Bioinspired Surface Treatments for Improved Decontamination: Anti-Ice Coatings

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## Bioinspired Surface Treatments for Improved Decontamination: Anti-Ice Coatings

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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, anti-ice 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. The intention was to provide 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 series of durable anti-ice coatings developed by the University of Houston. 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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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. The intention was to reduce 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 developed by the University of Houston (UH) and providing the basis for a technology from SurfEllent, Inc. This product is a durable anti-ice coating demonstrated for use on a range of surfaces under varying environmental conditions. Current applications for the technology focus on protection of aircraft, surface vessels, and power lines from threats inherent in formation of ice layers.

The materials provided by Dr. H. Ghasemi of UH were inspired by the North American Wood Frog. [1] This animal can tolerate freezing of 65% of their total body water during winter. The coatings are based on ferrofluids. Deposition includes application of a magnetic field to lock the fluid in place. These oil based fluids have been shown to have low evaporation rates and to withstand high shear stresses. The materials can be self-healing in the presence of a magnetic field. For the complete system, aluminum coupons were coated with a polyurethane paint system by NRL and were provided to Dr. H. Ghasemi (Figure 1). Following deposition of the coatings, 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. Three anti-ice variants were provided; the primary difference between the materials was intended to be in durability, A1-10 offering the least durability, followed by A1-11, and A1-21 offering the greatest durability.

![Fig. 1 — Images of a painted coupon (A), a painted coupon with Fomblin Y (B), a painted coupon with smooth fluoropolymer coating (C), a painted coupon with A1-10 (D), a painted coupon with A1-11 (E), and a painted coupon with A1-21(F).](image)

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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
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). [3]
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. [4] 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 control surfaces below 60°. Shedding angles for the oiled surface were
between 35° and 50° for test liquids. For the UH coatings, no sliding or shedding behaviors were observed for the 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>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 ± 0.6</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 ± 0.8</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>A1-11</td>
<td>water</td>
<td>100.2 ± 2.0</td>
<td>&gt;60</td>
<td>&gt;60</td>
<td>12.7 ± 0.89</td>
</tr>
<tr>
<td></td>
<td>ethylene glycol</td>
<td>89.7 ± 0.8</td>
<td>&gt;60</td>
<td>&gt;60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n-heptane</td>
<td>11.6 ± 1.1</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>A1-12</td>
<td>water</td>
<td>98.9 ± 2.7</td>
<td>&gt;60</td>
<td>&gt;60</td>
<td>13.3 ± 2.24</td>
</tr>
<tr>
<td></td>
<td>ethylene glycol</td>
<td>90.9 ± 1.8</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>A1-21</td>
<td>water</td>
<td>95.9 ± 2.3</td>
<td>&gt;60</td>
<td>&gt;60</td>
<td>16.8 ± 2.9</td>
</tr>
<tr>
<td></td>
<td>ethylene glycol</td>
<td>87.1 ± 2.8</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>
</tbody>
</table>

Fig. 2 — Geometric surface energy for the evaluated coatings.

The tendency of droplets to spread across the surfaces was also evaluated (Figure 3; Appendices A through F). 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 UH coatings A1-10 and A1-11 reduced the spread of paraoxon and MES. DMMP spread across the A1-11 was slightly greater than that on the paint only surface, similar to that of the oiled surface. The A1-21 surface increased spread of DMMP and reduced the spread of MES as compared to the painted surface. The DFP droplet appeared to be adsorbed by this surface at 15 min and the DMMP droplet appeared to be adsorbed at 25 min.
When the soapy water process (CARM) 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 coupons treated with A1-10 retained significantly less paraoxon than the paint only or the fluoropolymer treated coupons. All three variants, A1-10, A1-11, and A1-21 provided slight reductions in retention of DMMP. MES retention by the UH coatings was similar to that observed for the oiled and fluoropolymer coated coupons. Unfortunately, DFP retention by the UH coatings was significantly higher than that noted for the control surfaces. The coupons were subjected to several cycles of simulant exposure (10 g/m²), aging, washing, and drying over a period of a week. Some marking of the surfaces following DFP exposure was noticed, but all changes to appearance were minimal.

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.
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), a painted coupon with A1-10 (D), a painted coupon with A1-11 (E), and a painted coupon with A1-21 (F).
CONCLUSIONS

The anti-ice coatings from the University of Houston provide significant reduction in surface energy over the paint only surfaces though no sliding or shedding behaviors were noted. The materials reduced retention of paraoxon, had little impact on DMMP retention, and had a negative impact on DFP retention. As with many of the treatments evaluated under this effort, the UH coatings produced changes in the appearance of the painted coupons (Figure 1 and Appendices). Spectrophotometric analysis is necessary to determine the overall impact on color and reflectivity. While the utility of the UH coatings in prevention of icing has been thoroughly demonstrated by their previous work, the aspects of the materials contributing to those behaviors did not translate to reduced target retention. This lack of relationship between wetting behavior and retention has been noted for previously evaluated surfaces.[4] The UH coatings evaluated under this study are unlikely to meet the goals of the effort in improved performance under standard decontamination conditions.
ACKNOWLEDGEMENTS

The authors would like to thank Dr. Hadi Ghasemi of the University of Houston and SurfEllent, 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 A1-10 TREATED COUPONS
Fig. A1 — DFP on the A1-10 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. A2 — MES on the A1-10 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. A3 — DMMP on the A1-10 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 B

IMAGES OF A1-11 TREATED COUPONS
Fig. B1 — DFP on the A1-11 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. B2 — MES on the A1-11 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. B3 — DMMP on the A1-11 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 C

IMAGES OF A1-21 TREATED COUPONS
Fig. C1 — DFP on the A1-21 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. C2 — MES on the A1-21 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 A1-21 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 PAINTED COUPONS
Fig. D1 — 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. D2 — 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. D3 — 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 E

IMAGES OF FOMBLIN Y OILED COUPONS
Fig. E1 — 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. E2 — 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. E3 — 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 F

IMAGES OF FLUOROPOLYMER TREATED COUPONS
Fig. F1 — 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. F2 — 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. F3 — 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.