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Bioinspired Surface Treatments for Improved Decontamination: Adaptive Surface Technologies

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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 slippery liquid-infused porous surface (SLIPS) treatments. 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 developed by Adaptive Surface Technologies, Inc. The coatings are based on slippery liquid infused porous surface (SLIPS) approaches. The materials were 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: ADAPTIVE SURFACE TECHNOLOGIES

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, slippery liquid-infused porous surfaces (SLIPS).

Slippery liquid-infused porous surfaces (SLIPS) comprise a film of lubricating liquid with a textured substrate (micro/nano or both).[1-4] This provides a surface that is effectively smooth on the molecular scale and a liquid-liquid interaction interface. This is in contrast to the commonly harnessed lotus leaf effect that is achieved through use of a textured surface, providing air-liquid and air-solid interfaces. In addition, SLIPS coatings can offer a self-healing mechanism for damage to the surfaces, especially damage with a long, narrow surface profile. The liquid lubricant of the SLIPS treatment may flow to fill the region of damage, maintaining the overall liquid-liquid surface interactions. The solid and liquid components of a SLIPS system are selected to repel liquids of interest and for compatibility within the coating.

This effort has previously evaluated several different SLIPS based coatings.[5-8] Here, two types of coating were prepared by Adaptive Surface Technologies, Inc. For the first (Coating #1), the SLIPS® Repel product developed for use in mixers, tanks, and industrial process vessels was used. This coating is designed to repel viscous fluids, like paint and oil, reducing lost product, cleaning times, and waste streams. It uses a polymeric coating to support the lubricating layer. Coating #2 is a variation of this product, intended to improve performance in the open environment experienced by the relevant painted surfaces. For the complete evaluated systems, aluminum coupons were coated with a polyurethane paint system by NRL and were provided to Adaptive. Following deposition of the Adaptive coatings, coupons were returned to NRL (Figure 1) for evaluation using standard approaches including measurement of sessile, sliding, and shedding contact angles and quantification of retention for the simulant compounds. The coatings had some impact on the visible characteristics of the coupons, giving them a slightly wet appearance.

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

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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.

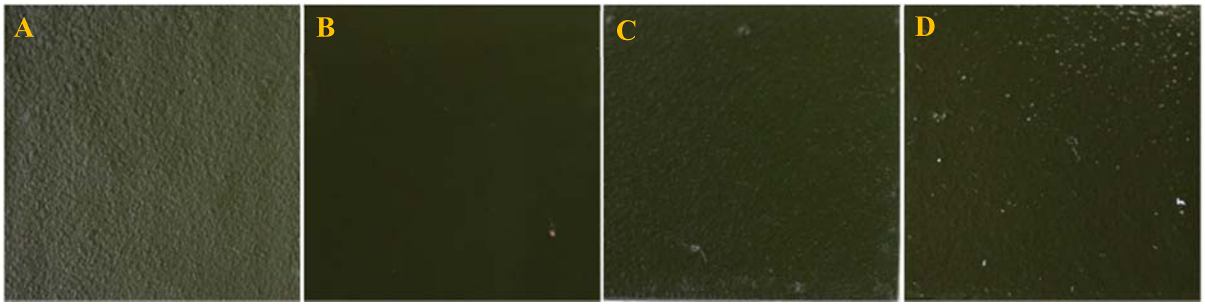

Fig. 1 — Images of a painted coupon (A), a painted coupon with Fomblin Y (B), a painted coupon with Coating #1 (C) and a painted coupons with Coating #2 (D).

Simulant exposure and evaluation methods were based on the tests developed by Edgewood Chemical Biological Center referred to as Chemical Agent Resistance Method (CARM).[9] 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°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. The fluorinated oil reduces the surface energy of the coupons (Table 1 and Figure 2). Application of Coating #1 significantly reduced the surface energy of the painted coupon, increasing contact angles for the three test liquids. Coating #2 produced behaviors more similar to that of the oiled coupon. Sliding on the painted coupon with and without oil and Coating #1 was not noted below 60°. For Coating #2, sliding of water was noted at 47°; sliding of ethylene glycol was noted at 33°. Shedding angles for the oiled surface were between 35° and 50° for test liquids while for Coating #1 they were between 35° and 45°. Coating #2 produced a similar water shedding angle with a slightly lower ethylene glycol shedding angle.

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	
Coating #1	water	100.9 ± 0.9	>60	40.5 ± 0.8	12.6 ± 0.5
	ethylene glycol	94.6 ± 0.5	>60	33.2 ± 0.6	
	n-heptane	39.4 ± 1.0	>60	>60	
Coating #2*	water	95.6 ± 1.0	47.0 ± 0.8	39.5 ± 3.3	37.4 ± 1.8
	ethylene glycol	61.4 ± 0.5	32.5 ± 3.5	26.3 ± 0.4	
	n-heptane	32.1 ± 0.2	>60	>60	

*Shedding may not be clean; it is difficult to tell on this surface

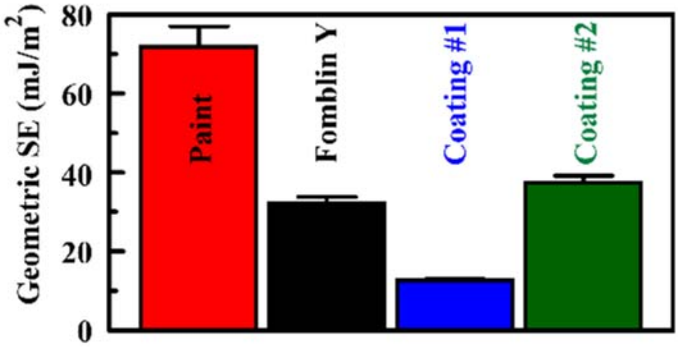

Fig. 2 — Geometric surface energy (mJ/m^2) for the evaluated coatings.

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. Coating #1 prevents spread of the three targets on the coupon. The initial droplet diameters for the targets are slightly smaller on Coating #1 than those noted for the Fomblin Y oiled coupons. Coating #2 also prevents spread of the three targets; however, droplet sizes for DMMP and DFP are slightly larger than those noted for Coating #1.

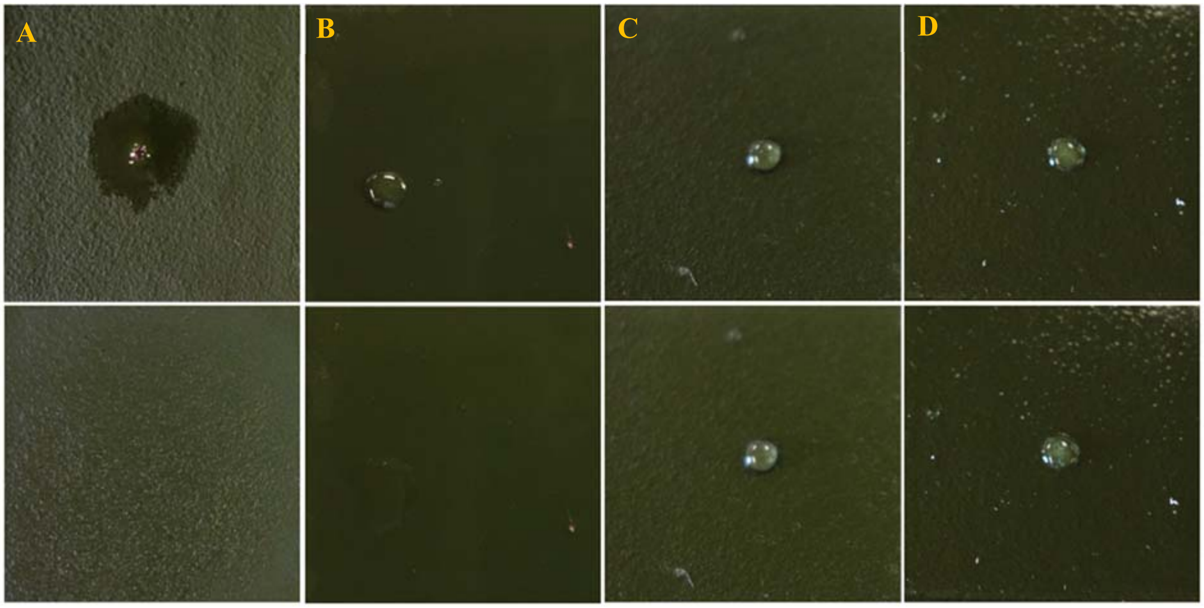

Fig. 3 — Images of coupons immediately following MES deposition (top) and images of the coupons at 30 min following deposition (bottom): for a painted coupon (A), a Fomblin Y oiled coupon (B), a Coating #1 treated coupon (C), and a Coating #2 treated coupon (D).

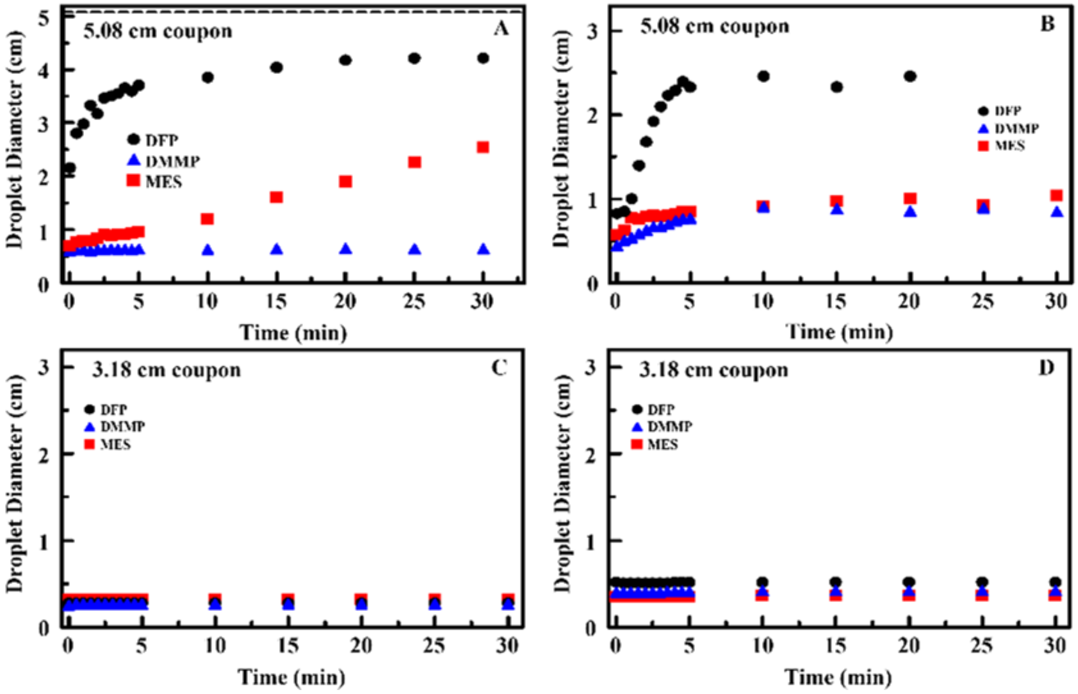

Fig. 4 — Droplet diameters over time following exposure to DFP (black), MES (red), and DMMP (blue) for a painted coupon (A), a painted coupon oiled with Fomblin Y (B), a painted coupon with Coating #1 (C), and a painted coupon with Coating #2 (D).

The coupons were subjected to several cycles of simulant exposure (10 g/m^2), aging, washing, and drying over a period of one week. 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. Coating #1 provided significantly greater reduction in retention for all four targets considered under this study than the oiled surface. Retention of paraoxon, MES, DMMP, and DFP was more than an order of magnitude less for Coating #1 than that noted for the painted surface. Coating #2 produced further reduction in the retained MES and DMMP with DFP retention similar to that of the oiled coupon.

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/m^2, MES – 9.54 g/m^2, DMMP – 9.90 g/m^2, DFP - 7.39 g/m^2. Though the nominal target application was 10 g/m^2, 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.

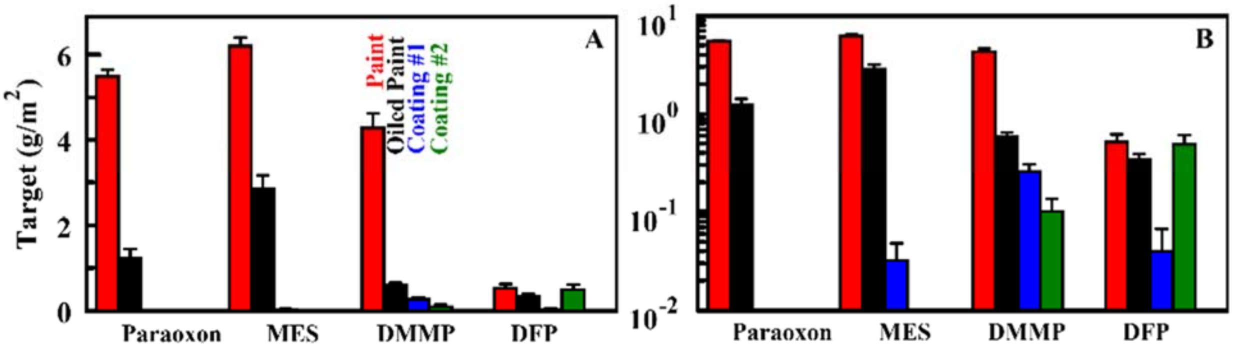

Fig. 5 — Target retention by coupons following treatment with an air stream and rinsing with soapy water: paint (red), oiled paint (black), smooth fluorinated polymer (blue), and the Luna Gentoo coating (green) plotted on a linear (A) and a log scale (B).

Table 2 – Target Retention (g/m^2) 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
Coating #1	ND	0.03	0.26	0.04
Coating #2	ND	ND	0.10	0.49

ND = not detected

CONCLUSIONS

The SLIPS coatings provided by Adaptive Surface Technologies, Inc. provide reduction in surface energy and significantly improved performance during evaluation over that noted for the paint only surfaces. As with many of the coatings evaluated under this effort, the coatings produce 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 used here, additional studies on performance of Coating #1, including aging and chemical agent evaluations should be considered.

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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.

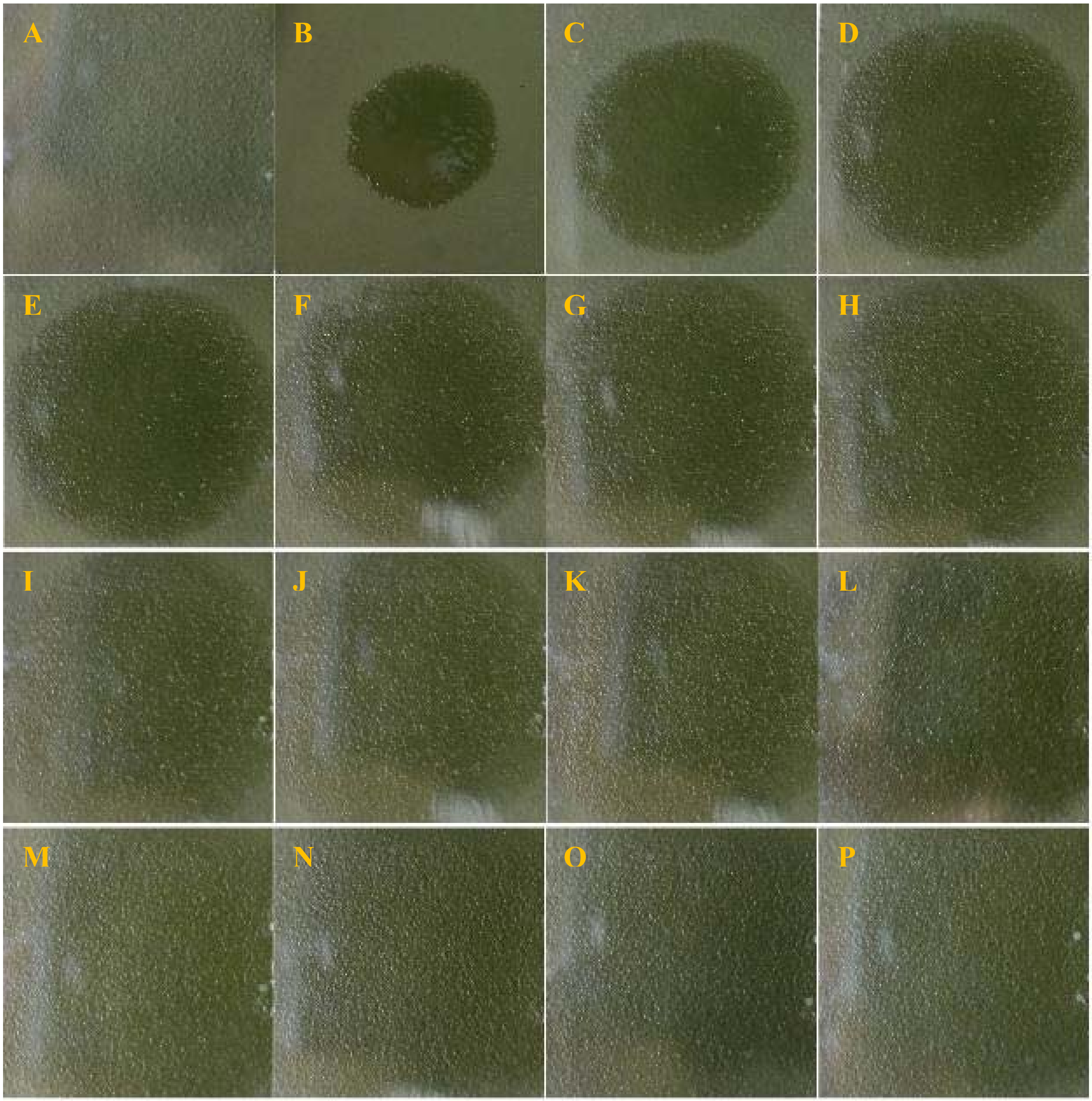


Fig. A2 — MES on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

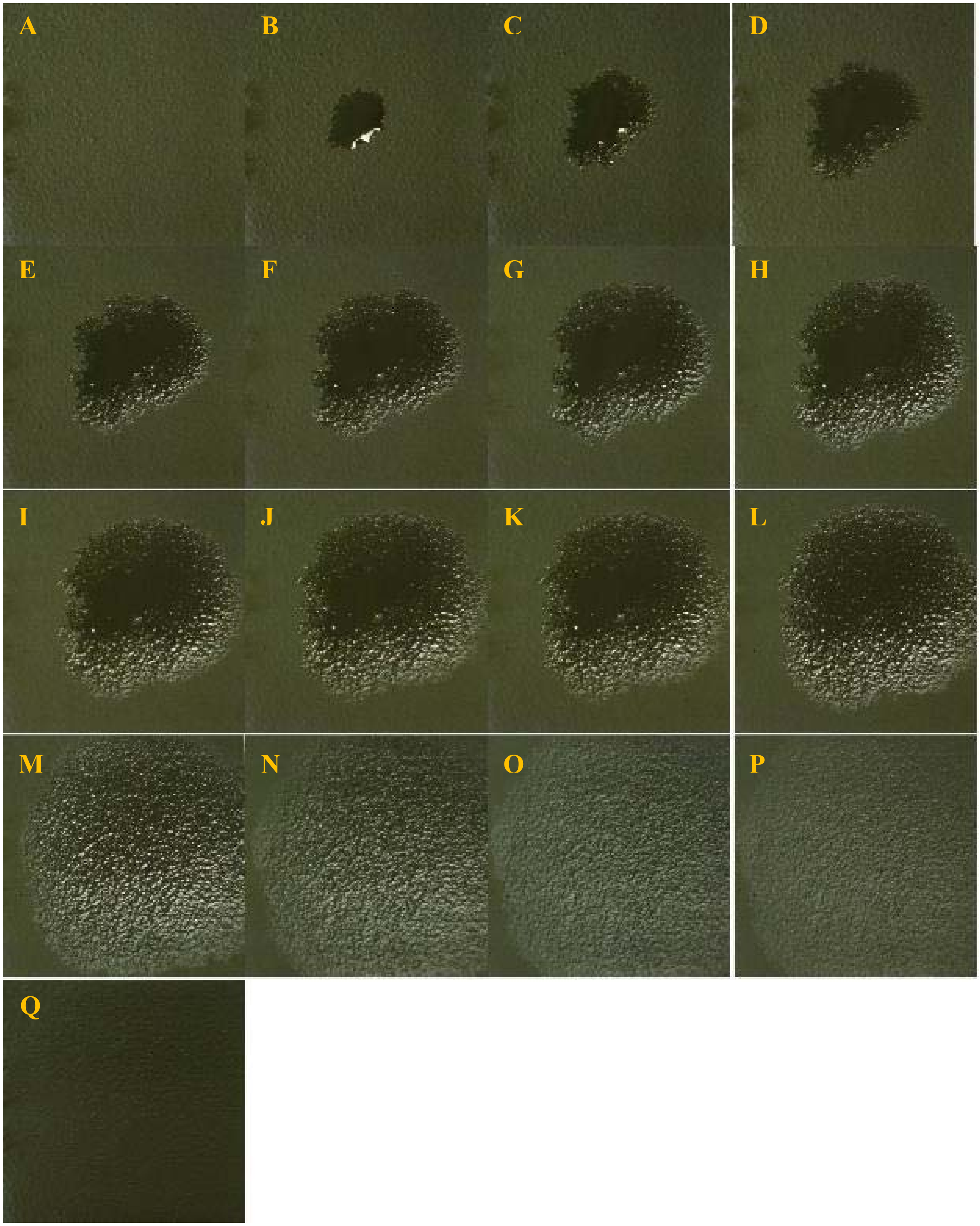
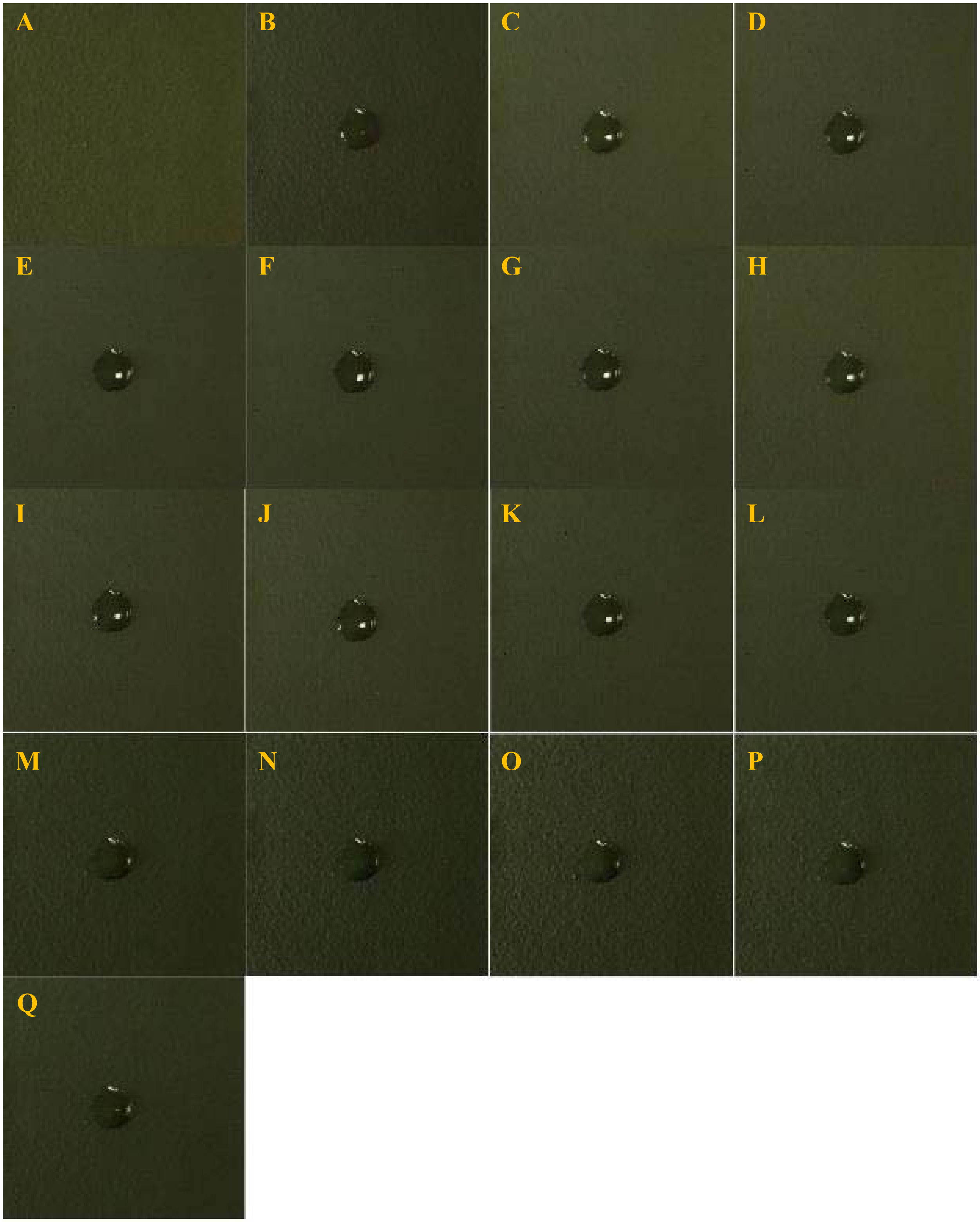


Fig. A3 — DMMP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



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.

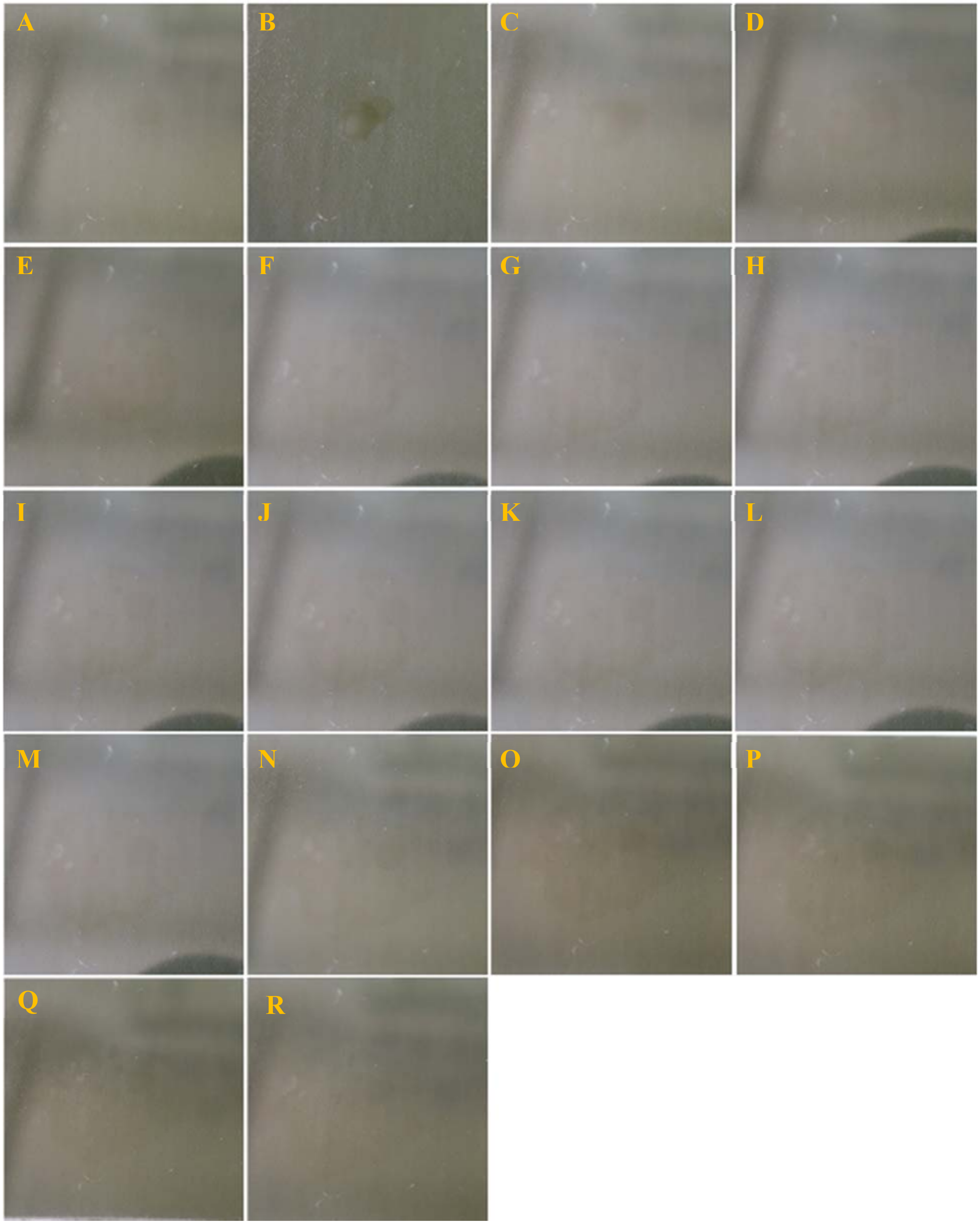
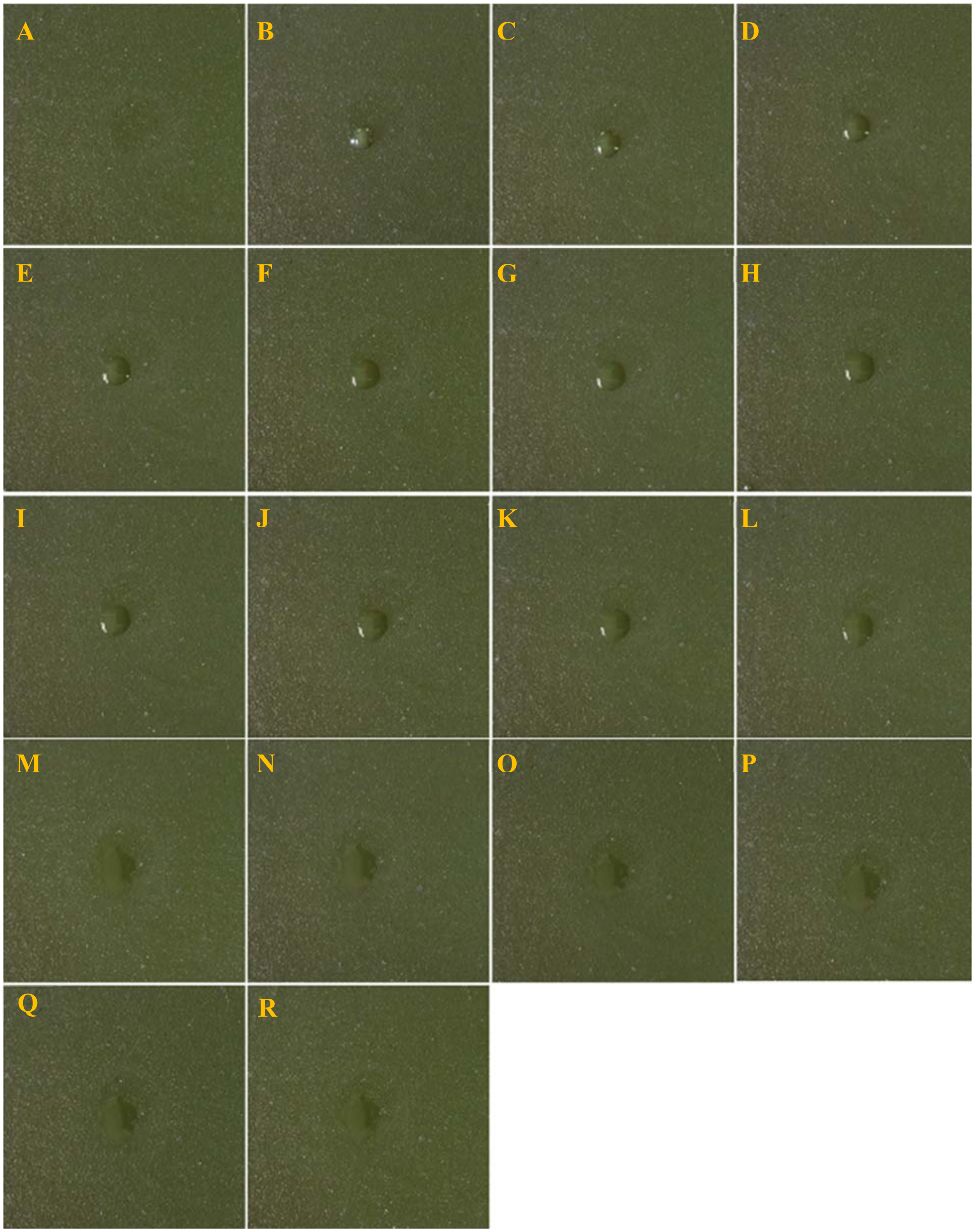


Fig. B2 — MES on Fomblin Y oiled paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) min following application of the target.

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) min following application of the target.



Appendix C

IMAGES OF ADAPTIVE SURFACE TECHNOLOGIES COATING #1

Fig. C1 — DFP on Coating #1. 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.

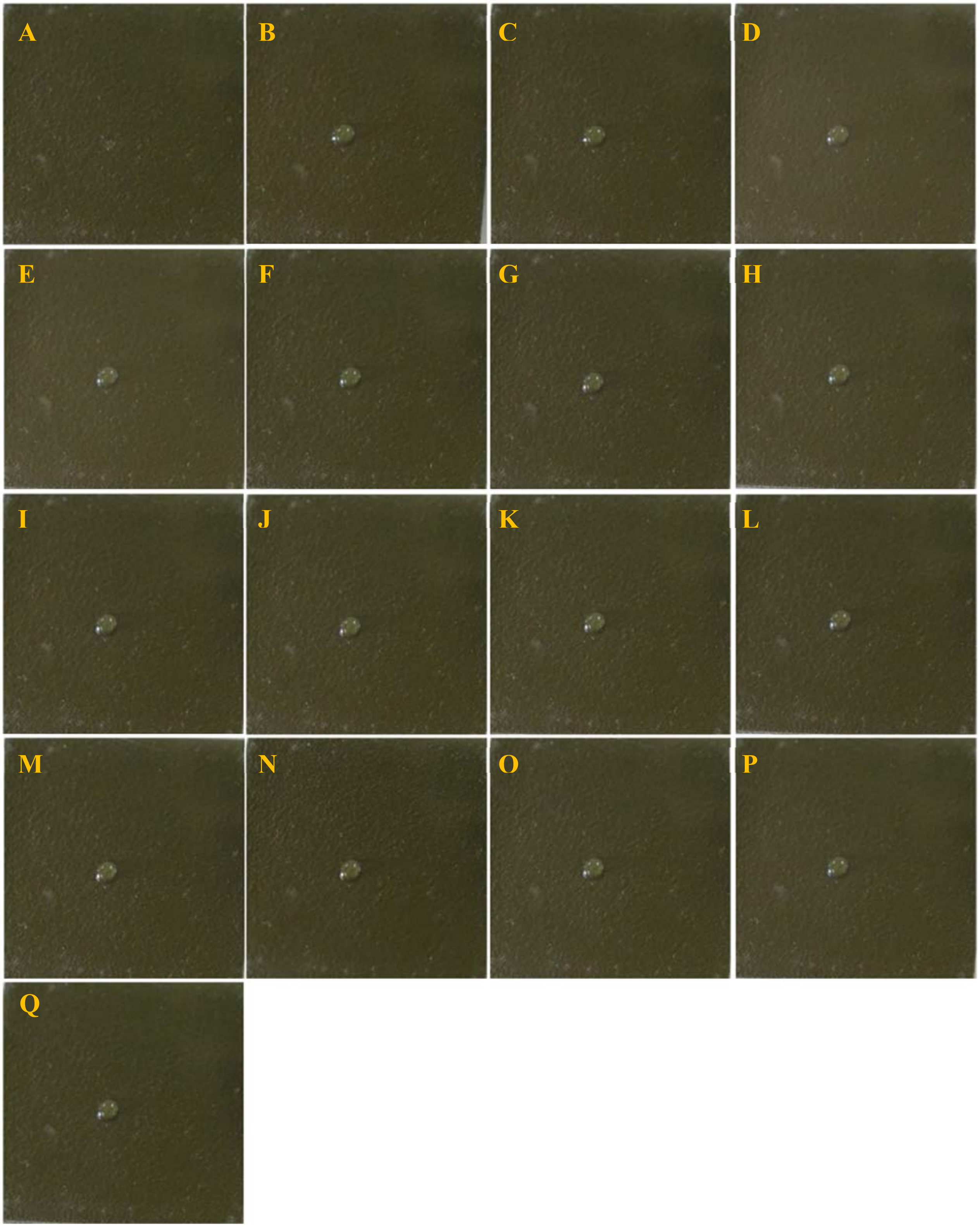


Fig. C2 — MES on Coating #1. Images of a coupon at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

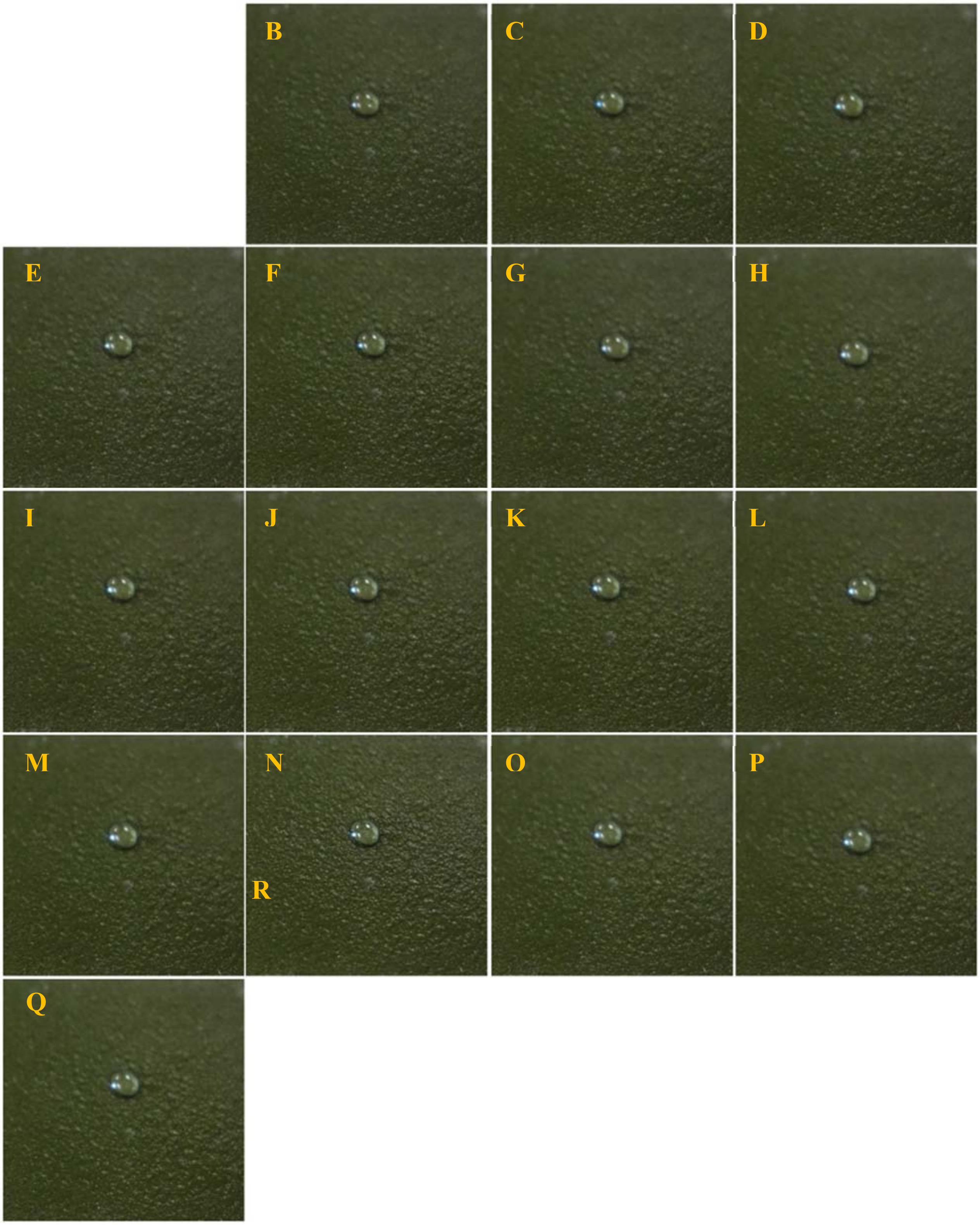
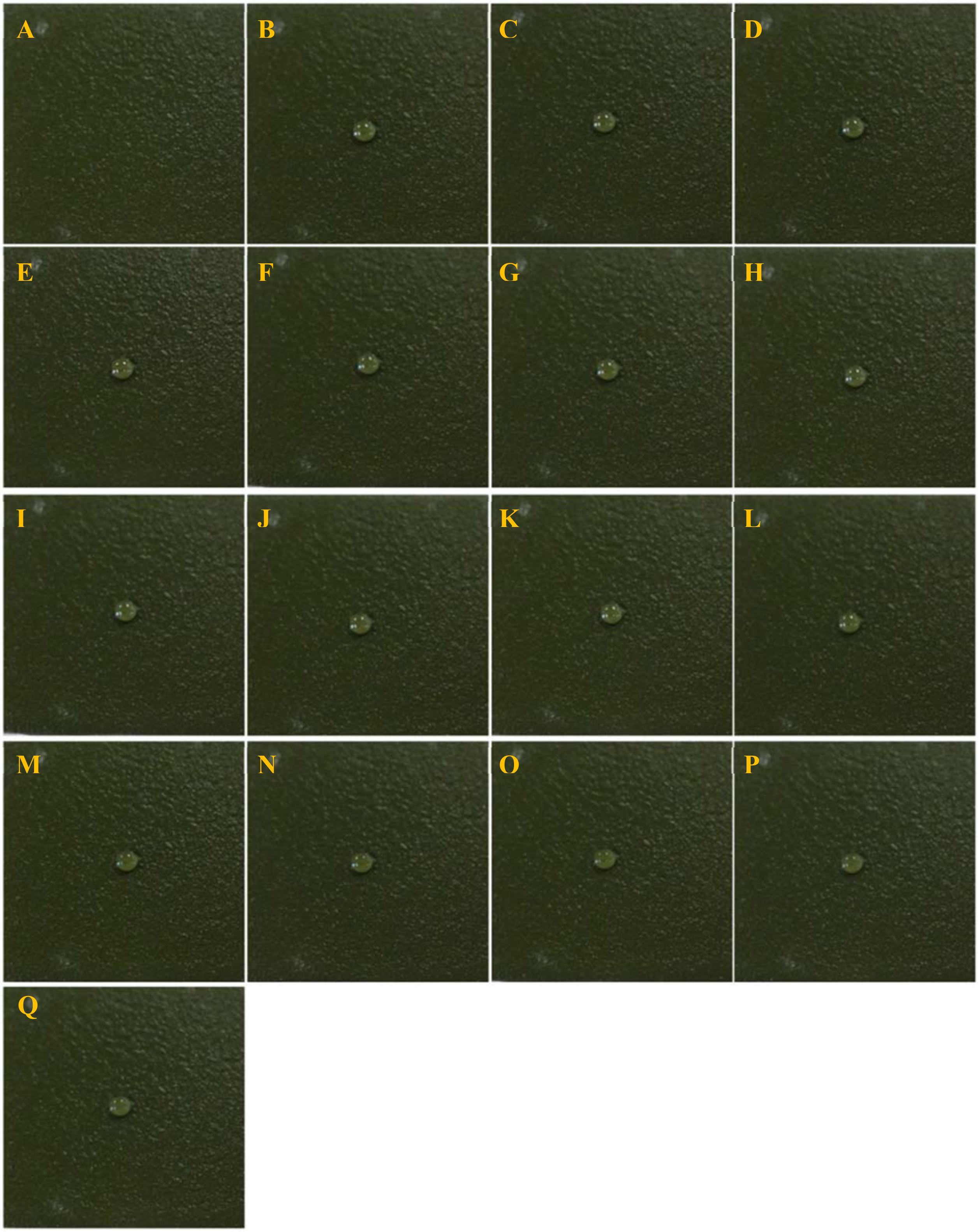


Fig. C3 — DMMP on Coating #1. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix D

IMAGES OF ADAPTIVE SURFACE TECHNOLOGIES COATING #2

Fig. D1 — DFP on Coating #2. 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.

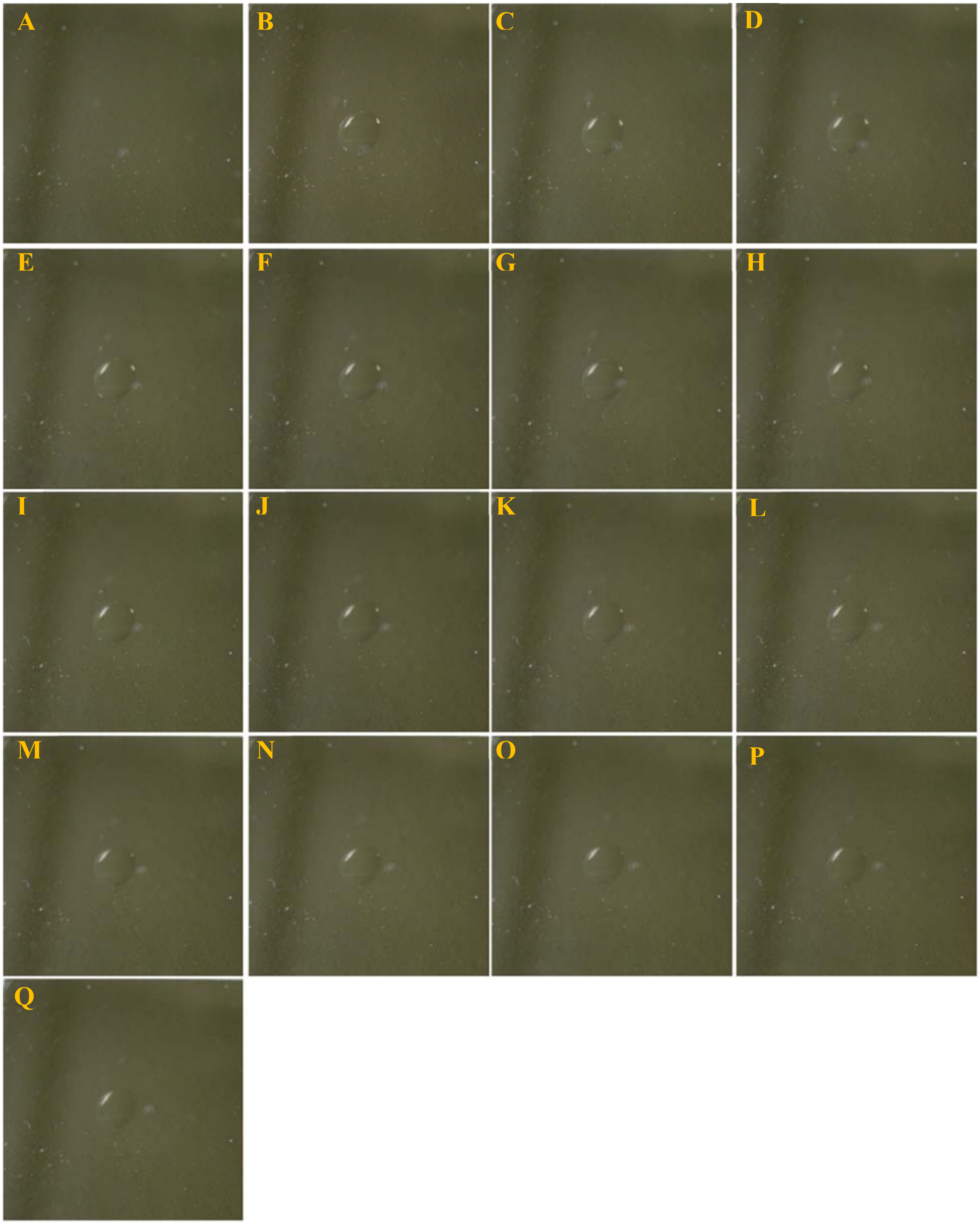


Fig. D2 — MES on Coating #2. Images of a coupon at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

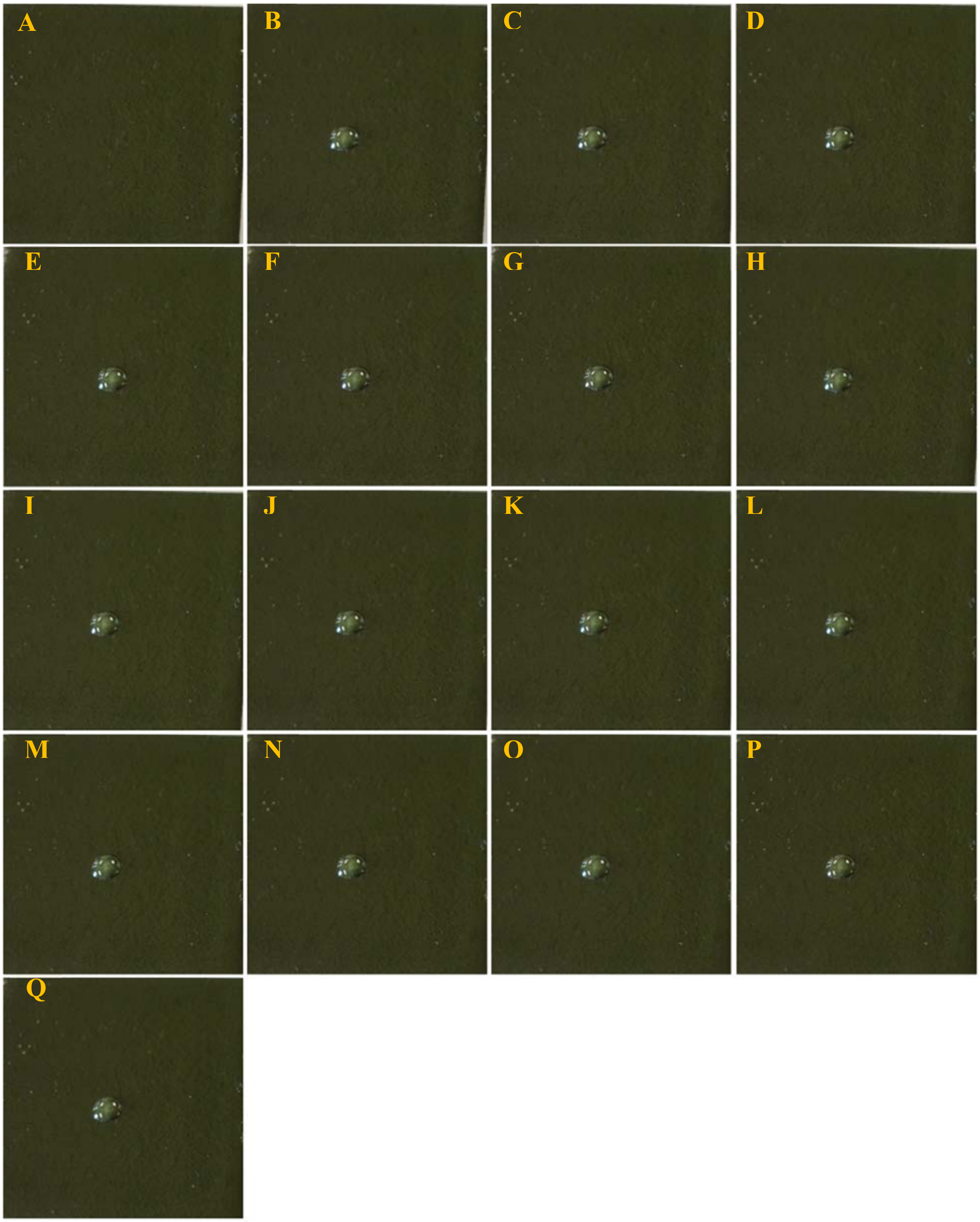


Fig. D3 — DMMP on Coating #2. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.