

# Reduced Chemical Warfare Agent Sorption in Polyurethane-Painted Surfaces via Plasma-Enhanced Chemical Vapor Deposition of Perfluoroalkanes

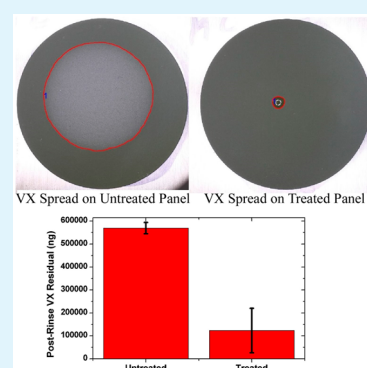
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## S Supporting Information

**ABSTRACT:** Perfluoroalkylation via plasma chemical vapor deposition has been used to improve hydrophobicity of surfaces. We have investigated this technique to improve the resistance of commercial polyurethane coatings to chemicals, such as chemical warfare agents. The reported results indicate the surface treatment minimizes the spread of agent droplets and the sorption of agent into the coating. The improvement in resistance is likely due to reduction of the coating's surface free energy via fluorine incorporation, but may also have contributing effects from surface morphology changes. The data indicates that plasma-based surface modifications may have utility in improving chemical resistance of commercial coatings.



**KEYWORDS:** chemical warfare agent resistance, plasma treatment, paint, polyurethane

Chemical warfare agents (CWAs) are among the more lethal substances known to mankind.<sup>1</sup> Not only do they pose an immediate threat to both civilian and military populations upon release<sup>2,3</sup> but they also pose a threat via sorption on and into porous surfaces, creating equally lethal off-gassing and contact hazards over extended periods of time. Painted surfaces in particular, such as those found on vehicles and on buildings, provide a sufficient sink for agent uptake.<sup>4,5</sup> Perfluoroalkylation via plasma chemical vapor deposition (PECVD) is a well-known method for creating hydrophobic coatings.<sup>6</sup> Furthermore, plasma based surface treatments have been used to alter surface and bulk properties of other materials.<sup>7–11</sup> Herein we present a method for treating urethane-painted surfaces with a perfluoroalkane plasma, and the resulting impact on the agent resistant properties of the material. PECVD with perfluoroalkanes has been shown to modify many substrates, altering their surface, as generally shown in Figure 1.

Scanning electron microscopy (SEM) images shown in Figure 2 illustrate the difference between treated and untreated panels. In both cases, materials are comprised of metal oxide and other particles dispersed throughout the urethane coating. The untreated coating exhibits large pores in the 1–30  $\mu\text{m}$  range that could provide sites for CWA sorption, as determined by mercury porosimetry (Figure S1 in the Supporting Information). The plasma-treated sample, however, shows the effects of two mechanisms. First, prior to plasma treatment the SEM image shows metal oxide pigments and fillers were mostly

enclosed by organic material. Post treatment, the pigments and fillers are more exposed, likely due to etching away of the organic component of the paint. This likely increases the roughness of the surface of the paint on the submicrometer scale, which may decrease wetting properties of the surface with respect to water and other chemicals.

In addition to SEM images, the treated and untreated panels were analyzed by confocal optical profilometry to determine if there was any observable macroscopic (0.05–1 mm) scale changes in the paint morphology and roughness. No clear differences were observed (Figure S2 in the Supporting Information).

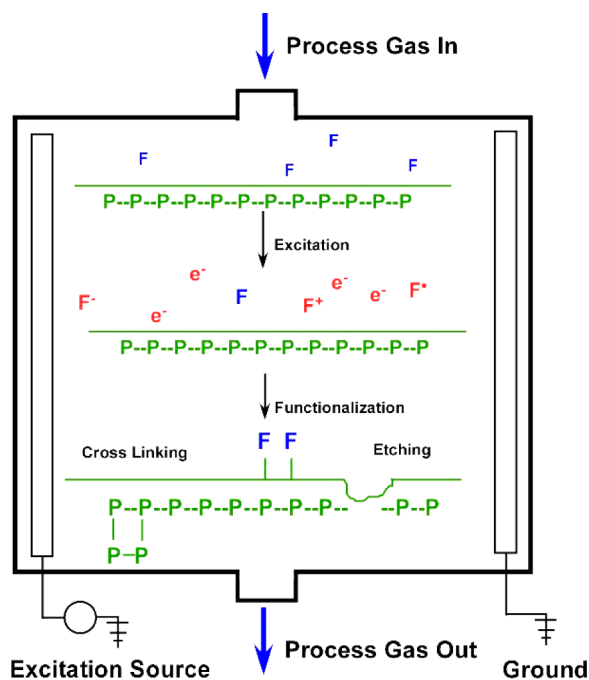
X-ray photoelectron spectroscopy (XPS) was also performed on untreated and treated paint panels. The results in Table 1 and Figure S8 in the Supporting Information suggest that the PECVD treatment incorporates a significant amount of fluorine onto the surface of the paint panel. The presence of fluorine most likely contributes to the diminished surface energy and promotes sessile drop formation.

As seen in Table 1, the relative amount of carbon near the surface of the film dramatically decreased after the plasma treatment, while the concentration of oxygen and nitrogen in the polyurethane increases slightly. These results suggest that

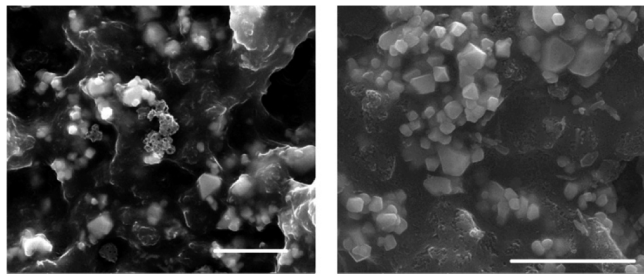
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**Figure 1.** Schematic showing potential mechanisms of surface modification using PECVD.



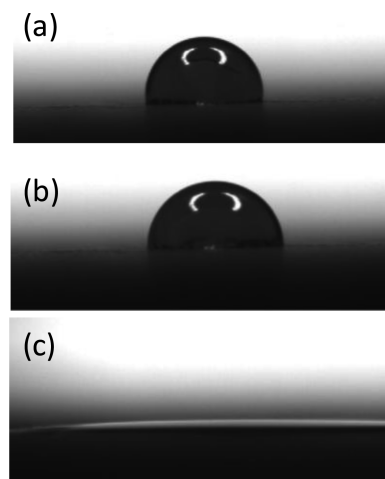
**Figure 2.** SEM images of untreated (left) and plasma-treated (right) urethane surfaces. The bar in the lower right corner shows a 5 μm scale.

**Table 1.** Near Surface Atomic % Values as Calculated via XPS Analysis; Trace Species from Paint Additives Were Excluded

peak	untreated	plasma
C 1s	77.4	48.5
O 1s	21.4	37.9
N 1s	1.2	3.7
F 1s	0.0	9.9

some carbon is removed from the polymer in the etching process and that fluorine is incorporated into the paint surface. Shifts in the binding energy of ca. 2 eV to higher values for both the C 1s and O 1s peaks are consistent with incorporation of CF species during treatment.

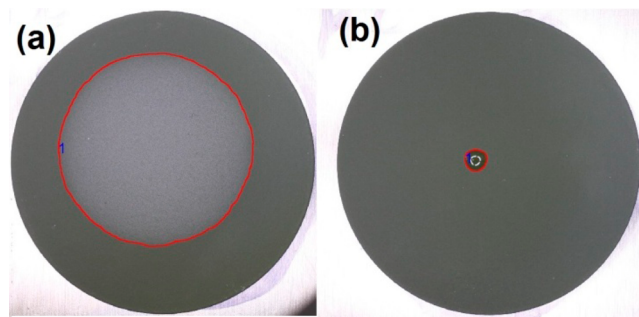
Contact angle measurements were performed on both untreated and treated panels contaminated with a 2 μL droplet of VX. On the treated panel (Figure 3a), the VX droplet had a contact angle of 97.40°; an hour later, the VX droplets remained sessile, with a slightly reduced contact angle of 90.97° (Figure 3b). This compares to immediate sorption into the untreated polyurethane sample. The contact angle of the VX droplet on the untreated panel was not reliably measured at any



**Figure 3.** Two microliter VX drops on urethane painted surface for (a) plasma-treated surface after 12 s, (b) plasma-treated surface after 60 min, and (c) untreated surface after 12 s.

time point, but was estimated to be below 6° at 6 s and below 5° at 12 s (Figure 3c).

Remaining agent studies were conducted to quantify resistance to agent sorption into the substrate due to the plasma treatment (detailed in the Supporting Information). Briefly, as-obtained and PECVD-treated panels were equilibrated at 50% RH and 25 °C for 24 h, challenged with 2 μL of VX, and aged for 1 h in a covered in a Petri dish. Top-down images were collected at the end of the age period; typical examples of which are shown in Figure 4. Following the age



**Figure 4.** Two microliter VX drops on 2 in. diameter polyurethane painted panels 58 min after contamination: (a) untreated surface, (b) plasma-treated surface. The extent of liquid spreading is indicated by the red outline.

period, the panels were rinsed with 3 aliquots of 20 mL 18 MΩ deionized water, and then placed in a jar with 20 mL of isopropyl alcohol to extract remaining VX for 1 h. Both the rinsate and the extraction solvent were analyzed via an Agilent triple quadrupole LC/MS to determine the amount of VX that was rinsed off and the amount remaining in the panel after rinsing with low detection limits (<1 ng/mL). Positive control experiments are summarized in the Supporting Information. The average results along with relative standard deviations of three replicate panel tests are shown in Table 2. Although uncertainties due to liquid delivery and variability in performance of the commercial coating do exist, the two-tailed P value of an unpaired *t* test is 0.0015 for the remaining agent values, meaning the values are considered to be statistically significant. A greater amount of VX was rinsed off of the treated panels,

**Table 2. Mass (ng) VX Measured in the Rinsate and Extracts from Treated and Untreated Panels**

parameter	untreated panel	std. dev.	treated panel	std. dev.
rinsate	1 113 495	16 1651	1 571 221	110 415
remaining Agent	569 261	24 636	123 725	96 703

showing improved decontamination efficacy, and less VX was found to remain in the panel, demonstrating the treated panel's improved resistivity to VX.

Droplets are classically described as existing in the Wenzel or Cassie–Baxter states. The Wenzel model describes a homogeneous wetting regime, where the microstructure of a porous substrate is fully wetted by the liquid.<sup>12</sup> In contrast, the Cassie–Baxter model is appropriate when the liquid does not fully wet the microporous surface, resulting in air pockets at the liquid–solid interface. In this model, the droplet should roll off at a certain angle as is observed by the lotus effect. In this case, the droplets of chemical agent do not roll off and instead are pinned, suggesting that the droplet may exist in the Wenzel or combined Cassie–Wenzel wetting regime, where larger size pores are wetted. This increases the liquid solid contact area and correspondingly the adhesive force due to electrostatic forces.

In summary, we have demonstrated the use of PECVD of perfluorocarbons to dramatically improve the oleophobicity of commercial polyurethane paints. XPS demonstrates that there is a significant amount of fluorine at the surface after treatment, and that a significant amount of the carbon near the surface is in fact fluorinated to some degree. SEM results suggest etching of the carbon surface, revealing pigment, flattener, and filler particles and therefore increasing the surface roughness on the micrometer and nanometer scales. Optical profilometry does not suggest a macroscale change in surface morphology.

Testing against chemical warfare agents, it has been found that the PECVD treatment improves coating resistance against one of the more challenging threats, VX. The fact that VX droplets are pinned to the surface and do not roll off upon rotation of the substrate (Figure S6 in the Supporting Information) supports the hypothesis that there are two mechanisms leading to the improved resistance: (1) reduction in surface energy due to incorporation of the fluorinated functional groups, and (2) increase in the nano- or micrometer scale roughness, which has been shown to affect droplet spreading in several studies.<sup>13,14</sup> The fact that the droplets do not move even upon gentle shaking suggests that the droplets exist in the Wenzel state or a combined Cassie–Wenzel state. In this state, the liquid has at least partially penetrated into the roughness of the surface, however pockets of air may remain in smaller cavities.<sup>15</sup> This results in a high-liquid-surface contact area, in which case electrostatic forces are a major driver in droplet adhesion.

In conclusion, these results for the first time show that PECVD and similar techniques may be able to be used to improve resistance of commercial coatings against chemical agents and other undesirable contaminants. Future work will focus on the use of contact angle hysteresis measurements and more detailed study of the impact of the PECVD on commercial paints and if this treatment negatively impacts other paint properties.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Detailed experimental details, mercury porosimetry data of the untreated coating, confocal optical profilometry data of untreated and PECVD treated polyurethanes, contact angle measurements of the simulant DMMP on treated coatings, preliminary testing comparing the spread of DMMP droplets on two different treated panels, images of preliminary results with VX showing drop pinning, and images of deionized water and chemical agent HD droplets on treated polyurethane. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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### Notes

The authors declare no competing financial interest.

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## ■ ABBREVIATIONS

PECVD, plasma-enhanced chemical vapor deposition  
CWA, chemical warfare agent  
XPS, X-ray photoelectron spectroscopy  
SEM, scanning electron spectroscopy  
DMMP, nerve agent simulant dimethyl methylphosphonate  
VX, nerve agent O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate  
LC/MS, liquid chromatography mass spectrometry

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