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Bioinspired Surface Treatments for Improved Decontamination: Cyanoacrylate Coatings

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14. ABSTRACT 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 top coat applications based on an approach adapted from published literature. The coatings are use a mixture of perfluorohexyltrichlorosilane (PTFS) and either n-butyl 2-cyanoacrylate or ethyl 2-cyanoacrylate. 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 top coat applications based on an approach adapted from published literature. The coatings are use a mixture of perfluorohexyltrichlorosilane (PTFS) and either *n*-butyl 2-cyanoacrylate or ethyl 2-cyanoacrylate. The approach can be used to produce multi-re-entrant surfaces on fabrics. Here, the materials were deposited on polyurethane paint coated aluminum coupons; the method is not expected to produce texture on the surfaces. 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: CYANOACRYLATE 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 type of identified technology.

A recent publication described multi-re-entrant, hierarchically structured coatings based on fluorosilanes and cyanoacrylates.[1] The coatings can be applied using spray or immersion techniques. The coatings are described as transparent, robust, mechanically durable, and self-healing. They offer repellence to liquids, including those with low surface tension. The hierarchical structures are organized across local domains and can be applied to a wide range of support materials including fabrics. While described for liquid repellence with a focus on anti-ice coatings, these characteristics may also offer advantages to the application under consideration here.

Here, two types of coating were prepared. PTFS-BCA used perfluorohexyltrichlorosilane (PTFS) with *n*-butyl 2-cyanoacrylate. PTFS-ECA used PTFS with ethyl 2-cyanoacrylate. These acrylate derivatives are used in medical grade (BCA) and other adhesive products. The reported coatings used a dip-coating process that was not expected to produce the textures described for other deposition methods.[1] For the complete evaluated systems, aluminum coupons were coated with a polyurethane paint system. The coatings were applied to this support material following an accelerated cure process. Materials were evaluated using standard approaches including measurement of sessile, sliding, and shedding contact angles and quantification of retention for the simulant compounds. The coatings had little impact on the visible characteristics of the coupons (Figure 1).

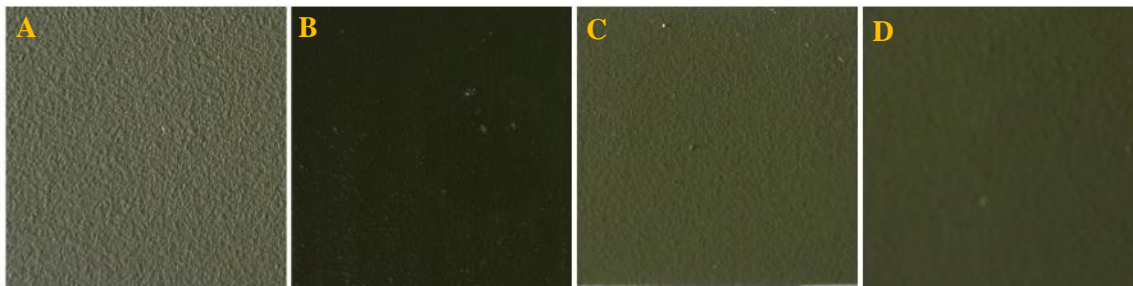


Fig. 1 — Images of a painted coupon (A), a painted coupon with Fomblin Y (B), a painted coupon with PTFS-BCA (C) and a painted coupons with PTFS-ECA (D).

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 μL 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).[2] Standard target exposures utilized a challenge level of 10 g/m^2 . The painted coupons were 0.00101 m^2 ; the 10 g/m^2 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 analysis of paraoxon, 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 $15^\circ\text{C}/\text{min}$ and then to 300°C at $20^\circ\text{C}/\text{min}$ where it was held for 5 min.

Coating Synthesis.

Synthesis of the cyanoacrylate coatings was adapted from a published report.[1] Painted coupons were rinsed with 2-propanol and dried at 65°C . Coupons were then soaked (5 min) in 20 wt % PFTS (nonafluorohexyltrichlorosilane) in dichloropentafluoropropane, with $\sim 10 \text{ mg/mL}$ BCA (*n*-butyl 2-cyanoacrylate) or ECA (ethyl 2-cyanoacrylate). Coated substrates were cured at 70°C for 2 h.

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. The fluorinated oil reduces the surface energy of the coupons (Table 1 and Figure 2). Application of the PFTS-BCA coating significantly reduced the surface energy of the painted coupon, increasing contact angles for water and ethylene glycol. PFTS-ECA further reduced the observed surface energy with a higher ethylene glycol contact angle and a similar water contact angle. Sliding behaviors were not observed on any of the

coupons. While shedding was observed for the oiled coupon, it was not observed on either of the PFTS coatings.

Table 1 – Sessile, Sliding, and Shedding Contact Angles on Aluminum Supports

Coupon	Liquid	Sessile Angle	Sliding Angle	Shedding Angle	Geometric Surface Energy (mJ/m ²)
Aluminum Support					
Paint Only	water	47.5 ± 1.1	>60	>60	71.9 ± 5.1
	ethylene glycol	55.7 ± 2.1	>60	>60	
	n-heptane	--	--	--	
Fomblin Y Oiled Paint	water	73.1 ± 2.1	>60	46.7 ± 3.3	32.2 ± 1.6
	ethylene glycol	52.5 ± 0.61	>60	49.8 ± 4.9	
	n-heptane	40.1 ± 2.9	>60	36.6 ± 3.3	
PFTS-BCA	water	109.3 ± 1.9	>60	>60	12.3 ± 2.1
	ethylene glycol	95.5 ± 2.6	>60	>60	
	n-heptane	--	--	--	
PFTS-ECA	water	104.8 ± 1.7	>60	>60	10.8 ± 1.5
	ethylene glycol	96.6 ± 2.1	>60	>60	
	n-heptane	--	--	--	

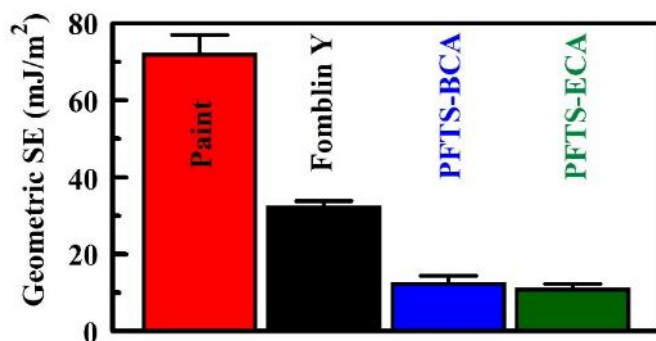


Fig. 2 — Geometric surface energy (mJ/m²) for the evaluated coatings.

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. DMMP and MES did not spread on either the PTFS-ECA or PTFS-BCA coated coupons. DFP spread was slowed on the coatings as compared to the painted surface. Initial droplet sizes for DFP were also smaller than those noted for the painted or oiled surfaces.

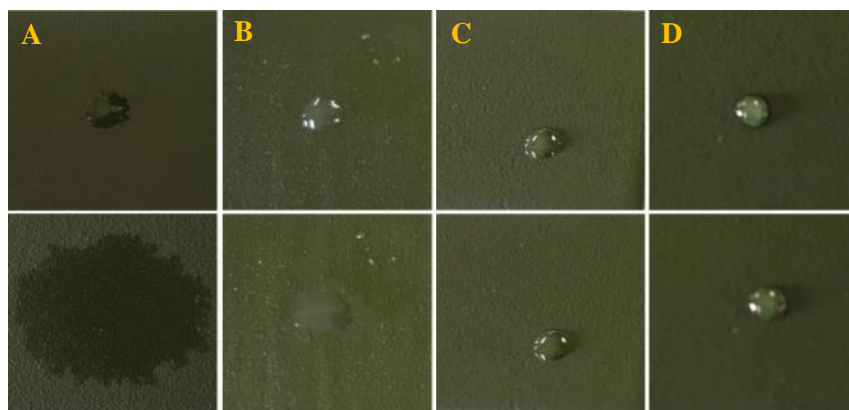


Fig. 3 — Images of coupons immediately following MES deposition (top) and images of the coupons at 30 min following deposition (bottom): for a painted coupon (A), a Fomblin Y oiled coupon (B), a PTFS-BCA treated coupon (C), and a PTFS-ECA treated coupon (D).

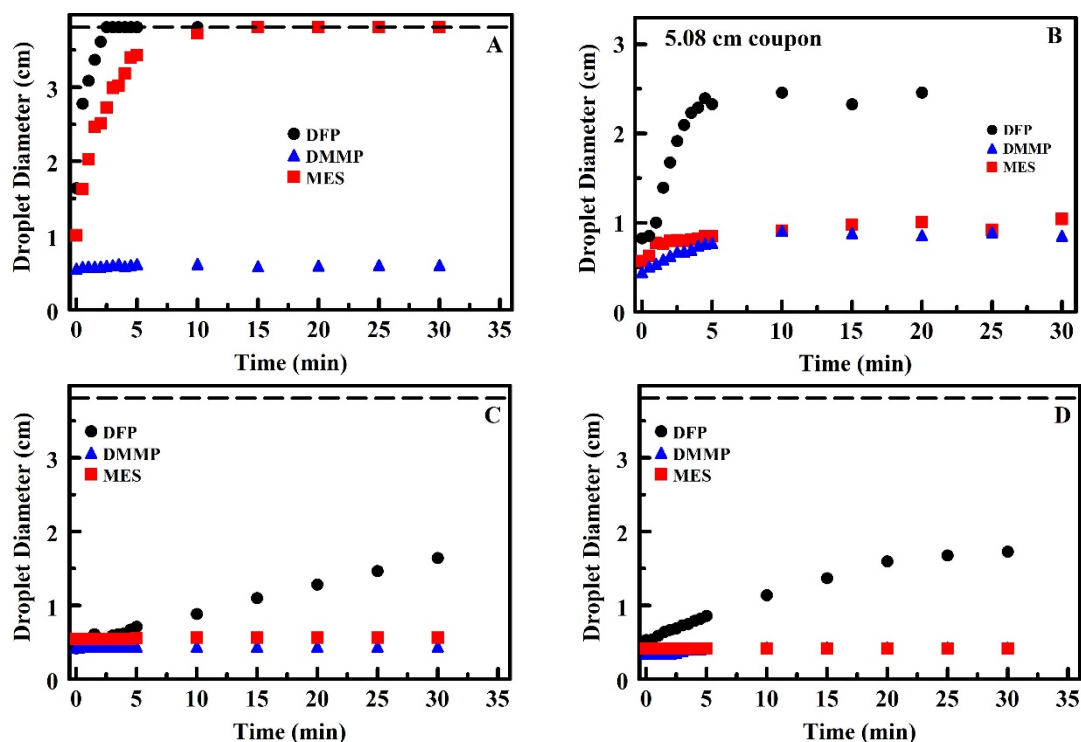


Fig. 4 — Droplet diameters over time following exposure to DFP (black), MES (red), and DMMP (blue) for a painted coupon (A), a painted coupon oiled with Fomblin Y (B), a painted coupon with Coating #1 (C), and a painted coupon with Coating #2 (D).

The coupons were subjected to several cycles of simulant exposure (10 g/m^2), aging, washing, and drying over a period of one week. Some change in appearance was noted following DFP exposures, but no changes in performance were 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. PTFS-BCA and PTFS-ECA provided lower retention for all four targets considered under

this study than that noted for the oiled surface. These materials also offer lower retention of all targets than the Fomblin Y oiled paint. Retention of all targets was approximately 4% of the 10 g/m² applied challenge.

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.

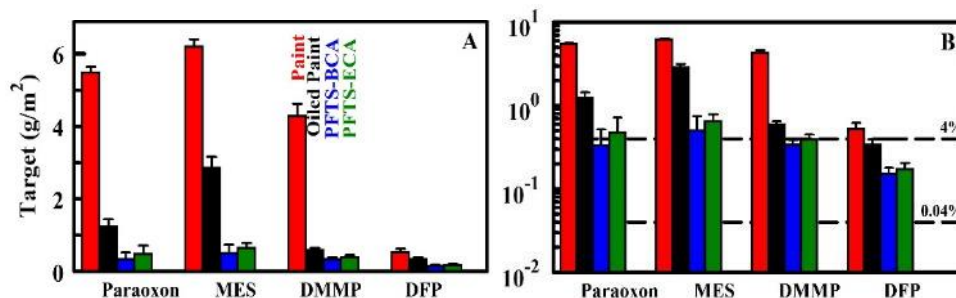


Fig. 5 — Target retention by coupons following treatment with an air stream and rinsing with soapy water: paint (red), oiled paint (black), PTFS-BCA (blue), and PTFS-ECA (green) plotted on a linear (A) and a log scale (B).

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

Coupon	Paraoxon	MES	DMMP	DFP
Aluminum Support				
Paint Only	5.48	6.20	4.28	0.52
Fomblin Y Oiled Paint	1.24	2.85	0.59	0.34
PTFS-BCA	0.33	0.50	0.34	0.15
PTFS-ECA	0.48	0.64	0.39	0.17

CONCLUSIONS

The perfluorohexyltrichlorosilane-cyanoacrylate coatings provided reduction in surface energy and significantly improved performance during retention evaluations over that noted for the paint only surfaces. Unlike many of the coatings evaluated under this effort, the coatings had little impact on the visible appearance of the painted surfaces (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 used here, additional studies are merited. It may be possible to improve performance through altering the composition of the deposition solutions. It may also be possible to use alternatives to the fluorinated component.

ACKNOWLEDGEMENTS

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Appendix A

IMAGES OF THE PFTS-BCA COUPONS

Fig. A1 — DFP on the PFTS-BCA Coupon. 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.

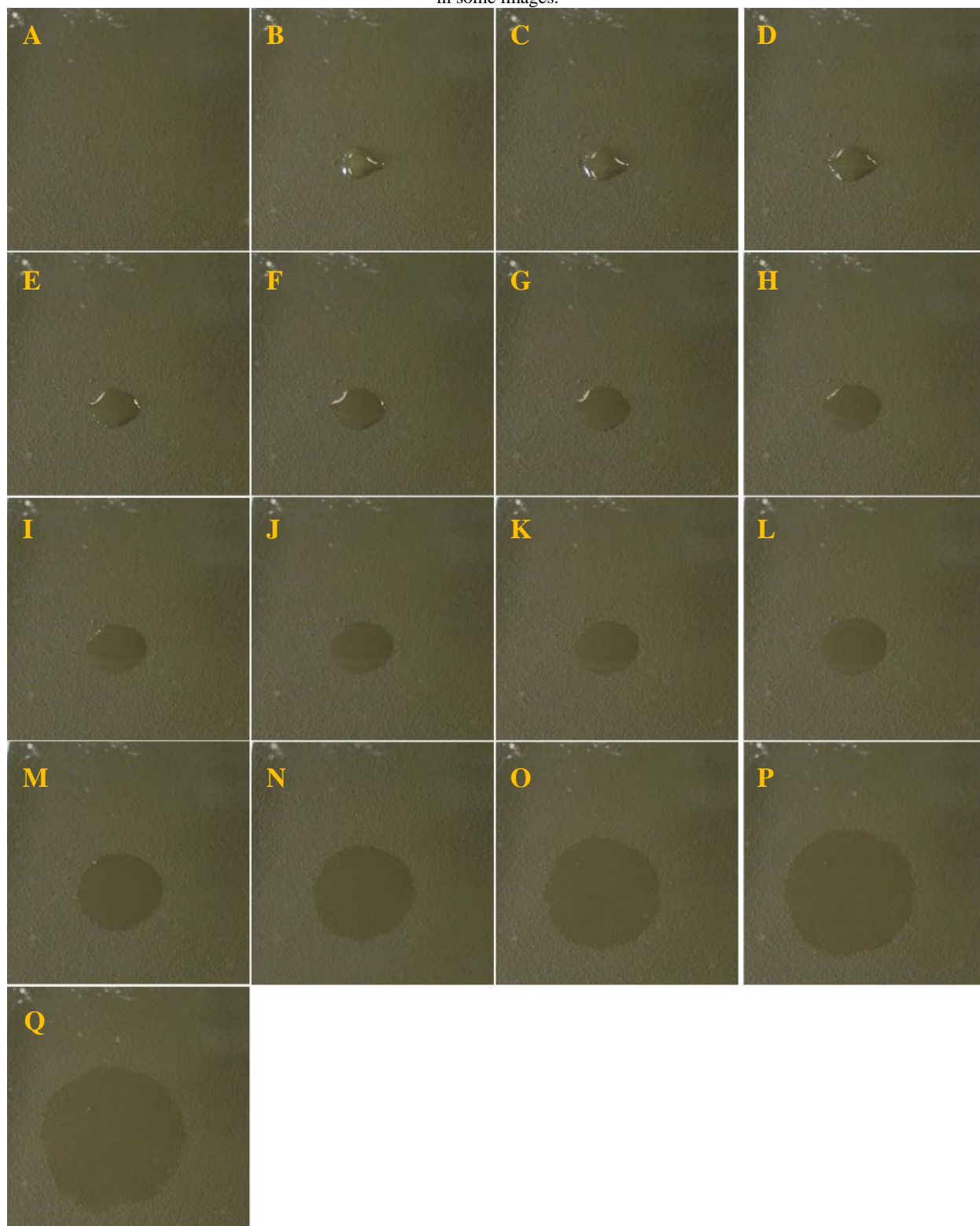


Fig. A2 — MES on the PFTS-BCA Coupon. Images of a coupon at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

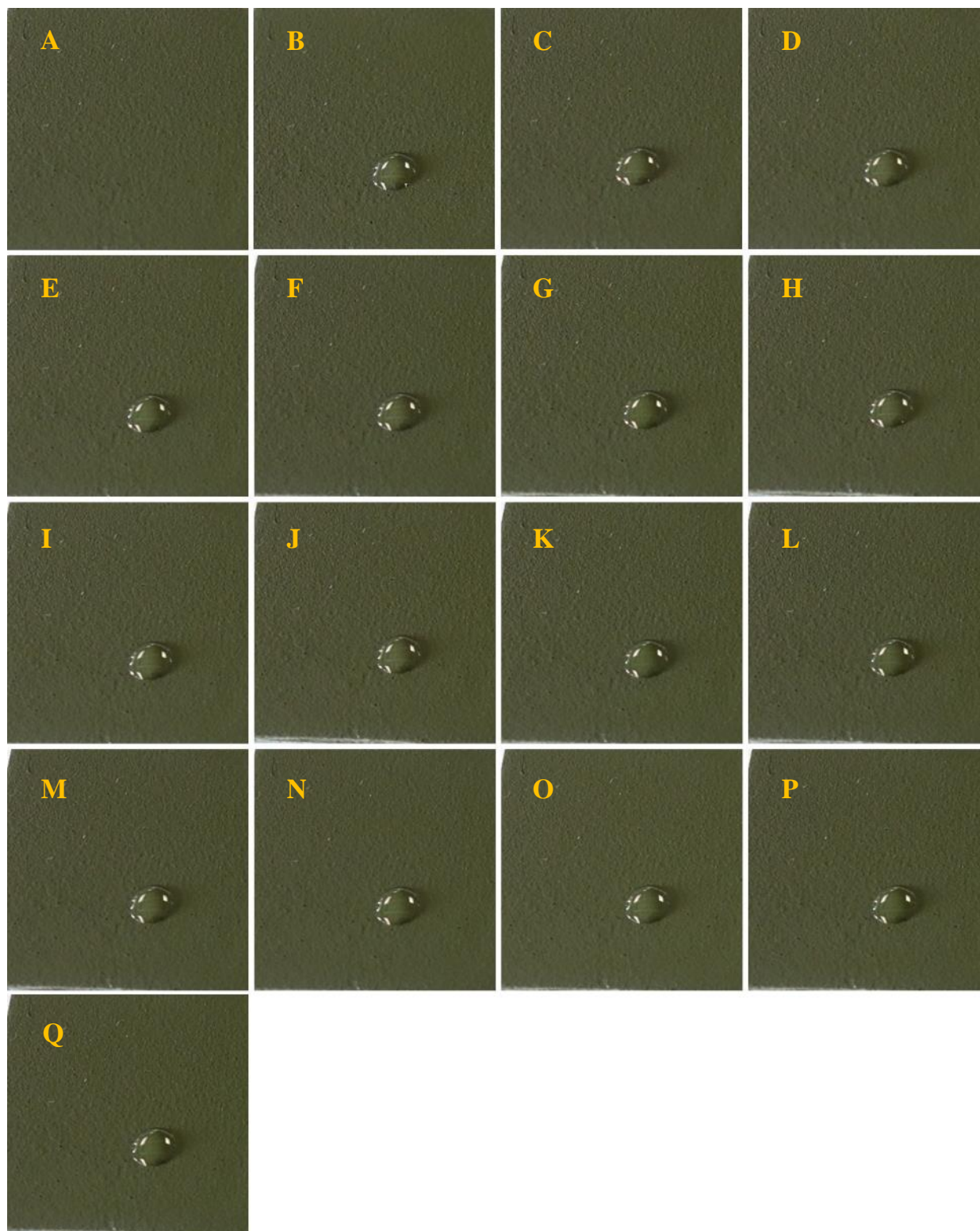
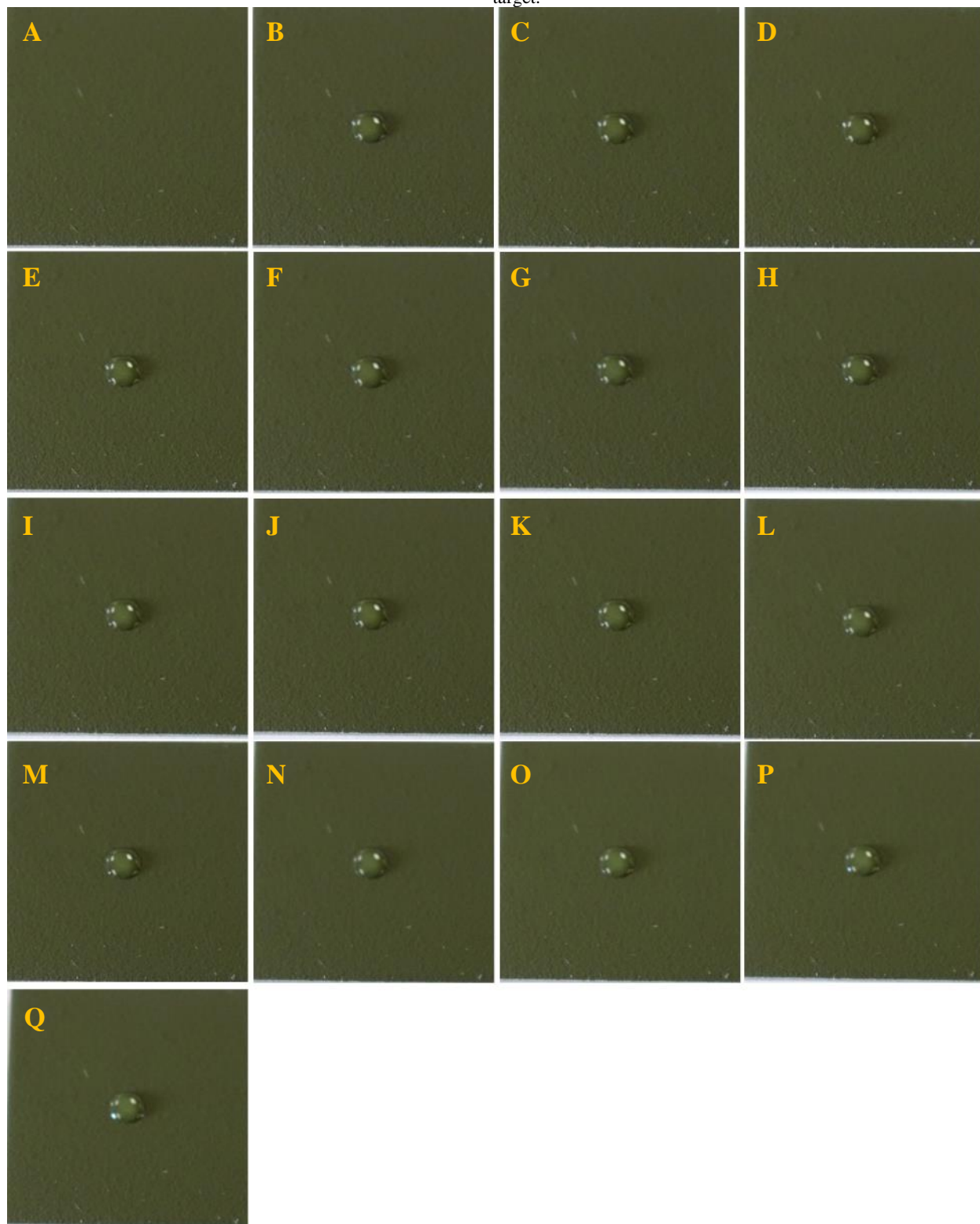


Fig. A3 — DMMP on the PFTS-BCA Coupon. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix B

IMAGES OF THE PFTS-ECA COUPONS

Fig. B1 — DFP on the PFTS-ECA Coupon. 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.

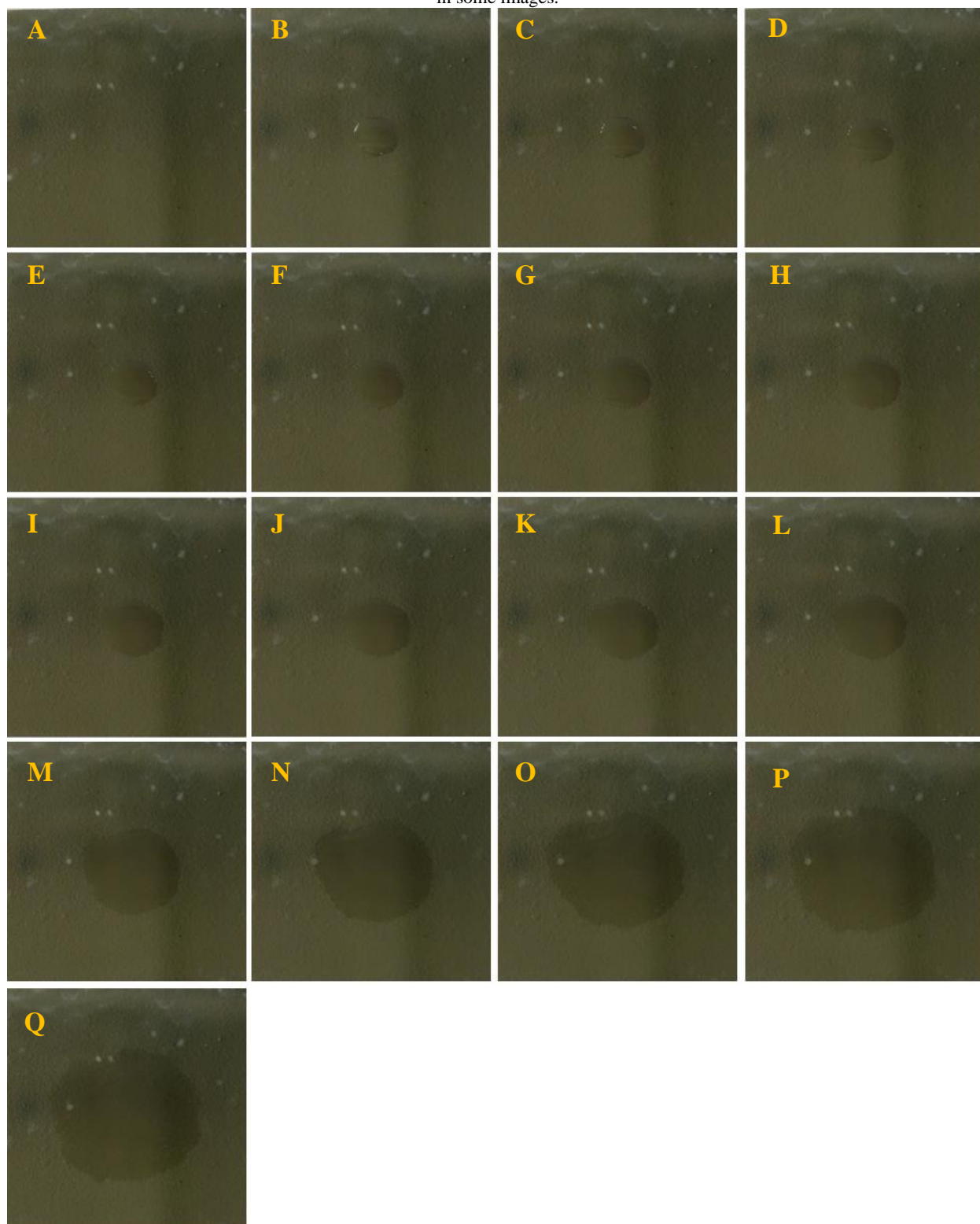


Fig. B2 — MES on the PFTS-ECA Coupon. Images of a coupon at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

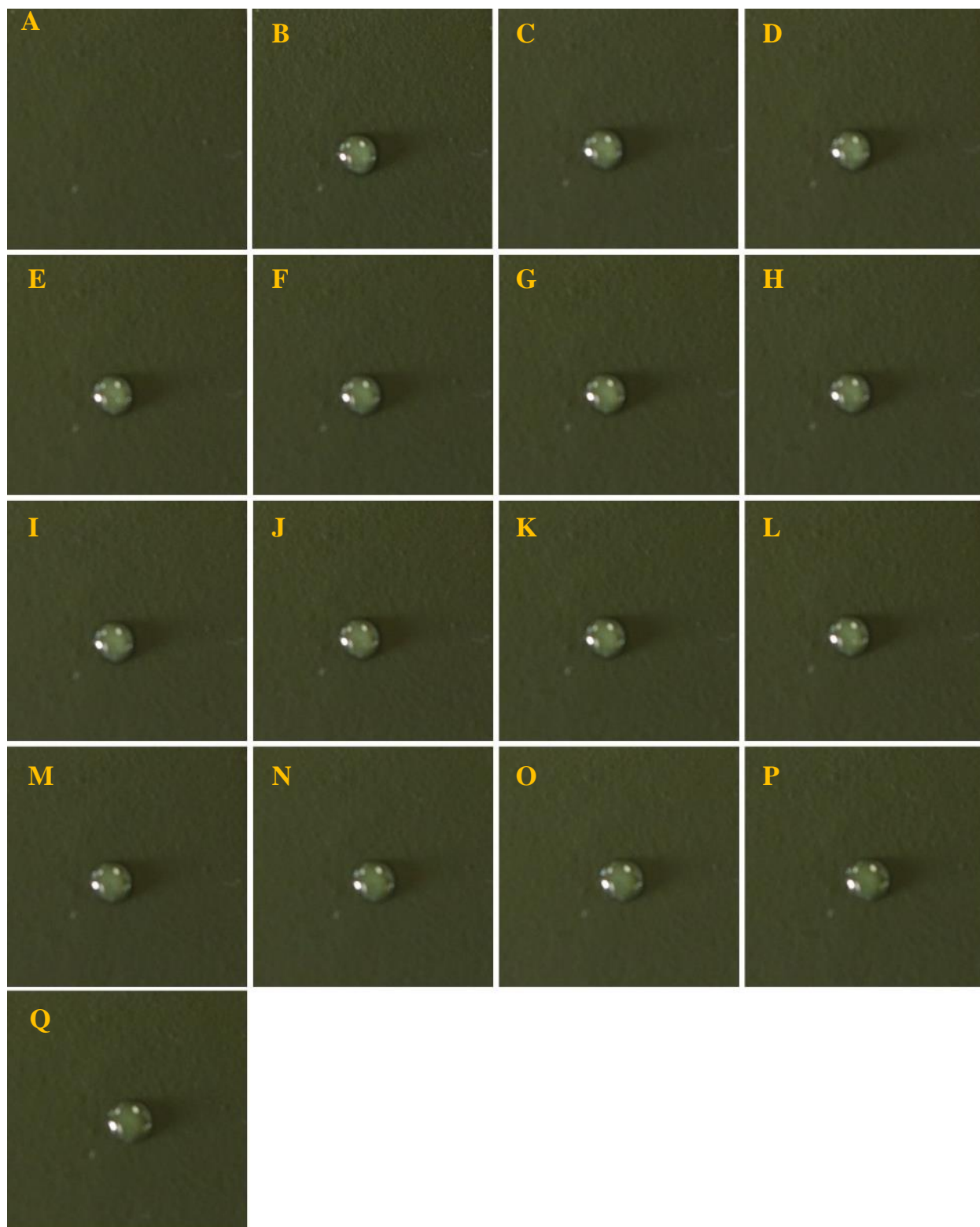
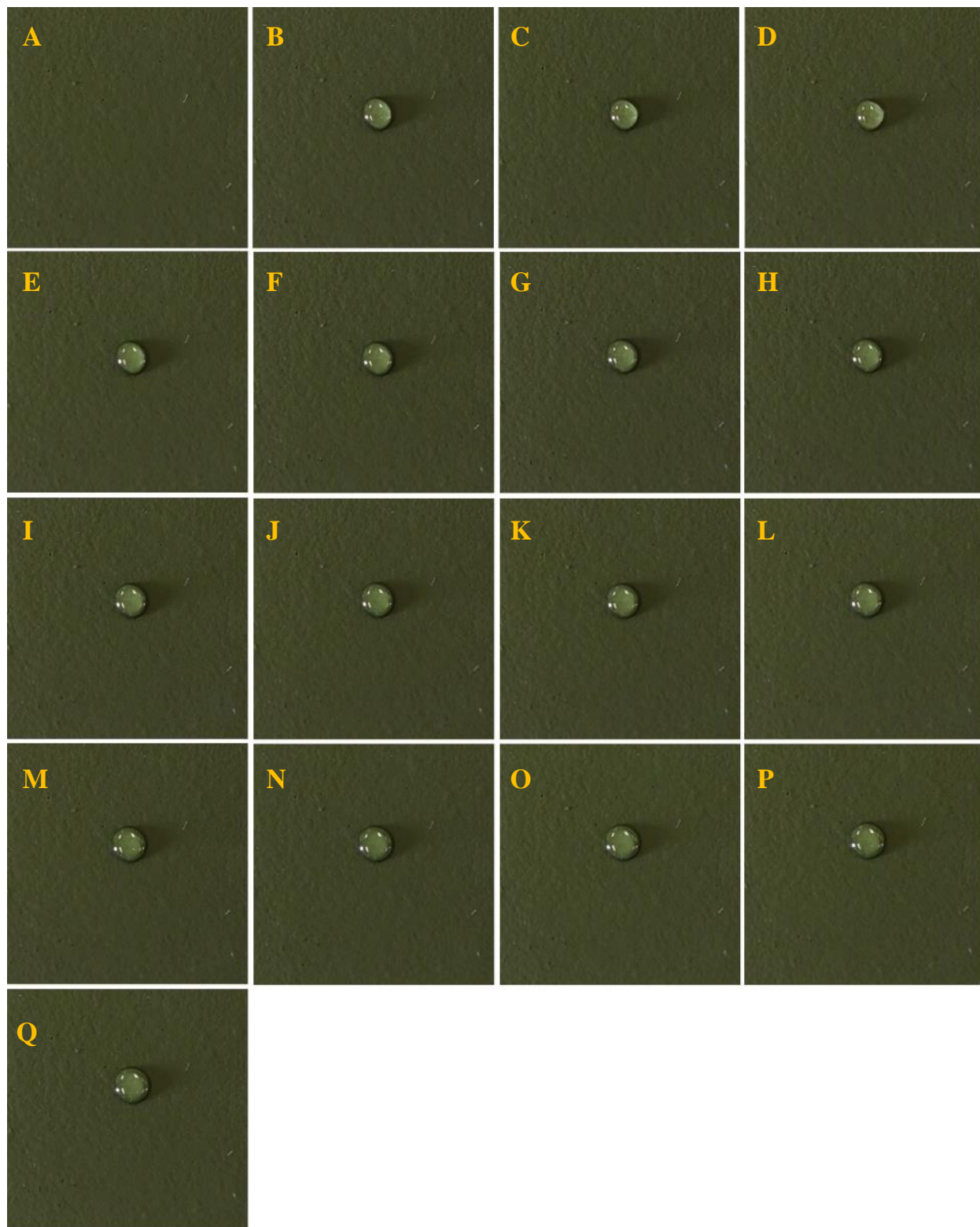


Fig. B3 — DMMP on the PFTS-ECA Coupon. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix C

IMAGES OF PAINTED COUPONS

Fig. C1 — 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.

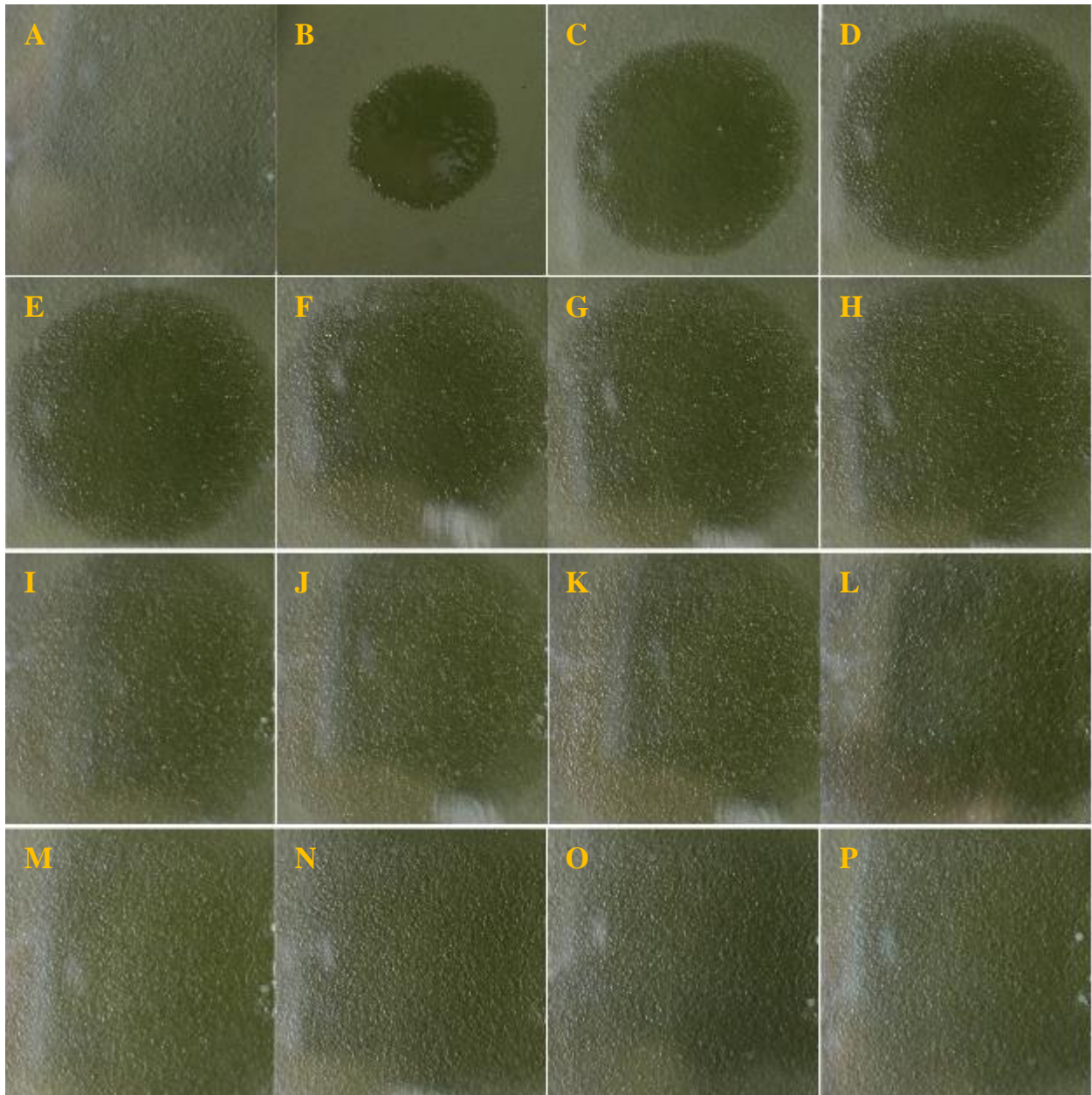


Fig. C2 — MES on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

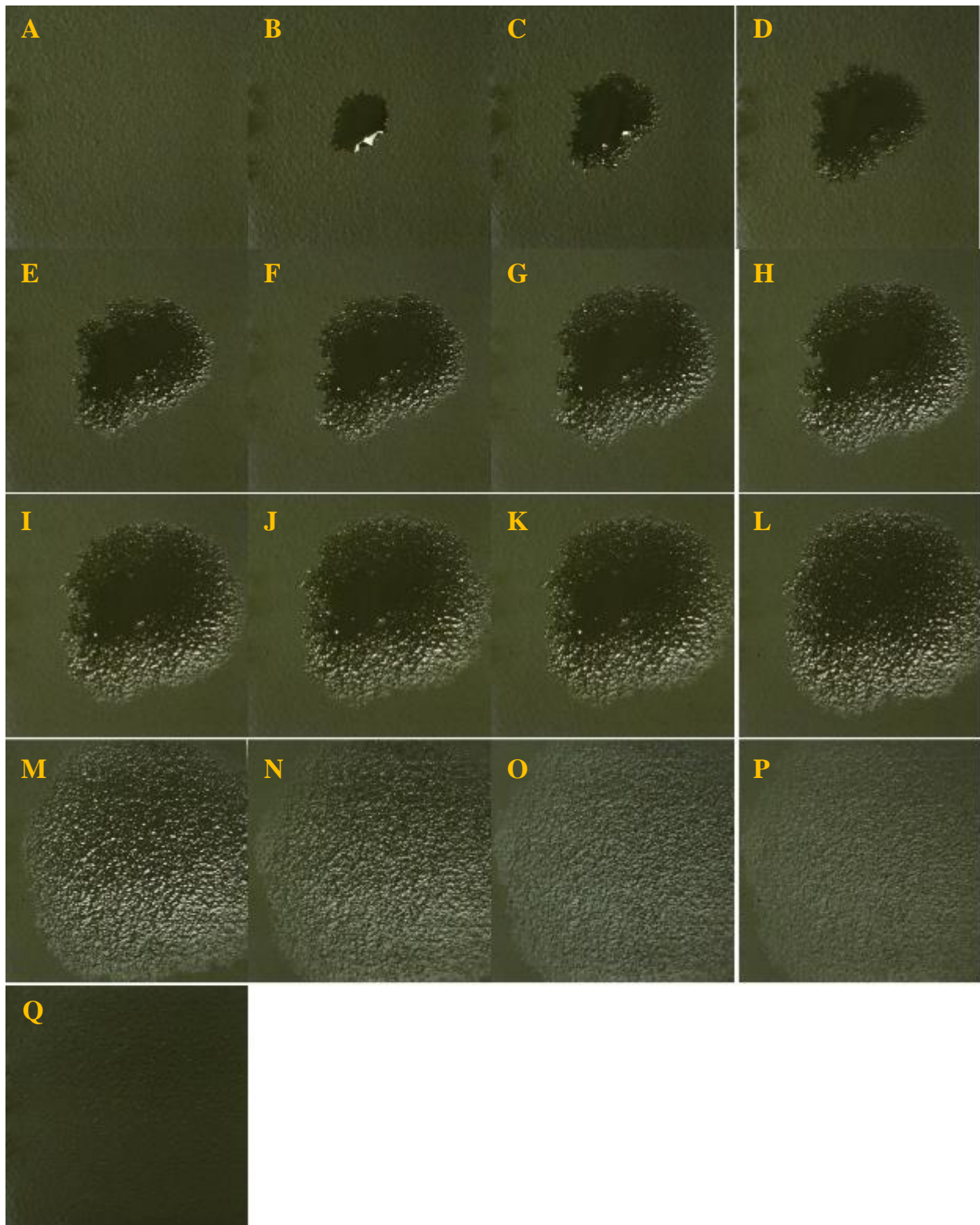
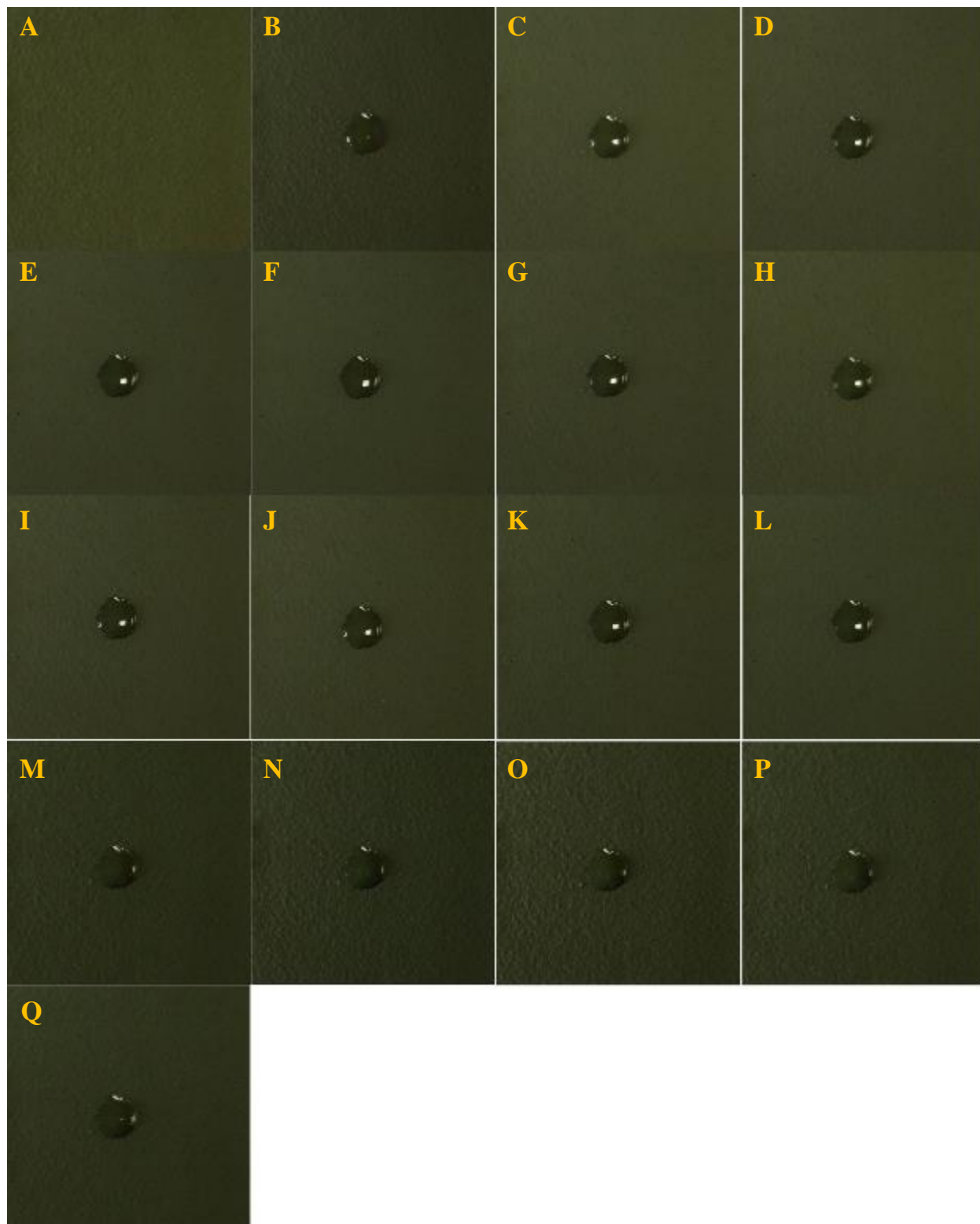


Fig. C3 — DMMP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix D

IMAGES OF FOMBLIN Y OILED COUPONS

Fig. D1 — 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. D2 — 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. D3 — 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.

