Bioinspired Surface Treatments for Improved Decontamination: Durable Hydrophobic Coating

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This effort evaluates bioinspired coatings for use in a top-coat type application to identify those technologies that may improve decontamination capabilities for painted surfaces. This report details results for evaluation of a commercially available, transparent, hydrophobic coating. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphate, and diisopropyl fluorophosphates following treatment of contaminated surfaces with a soapy water solution is reported. Wetting behaviors and target droplet diffusion on the surfaces are also discussed.
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EXECUTIVE SUMMARY

The Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) initiated a program in January 2015 for evaluation of bioinspired treatments suitable for use as a top coat on painted surfaces with the intention of achieving improved aqueous decontamination of these materials. Funding was provided by the Defense Threat Reduction Agency (DTRA, CB10125). This report details results for evaluation of a clear, durable hydrophobic coating generated through a sol-gel process. The coating is flexible, applicable to a range of substrates, and provides corrosion protection. The material was deposited on polyurethane paint coated aluminum coupons. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphonate, and diisopropyl fluorophosphate following treatment of contaminated surfaces with a soapy water solution is reported along with droplet diffusion on the surfaces and wetting angles.
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BIOINSPIRED SURFACE TREATMENTS FOR IMPROVED DECONTAMINATION: DURABLE HYDROPHOBIC COATINGS

INTRODUCTION

The DoD Chemical and Biological Defense Program (CBDP) seeks to provide protection of forces in a contaminated environment including contamination avoidance, individual protection, collective protection, and decontamination. In January 2015, the Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) began an effort funded through the Defense Threat Reduction Agency (DTRA, CB10125) intended to evaluate top-coat type treatments suitable for application to painted surfaces for reduction of chemical threat agent retention following standard decontamination approaches. The effort sought to survey relevant and related areas of research and evaluate identified technologies under appropriate methods to determine efficacy, scalability, and durability. The current document summarizes results for one of the identified technologies, a coating marketed as Gentoo. This product was developed by Luna Innovations, Inc and is based on a sol-gel process. The resulting material is a dense polymer coating that has been subjected to a number of industry standard evaluations including transparency and abrasion resistance. Gentoo is a two part coating system that is mixed and applied as a single coat using flow-coating, dip-coating, HVLP spraying, or deposition by brush or roller. The coating is 4 to 6 µm thick and can be applied to painted, plated, and bare metallic substrates as well as to glass and primed plastics.

For the complete system, aluminum coupons were coated with a polyurethane paint system by NRL and were provided to Luna Innovations, Inc. (Figure 1). Following deposition of the Luna Gentoo coating, coupons were returned to NRL for evaluation using standard approaches including measurement of sessile, sliding, and shedding contact angles and quantification of retention for the simulant compounds. The coating had little impact on the visible characteristics of the coupons.

METHODS

Sessile contact angles for samples evaluated under this effort used three 3 µL droplets per surface with each droplet measured independently three times for each of three targets, water, ethylene glycol, and n-heptane. Geometric surface energy was calculated based on the water and ethylene glycol interactions using software designed for the DROPimage goniometer package. Sliding angles were determined using 5
µL droplets. The droplet was applied at 0° after which the supporting platform angle was gradually increased up to 60°. Sliding angles for each of the liquids were identified as the angle for which movement of the droplet was identified. Shedding angles for each liquid were determined using 12 µL droplets initiated 2.5 cm above the coupon surface. Changes in base angle of 10° were utilized to identify the range of droplet shedding angle based on a complete lack of droplet retention by the surface (not sliding). The angle was then reduced in steps of 1° to identify the minimum required angle. Droplet diameters were determined using tools provided by Adobe Photoshop CS3. Droplets of 5 mL were applied to the surfaces and images were collected at 30 s intervals for 5 min followed by images at 5 min intervals for a total of 30 min. DFP samples were kept covered for the duration of the experiment to minimize evaporation. In some cases, reflections from the glass cover can be seen in the images.

Simulant exposure and evaluation methods were based on the tests developed by Edgewood Chemical Biological Center referred to as Chemical Agent Resistance Method (CARM). Standard target exposures utilized a challenge level of 10 g/m². The painted coupons were 0.00101 m²; the 10 g/m² target challenge was applied to the surfaces as two equally sized neat droplets. Following application of the target, coupons were aged 1 h prior to use of a gentle stream of air to expel target from the surface. Samples were then rinsed with soapy water (0.59 g/L Alconox in deionized water). The rinsed coupons were soaked in isopropanol for 30 min to extract remaining target; this isopropanol extract was analyzed by the appropriate chromatography method to determine target retention on the surface.

For paraoxon analysis, a Shimadzu High Performance Liquid Chromatography (HPLC) system with dual-plunger parallel flow solvent delivery modules (LC-20AD) and an auto-sampler (SIL-20AC; 40 µL injection volume) coupled to a photodiode array detector (SPD-M20A; 277 nm) was used. The stationary phase was a C18 stainless steel analytical column (Luna, 150 mm x 4.6 mm, 3 µm diameter; Phenomenex, Torrance, CA) with an isocratic 45:55 acetonitrile: 1% aqueous acetic acid mobile phase (1.2 mL/min). For analysis of methyl salicylate (MES), diisopropyl fluorophosphate (DFP), and dimethyl methylphosphonate (DMMP), gas chromatography-mass spectrometry (GC-MS) was accomplished using a Shimadzu GCMS-QP2010 with AOC-20 auto-injector equipped with a Restex Rtx-5 (30 m x 0.25 mm ID x 0.25 µm df) cross bond 5% diphenyl 95% dimethyl polysiloxane column. A GC injection temperature of 200°C was used with a 1:1 split ratio at a flow rate of 3.6 mL/min at 69.4 kPa. The oven gradient ramped from 50°C (1 min hold time) to 180°C at 15°C/min and then to 300°C at 20°C/min where it was held for 5 min.

RESULTS

Analysis of the support surface in the absence of additional coatings provides a point of comparison for evaluating the benefits of the surface treatment. Each table includes data on the relevant support material, a painted aluminum coupon as well as that for a Fomblin Y oiled painted aluminum coupon and that for a smooth fluoropolymer coating on the painted aluminum coupon. The fluoropolymer coating is a previously reported poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) layer. The fluorinated oil and the fluoropolymer coating reduce the surface energy of the coupons (Table 1 and Figure 2). No sliding was noted on any of the evaluated surfaces below 60°. Shedding angles for the oiled surface were between 35° and 50° for test liquids. For the Gentoo coating, no sliding or shedding was noted for water, ethylene glycol, or heptane. This is contrary to reported results for this coating; however, the painted support surface used here is not smooth. The polymer, glass, and metal support surfaces previously used are significantly more homogeneous than the surface resulting from deposition of the polyurethane paint system. Application of the Gentoo coating significantly reduced the surface energy of the painted coupon, increasing contact angles for the three test liquids.
Table 1 – Sessile, Sliding, and Shedding Contact Angles on Aluminum Supports

<table>
<thead>
<tr>
<th>Coupon</th>
<th>Liquid</th>
<th>Sessile Angle</th>
<th>Sliding Angle</th>
<th>Shedding Angle</th>
<th>Geometric Surface Energy (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Support</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paint Only</td>
<td>water</td>
<td>47.5 ± 1.1</td>
<td>&gt;60</td>
<td>&gt;60</td>
<td>71.9 ± 5.1</td>
</tr>
<tr>
<td></td>
<td>ethylene glycol</td>
<td>55.7 ± 2.1</td>
<td>&gt;60</td>
<td>&gt;60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n-heptane</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Fomblin Y Oiled Paint</td>
<td>water</td>
<td>73.1 ± 2.1</td>
<td>&gt;60</td>
<td>46.7 ± 3.3</td>
<td>32.2 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>ethylene glycol</td>
<td>52.5 ± 0.61</td>
<td>&gt;60</td>
<td>49.8 ± 4.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n-heptane</td>
<td>40.1 ± 2.9</td>
<td>&gt;60</td>
<td>36.6 ± 3.3</td>
<td></td>
</tr>
<tr>
<td>Smooth Fluoropolymer</td>
<td>water</td>
<td>116.8 ± 1.1</td>
<td>&gt;60</td>
<td>&gt;60</td>
<td>10.5 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>ethylene glycol</td>
<td>100.3 ± 1.5</td>
<td>&gt;60</td>
<td>&gt;60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n-heptane</td>
<td>19.1 ± 0.79</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Luna Gentoo Coating</td>
<td>water</td>
<td>99.5 ± 0.62</td>
<td>&gt;60</td>
<td>&gt;60</td>
<td>14.5 ± 0.34</td>
</tr>
<tr>
<td></td>
<td>ethylene glycol</td>
<td>86.4 ± 0.21</td>
<td>&gt;60</td>
<td>&gt;60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n-heptane</td>
<td>29.3 ± 0.92</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

The tendency of droplets to spread across the surfaces was also evaluated (Figure 3; Appendices A through D). For these studies, droplets of the simulants (5 µL) were utilized. The spread of the droplets was quantified by measuring the diameter of the droplets in the images over time (Figure 4). For the paint only samples, MES and DFP spread quickly reaching the edges of the coupon at 10 and 2 min, respectively. DMMP does not spread during the course of the 30 min incubation. Similar behavior is noted for the Fomblin Y oiled coupons. The fluoropolymer coating significantly reduces spread of the three targets on the coupon. The Gentoo coating completely prevents spread of all three targets. The initial droplet diameter for the DFP on this surface is slightly larger than that noted for the other targets, but it does not change over the course of the experiment.
Fig. 3 — Images of coupons immediately following MES deposition (top) and images of the coupons at 30 min following deposition (bottom): for a painted coupon (A), a Fomblin Y oiled coupon (B), a fluoropolymer treated coupon (C), and a Gentoo treated coupon (D).

Fig. 4 — Droplet diameters over time following exposure to DFP (black), MES (red), and DMMP (blue) for a painted coupon (A), a painted coupon oiled with Fomblin Y (B), a painted coupon with a smooth fluoropolymer coating (C), and a painted coupon with the Luna Gentoo coating (D).
The coupons were subjected to several cycles of simulant exposure (10 g/m²), aging, washing, and drying over a period of a week. No change in appearance or performance was noted for the cycled samples. When the soapy water process was employed (Figure 5; Table 2), retention of all targets was less for the Fomblin Y lubricated paint treatments than for the paint only surfaces. Similar reduction in target retention was noted for the fluoropolymer treated coupons. The Gentoo coating provided significantly greater reduction in retention for all four targets considered under this study than either the oiled or fluoropolymer treated surfaces. Retention of paraoxon, MES, DMMP, and DFP was more than an order of magnitude less for the Gentoo coating than the noted for the painted surface.

For paint only coupons, retention was significant but was less than that of paint only coupons that were extracted with no rinsing or decontamination steps. For comparison purposes, paint only coupons that were not rinsed prior to isopropanol extraction retained the following: paraoxon – 9.84 g/m², MES – 9.54 g/m², DMMP – 9.90 g/m², DFP - 7.39 g/m². Though the nominal target application was 10 g/m², recovery from surfaces was always less than this value. Losses due to evaporation would be expected, especially for DFP. Additional losses likely occur during rinse steps due to agent interaction with the untreated region of the coupon; the back of these coupons is unpainted aluminum.

![Figure 5](image-url)

**Fig. 5** — Target retention by coupons following treatment with an air stream and rinsing with soapy water: paint (red), oiled paint (black), smooth fluorinated polymer (blue), and the Luna Gentoo coating (green) plotted on a linear (A) and a log scale (B).

<table>
<thead>
<tr>
<th>Coupon</th>
<th>Paraoxon</th>
<th>MES</th>
<th>DMMP</th>
<th>DFP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Support</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paint Only</td>
<td>5.48</td>
<td>6.20</td>
<td>4.28</td>
<td>0.52</td>
</tr>
<tr>
<td>Fomblin Y Oiled Paint</td>
<td>1.24</td>
<td>2.85</td>
<td>0.59</td>
<td>0.34</td>
</tr>
<tr>
<td>Smooth Fluoropolymer</td>
<td>1.47</td>
<td>2.74</td>
<td>0.34</td>
<td>0.41</td>
</tr>
<tr>
<td>Luna Gentoo Coating</td>
<td>0.13</td>
<td>0.10</td>
<td>0.16</td>
<td>0.05</td>
</tr>
</tbody>
</table>

ND = not detected

**Table 2** – Target Retention (g/m²) Following 1 h Aging on Aluminum Supports

**CONCLUSIONS**

The Gentoo coating from Luna Innovations, Inc provides reduction in surface energy and significantly improved performance during processing than that noted for the paint only surfaces. The lack of noted sliding and shedding behavior is likely due to the textured nature of the underlying painted surface. Prior work, for example with deposition on aluminum substrates and aircraft canopies, returned low sliding and
shedding angles, especially for water. As with many of the coatings evaluated under this effort, the Gentoo coating produces a slightly wet look on the painted coupons (Figure 1 and Appendices). Spectrophotometric analysis is necessary to determine the overall impact on color and reflectivity. Given the reductions in target retention noted for the simulant compounds evaluated here, additional studies on performance of aged coupons and using chemical agents should be considered.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. Bryan Koene, Dr. Rebecca Martin, and Ms. Miranda Thornton of Luna Innovations, Inc. for supplying the samples evaluated under this study. This research was sponsored by the Defense Threat Reduction Agency (DTRA, CB10125).

REFERENCES

Appendix A

IMAGES OF PAINTED COUPONS
Fig. A1 — DFP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 10 (L), 15 (M), 20 (N), 25 (O), and 30 (P) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.
Fig. A2 — MES on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.
Fig. A3 — DMMP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.
Appendix B

IMAGES OF FOMBLIN Y OILED COUPONS
Fig. B1 — DFP on Fomblin Y oiled paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.
Fig. B2 — MES on Fomblin Y oiled paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) min following application of the target.
Fig. B3 — DMMP on Fomblin Y oiled paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) min following application of the target.
Appendix C

IMAGES OF FLUOROPOLYMER TREATED COUPONS
Fig. C1 — DFP on the fluoropolymer coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.
Fig. C2 — MES on the fluoropolymer coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.
Fig. C3 — DMMP on the fluoropolymer coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.
Appendix D

IMAGES OF GENTOO TREATED COUPONS
Fig. D1 — DFP on Gentoo coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.
Fig. D2 — MES on Gentoo coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.
Fig. D3 — DMMP on Gentoo coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.