Surface Modification to Improve Chemical Resistance of Coatings

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Abstract

Coatings are required to demonstrate chemical resistance in order to protect material, vehicles, and personnel. In addition, numerous other requirements for the development of new coatings often involve substantial reformulation efforts in order to adapt to changing conditions and applications. One method to improve chemical resistance of coatings is to modify the surface of the paint to reduce surface energy without changing the bulk; ensuring any bulk properties remain unaltered. 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. For example, there are several reports in the literature of superhydrophobic fabrics developed using PECVD. 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. Over 60 minutes, droplets remained pinned and were therefore more easily decontaminated or physically removed. Surface analysis confirms modification of the surface with fluorinated species and also shows etching of the organic components of the paint. 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. This is particularly true for military vehicles and equipment. In the case of many legacy coatings, chemical agents may rapidly spread and absorb into the paint bulk. This results in an increased decontamination challenge, while also increasing the contact and vapor hazards to the warfighter. 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.

In the past, researchers have often engaged in a major reformulation effort in order to respond to new requirements. We propose that a possible alternative to reformulation is to develop surface treatments or coatings for military paint systems. Surface treatments only impact the top few µm of paint, rather than change the properties of the bulk. 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 a reduction in time and funds spent on development of new paints.

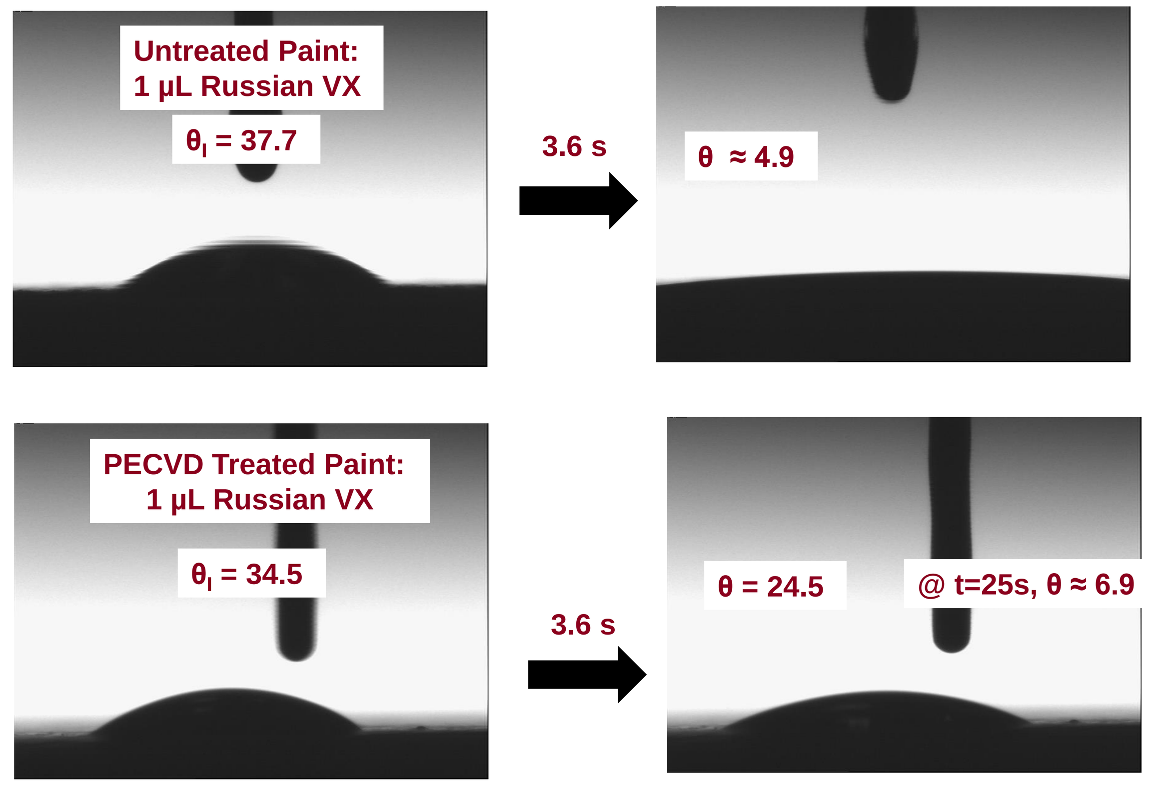
Strategies for improving chemical resistance include reduction in the surface energy and changing the surface morphology of the paint surface. By decreasing the surface energy, the spreading of liquid droplets, including chemical agents, will be reduced. This reduces the rate of absorption into the material by reducing the area of liquid-material contact. An additional benefit of this is that liquid agent will be more easily removed and/or decontaminated. Adjustment of the surface morphology at very small scales (classically known as the lotus effect) may also result in improved resistance.

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.

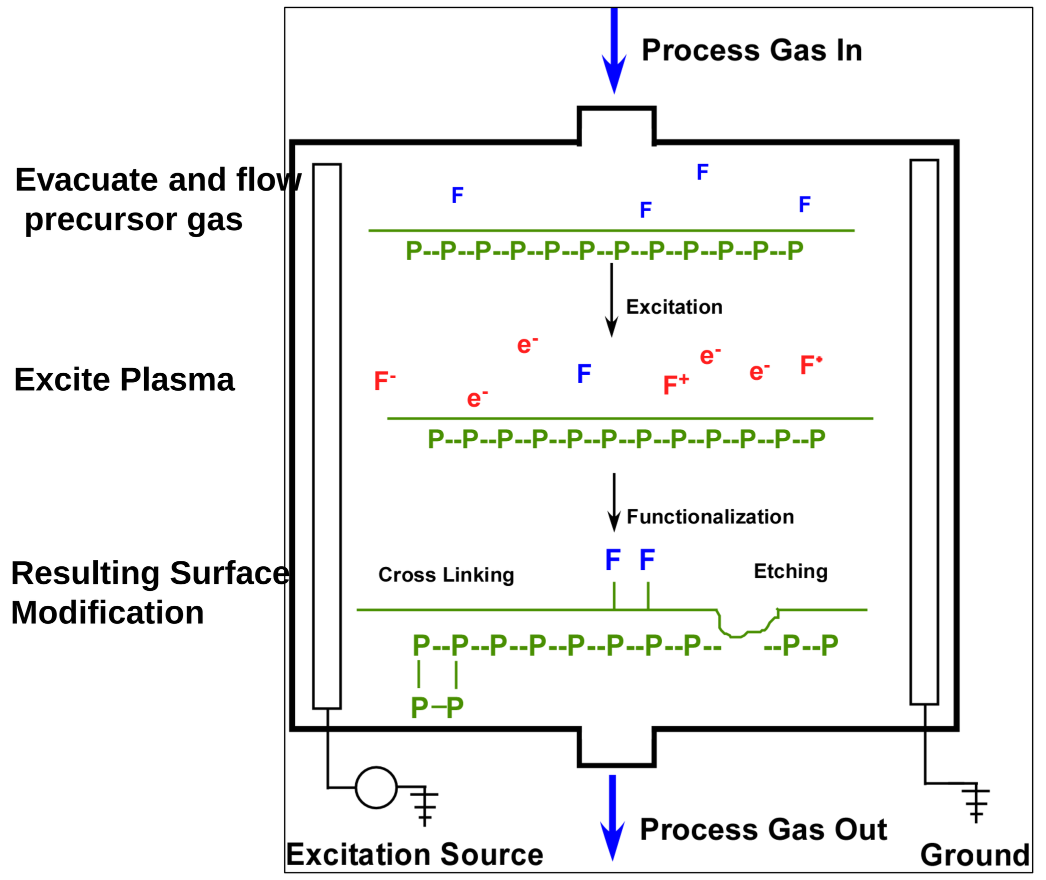
Materials and Methods

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 percursor 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.



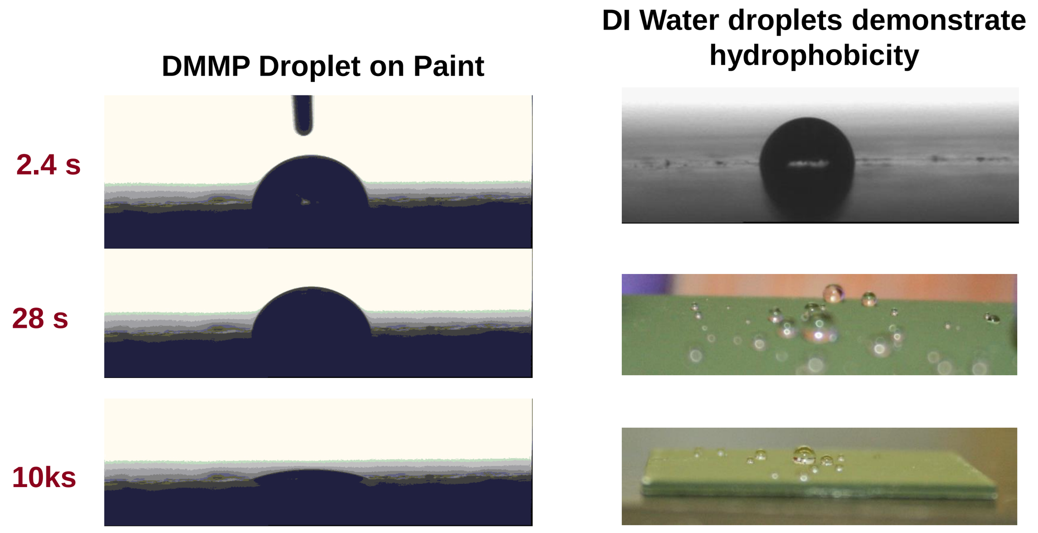
First formulation exhibited qualitative improvement with agent spreading.



Schematic of the PECVD process.

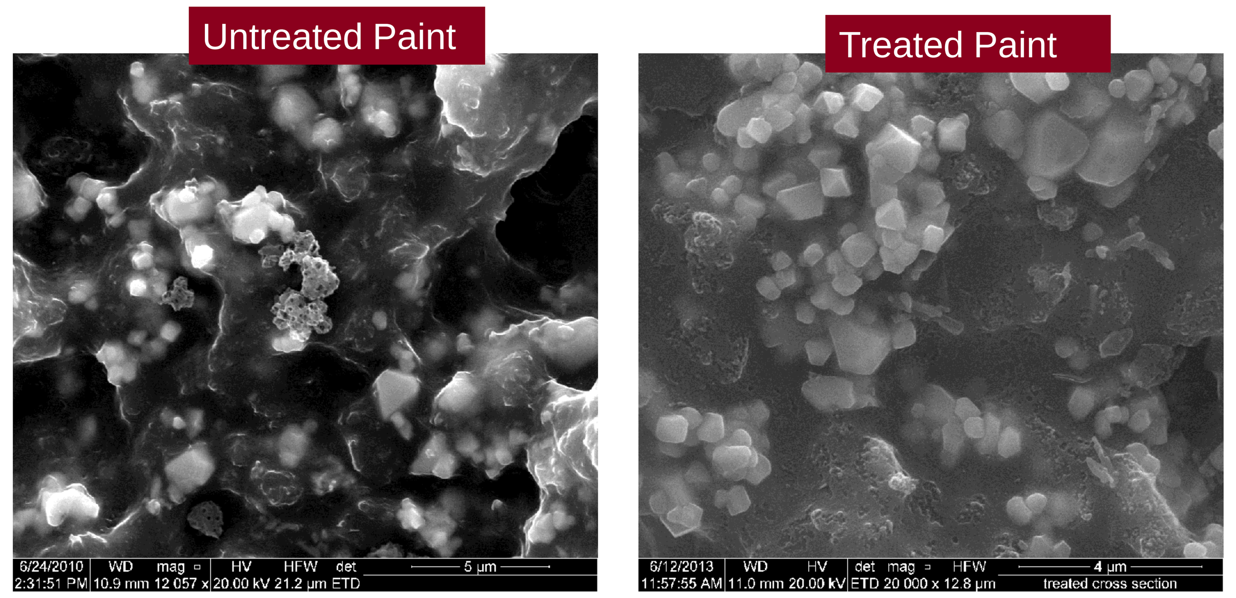
Set-up

Picture of Plasma Furnace



Preliminary Tests showing treated surface resistance to the simulant dimethyl methylphosphonate (DMMP) and demonstrated hydrophobicity of the surface (R).

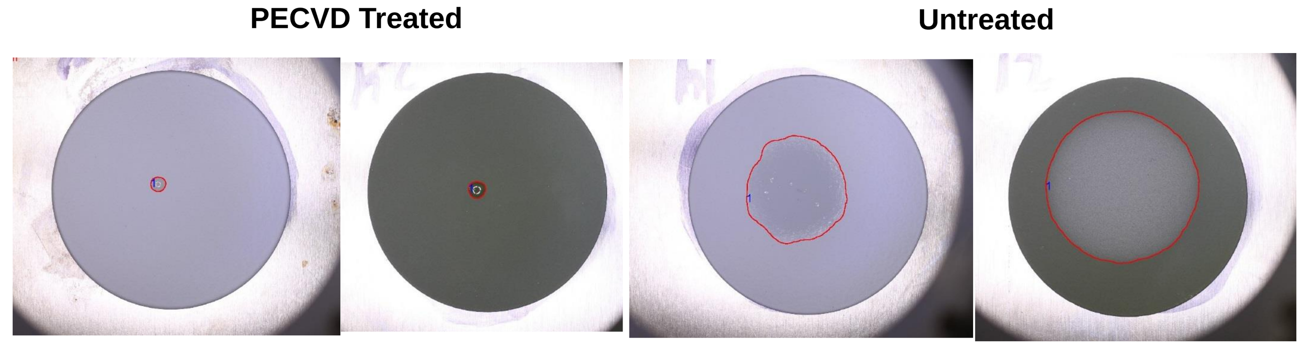
Surface Analysis



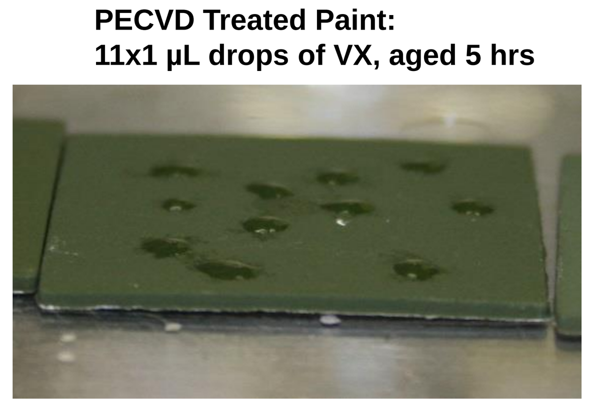
SEM, x-ray photoelectron spectroscopy, optical profilometry, and energy dispersive x-ray spectroscopy suggest:

1) Etching of the organic content of the Paint panel
2) Much more of the filler/pigment particles are exposed, possibly resulting in more textured surface (µm and nm scale). This may augment chemical functionalization leading to omniphobicity (oxides can readily fluorinate).
3) Chemical functionalization with F (~9 at. %) species occurs on the surface.
4) Bulk macro pore structure does not appear to be significantly changed.

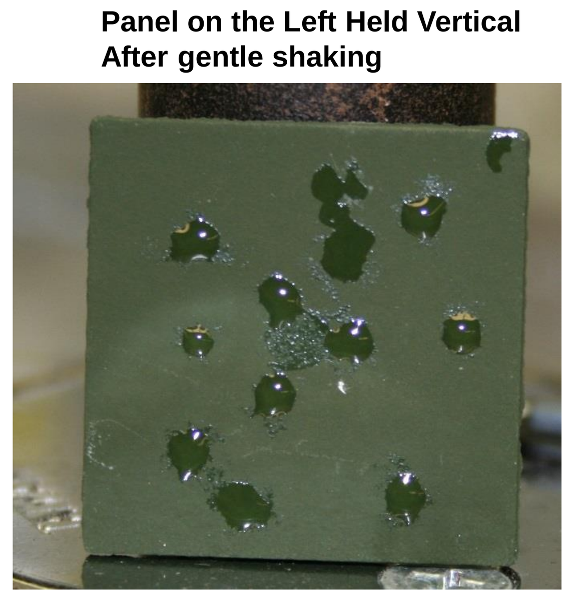
Data

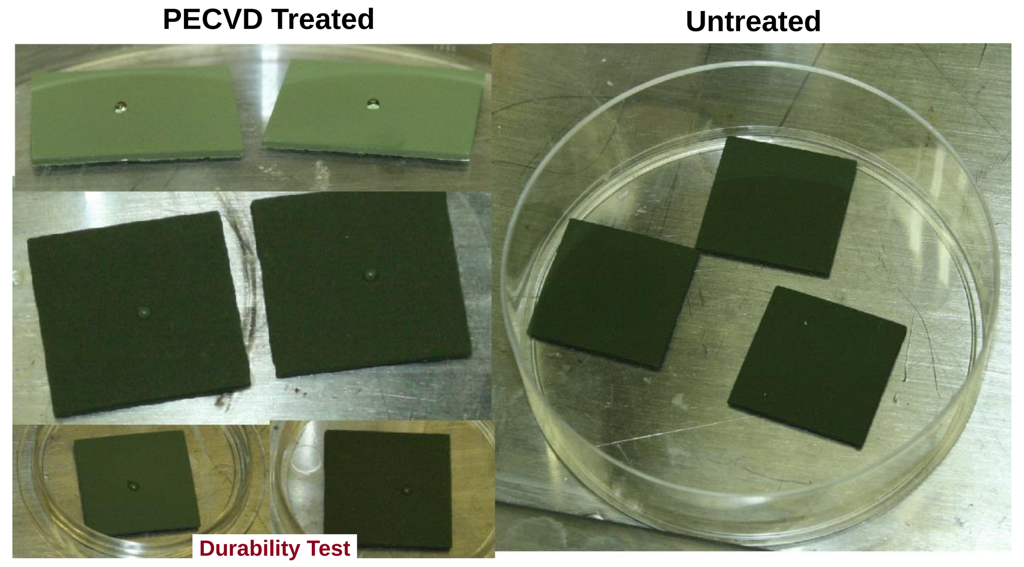


Spreading Challenge: Pictures taken 60 min after 2µL VX contamination. After 60 minutes, the panels were rinsed with 3 aliquots of deionized water. Depending on test methodology, the water rinse was found to remove ~30-200% more VX from the treated panels, and panel extractions showed agent absorption was reduced by ~5-10×. Other results suggest improvements much greater than this.

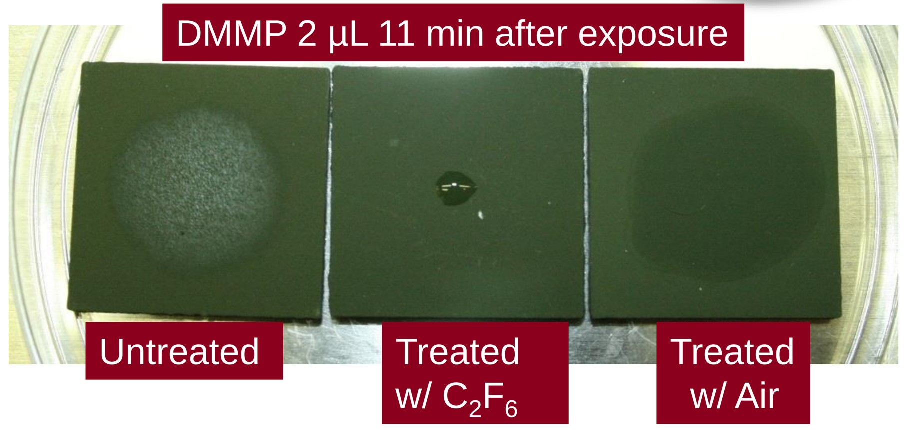


Prolonged Spreading Challenge: 5 hrs after VX contamination. Panel is agitated and changed from a horizontal to a vertical position.

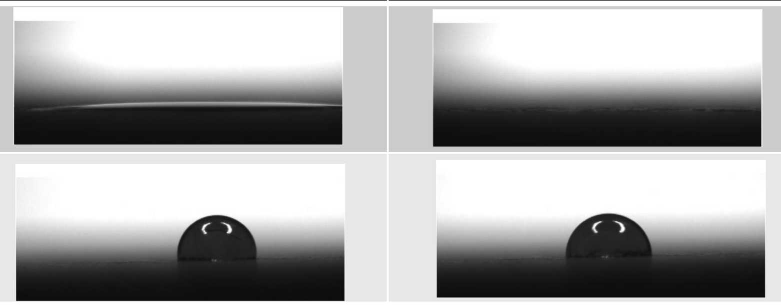




Absorption Challenge: Pictures taken ~27 min after 2µL HD contamination. Panels treated with a variety of perfluoronated alkanes resist spread by over 10×. An isopropyl alcohol rinse after 30 minutes removed >95% of the agent on the treated panels, which retained 10-35× less agent than the untreated coating.
Bottom left: Treated panels showed continued resistance to HD after being abraded by a laboratory wipe.



Precursor Assessment: Pictures of panels untreated, treated with air, and treated with precursor indicate the importance of precursor inclusion.



Time	12 s	3600 s
Untreated		
Treated		

Contact angle measurements of a 2µL VX droplet on treated and untreated paint.

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 5-35×.
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. This method can also be used to treat surfaces to increase hydrophobic properties (e.g. Air force coatings). While the vacuum plasma treatment method may not be applicable to 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. Therefore, the technology to develop a surface treatment or coating to dramatically improve agent resistance is possible, especially if developed for use at small scale (for protection of high at-risk assets).

References

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.

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