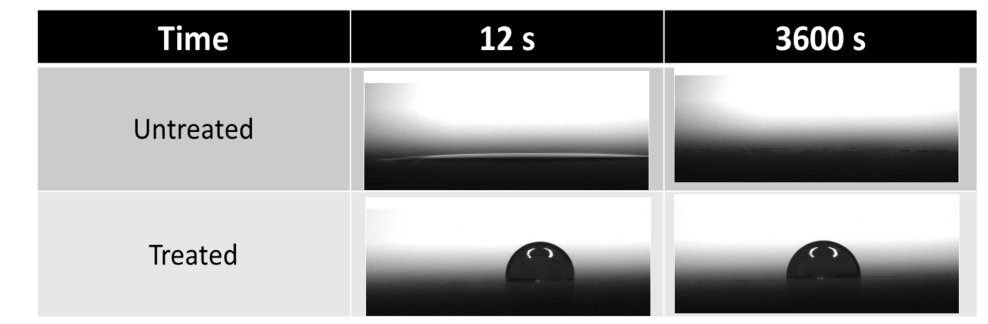
SEM, XPS, and EDX suggest:

1) Etching of the organic content of the Paint panel
2) F functionalization (9 at. %) near the surface.
3) Bulk macro pore structure does not appear to change

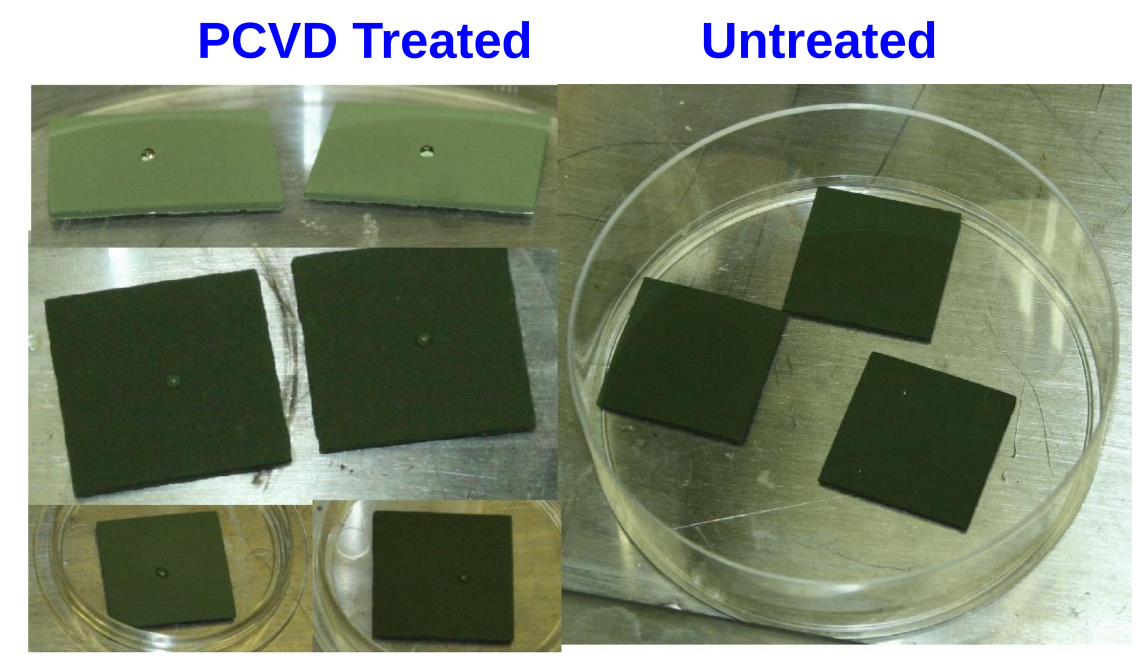
Data



Spreading Challenge: Pictures taken 60 min after 2μL VX contamination. DI water rinsing removed ~30-200% more VX from the panel,



Contact angle 2μL VX droplet on treated and untreated polyurethane.



LEFT: Absorption Challenge; Pictures taken ~27 min after 2μL HD contamination. Panels treated with a variety of perfluorinated alkanes resist spread by over 10×. An IPA rinse after 30 minutes removed >95% of the agent on the treated panels, which retained 10-35× less agent than the untreated coating.

Results: PECVD treatment of a polyurethane paint system was found to improve the resistance of the paint to CWA spread by >10×, and CWA absorption by 10-35×. CWA drops spread very little and therefore are more available for physical removal or decontamination. Drops remained pinned, even though the apparent surface energy has been decreased. Surface analysis confirms that both functionalization of the surface with fluorinated compounds and etching of the organic components occur during the PECVD process. The perfluorinated alkane was found to be critical to the process, and varying the alkane chain length had minor impact on treated coating performance.

Conclusions: Our results indicate PECVD treatment improves agent resistant qualities of a polyurethane coating. While the vacuum plasma treatment method may not be applicable for the treatment of vehicles, atmospheric plasma methods, which result in similar chemistries, do exist.[1] Furthermore, the (presumed) primary driver of the improvement of chemical resistance (surface fluorination) can be achieved by other methods,[2] possibly on an industrial scale.

1. Francoise, M.; et al. *Plasma Processes and Polymers* **2012,** *9* (11-12), 1041-1073.
2. Kharitonov, A. P.; Kharitonova, L. N., *Pure Appl. Chem.* **2009,** *81* (3), 451-471.

Acknowledgements: Funding provided by JSTO; Patrick Riley, Stephanie Quinones, and Janlyn Eikenberg (Leidos, Inc.) for Testing Support

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.