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Bioinspired Surface Treatments for Improved Decontamination: Bioceramic Coating

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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 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 oleophobic coating. The coating is provided as a single component, low viscosity material applicable to a range of substrates and provides corrosion protection for metals. 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: BIOCERAMIC COATING

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 AVIRAL. This product was developed by Flora Coatings LLC and is based on a bioceramic. The product is provided as a single component, low viscosity solution that yields a transparent, oleophobic coating. It is suitable for deposition on a range of surfaces and has previously been subjected to a number of industry standard evaluations including abrasion resistance and salt spray tests.

For the complete system, aluminum coupons were coated with a polyurethane paint system by NRL and were provided to Flora Coatings LLC. (Figure 1). Following deposition of the AVIRAL 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. Two AVIRAL coating thicknesses were supplied. The coating had little impact on the visible characteristics of the coupons in either case.

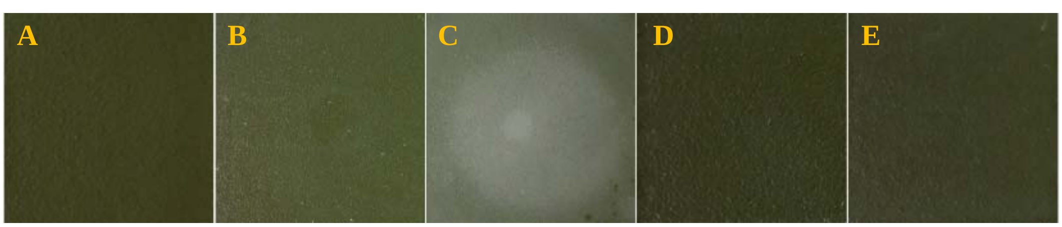

Fig. 1 — Images of a painted coupon (A), a painted coupon with Fomblin Y (B), a painted coupon with smooth fluoropolymer coating (C), a painted coupon with the thick AVIRAL coating (D), and a painted coupons with the thin AVIRAL coating (E).

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

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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). [1] 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 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). [2] 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. [3] 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 AVIRAL coating, the surface energies noted on the two variants were similar and slightly higher than that of the fluoropolymer. No sliding behavior was noted for water, ethylene glycol, or heptane. Shedding angles of 40° to 50° were noted for water and ethylene glycol on the thick version of the coating. Shedding angles for the thin coating were slightly higher. Reported results for this coating indicate greater water shedding behavior. The difference noted here is likely due to the nature of the painted support surface. The polymer, glass, and metal support surfaces previously used are significantly more homogeneous than the surface resulting from deposition of the polyurethane paint system.

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	
Smooth Fluoropolymer	water	116.8 ± 1.1	>60	>60	10.5 ± 1.1
	ethylene glycol	100.3 ± 1.5	>60	>60	
	n-heptane	19.1 ± 0.79	--	--	
AVIRAL, thick	water	102.0 ± 0.70	>60	46.0 ± 1.3	13.5 ± 0.45
	ethylene glycol	86.8 ± 0.74	>60	40.3 ± 0.76	
	n-heptane	35.1 ± 1.2	--	--	
AVIRAL, thin	water	99.9 ± 1.6	>60	>60	12.5 ± 0.81
	ethylene glycol	91.0 ± 0.48	>60	51.0 ± 4.8	
	n-heptane	21.5 ± 1.4	--	--	

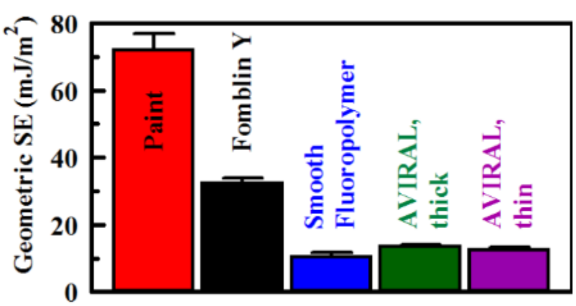

Fig. 2 — Geometric surface energy for the evaluated coatings.

The tendency of droplets to spread across the surfaces was also evaluated (Figure 3; Appendices A through 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 AVIRAL coatings completely prevent spread of all three targets.

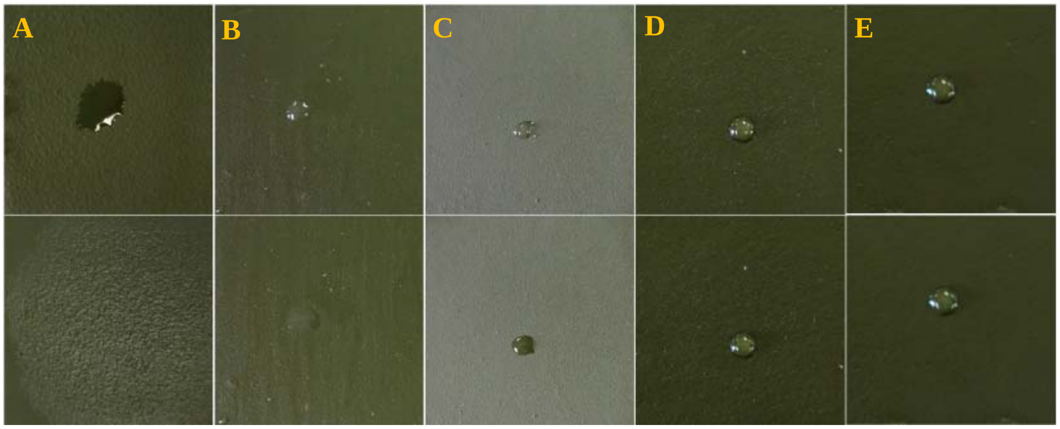

Fig. 3 — Images of coupons immediately following MES deposition (top) and images of the coupons at 30 min following deposition (bottom): for a painted coupon (A), a Fomblin Y oiled coupon (B), a fluoropolymer treated coupon (C), a thick AVIRAL coating treated coupon (D), and a thin AVIRAL coating treated coupon (E).

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 AVIRAL coatings 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, and DMMP was approximately two orders of magnitude less for the AVIRAL coating than that noted for the painted surface. DFP retention was reduced by an order of magnitude on the AVIRAL treated coupons. The coupons were subjected to several cycles of simulant exposure (10 g/m^2), aging, washing, and drying over a period of a week. No change in appearance or performance was noted for the cycled samples.

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.

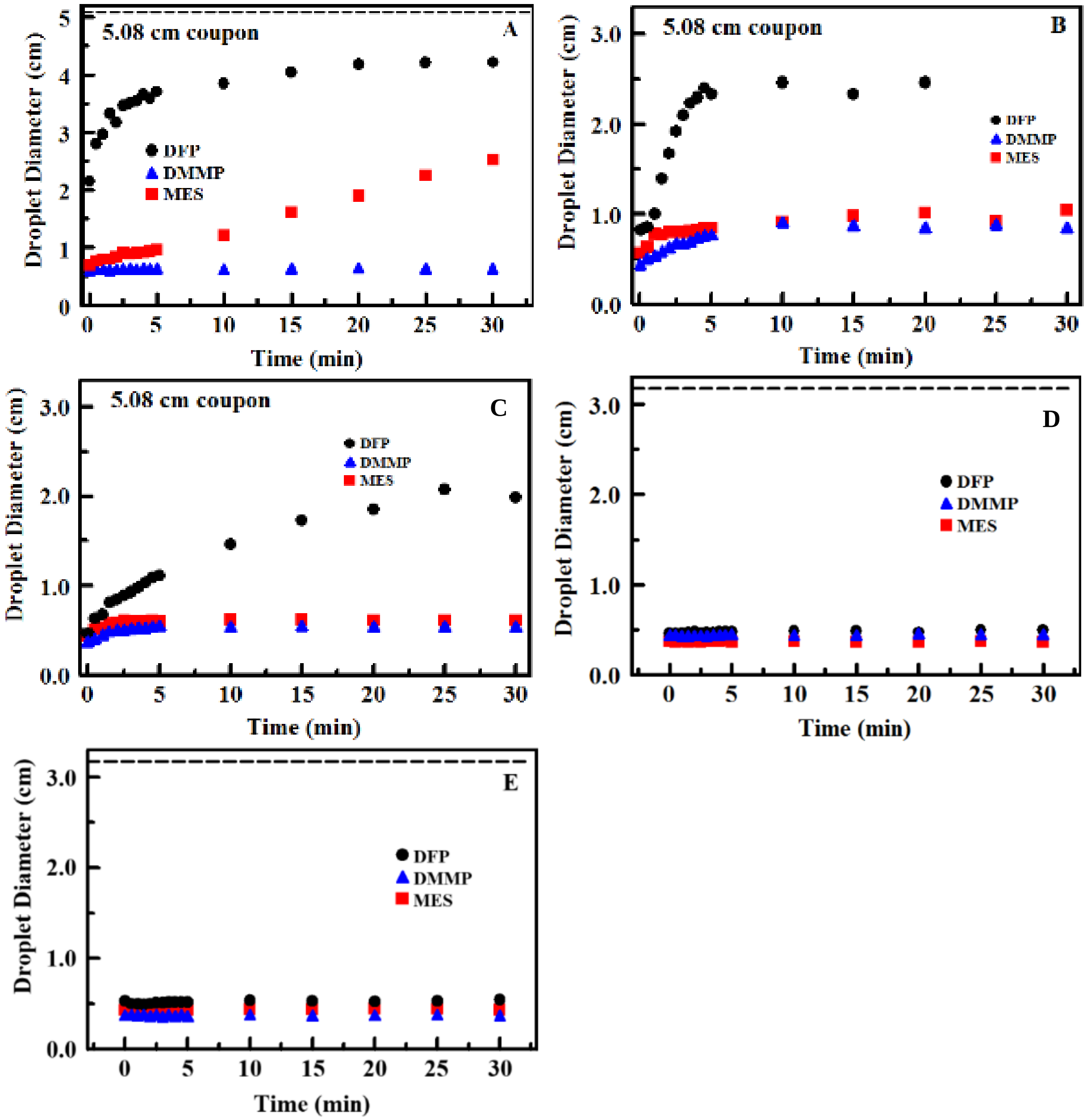

Fig. 4 — Droplet diameters over time following exposure to DFP (black), MES (red), and DMMP (blue) for a painted coupon (A), a painted coupon oiled with Fomblin Y (B), a painted coupon with a smooth fluoropolymer coating (C), and a painted coupon with the thick AVIRAL coating (D) and a painted coupon with the thin AVIRAL coating (E).

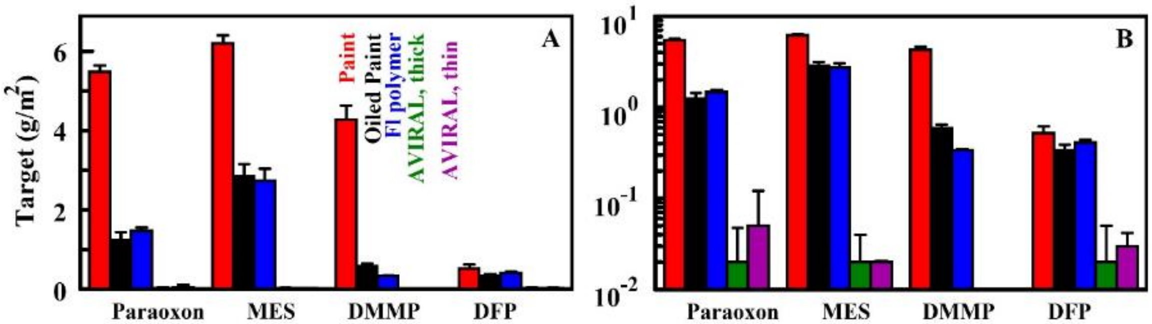

Fig. 5 — Target retention by coupons following treatment with an air stream and rinsing with soapy water: paint (red), oiled paint (black), smooth fluorinated polymer (blue), the thick AVIRAL coating (green), and the thin AVIRAL coating (purple) plotted on a linear (A) and a log scale (B).

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
Smooth Fluoropolymer	1.47	2.74	0.34	0.41
AVIRAL, thick	0.02	0.02	ND	0.02
AVIRAL, thin	0.05	0.02	ND	0.03

ND = not detected

CONCLUSIONS

The AVIRAL coating from Flora Coatings LLC provides reduction in surface energy and significantly improved performance during processing than that noted for the paint only surfaces. The noted discrepancies between the results observed under this study and prior sliding and shedding angle evaluations is likely due to the textured nature of the underlying painted surface. Prior work, for example with deposition on aluminum substrates, returned low sliding and shedding angles, especially for water. In contrast to many of the coatings evaluated under this effort, the AVIRAL coating produces little change in the appearance of the painted coupons (Figure 1 and Appendices). Spectrophotometric analysis is necessary to determine the overall impact on color and reflectivity. It should also be noted that Flora Coatings LLC has additional products including a variant of AVIRAL, incorporating nanoparticles, which should produce less change to the appearance of the underlying surface. Given the reductions in target retention noted for the simulant compounds evaluated here, additional studies on the performance of aged coupons and under chemical agent challenge should be considered.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. Atul Tiwari of Flora Coatings LLC for supplying the samples evaluated under this study. This research was sponsored by the Defense Threat Reduction Agency (DTRA, CB10125).

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3. White, B.J.; Melde, B.J.; Moore, M.H.; Malanoski, A.P.; Campbell, C.; Mantooth, B.A.; Stevenson, S.M.; Smallwood, S.; Eikenberg, J. "Bioinspired Surface Treatments for Improved Decontamination: Polymer-Based Slippery Liquid-Infused Porous Surfaces (SLIPS)," US Naval Research Laboratory, **2018**; NRL/MR/ 6930-18-9773.

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.

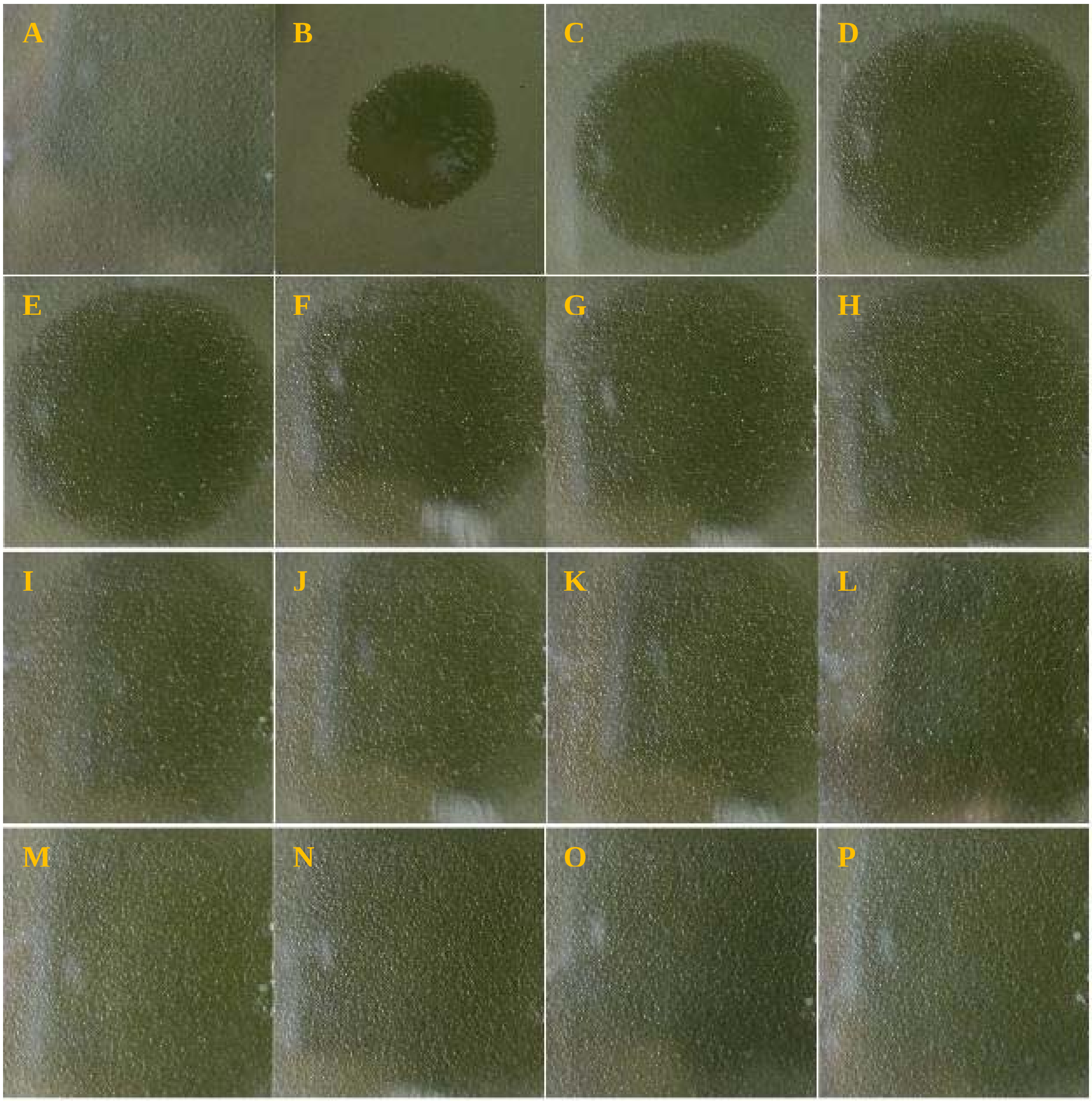


Fig. A2 — MES on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

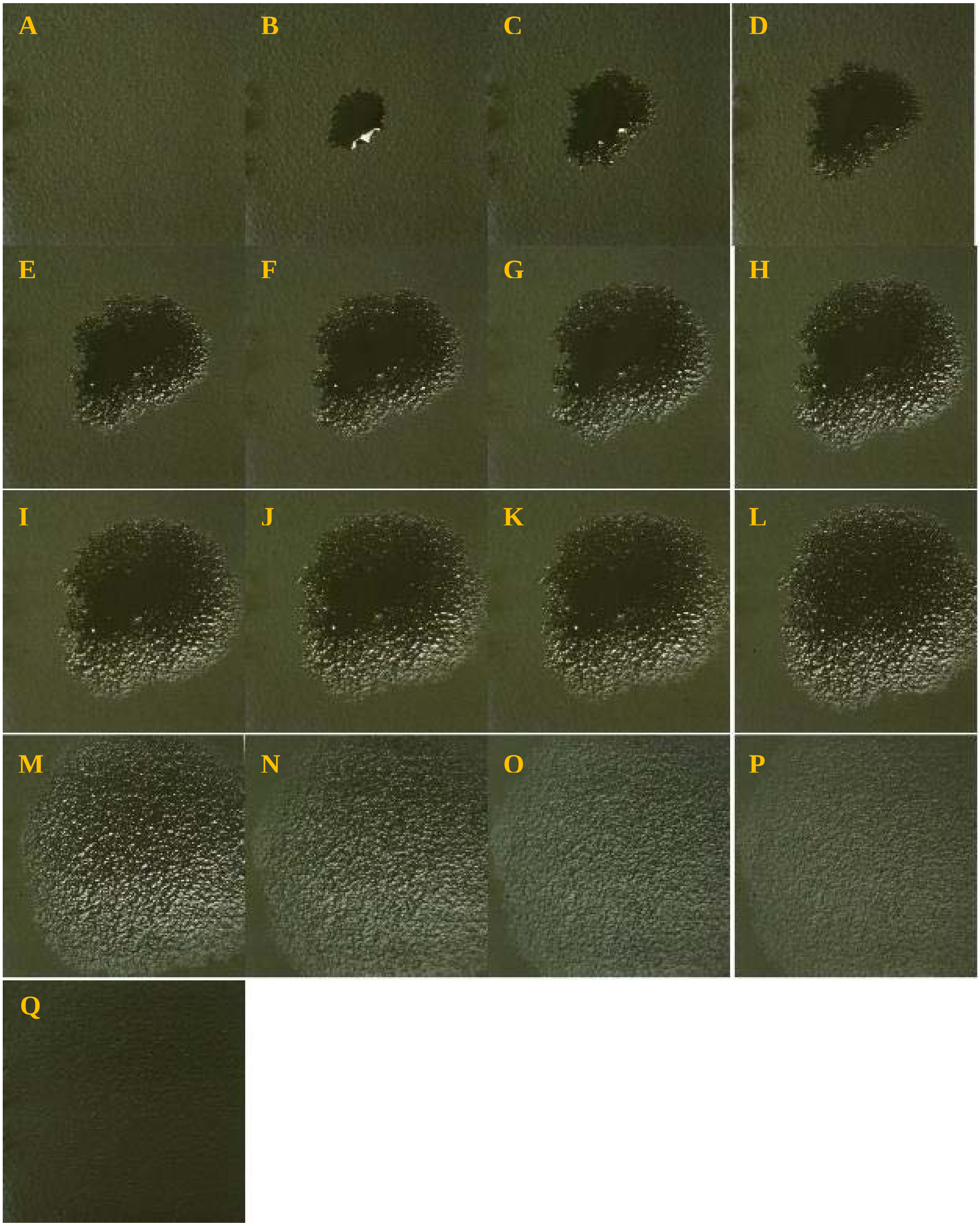
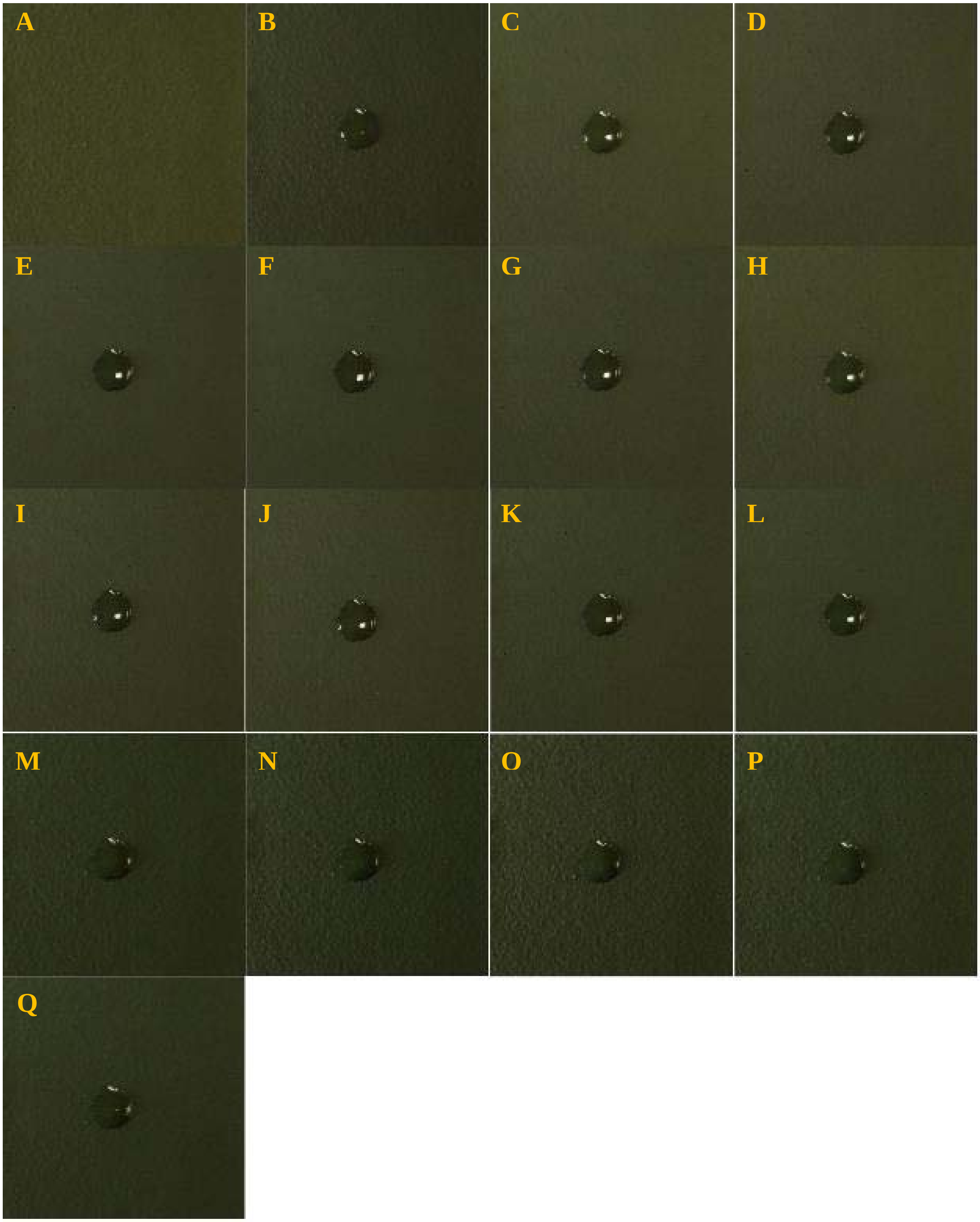


Fig. A3 — DMMP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



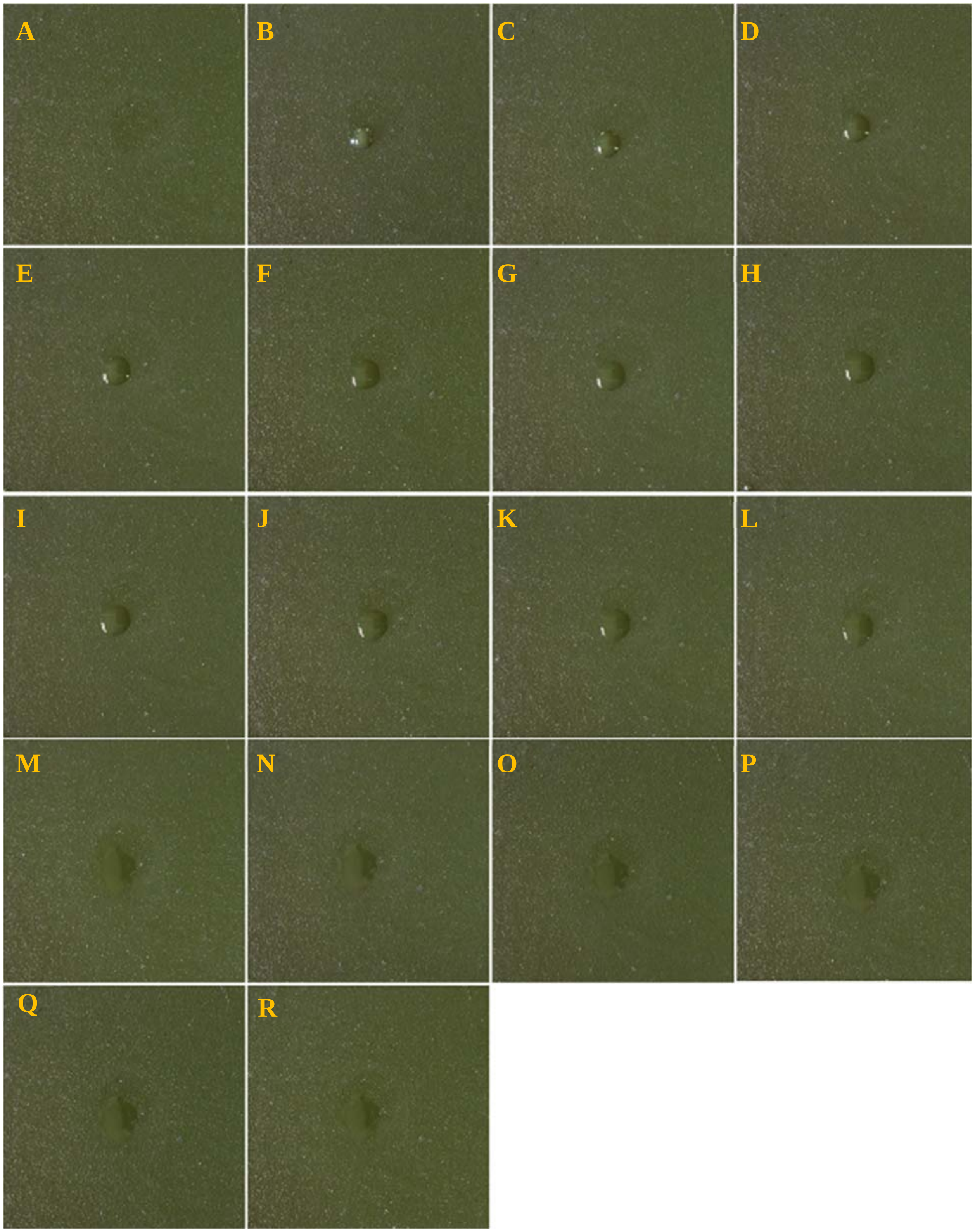
Appendix B

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 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.

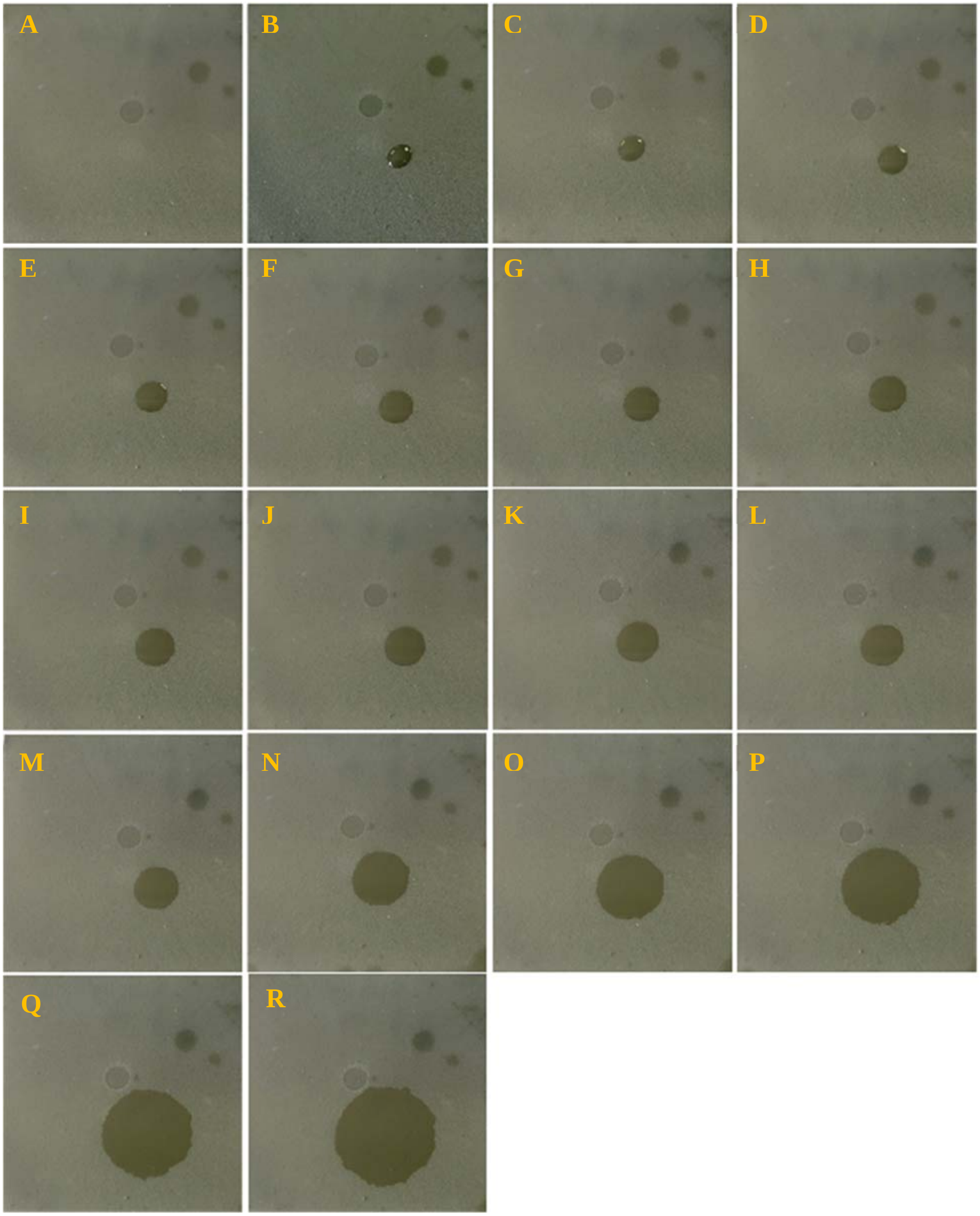


Fig. C2 — MES on the fluoropolymer coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

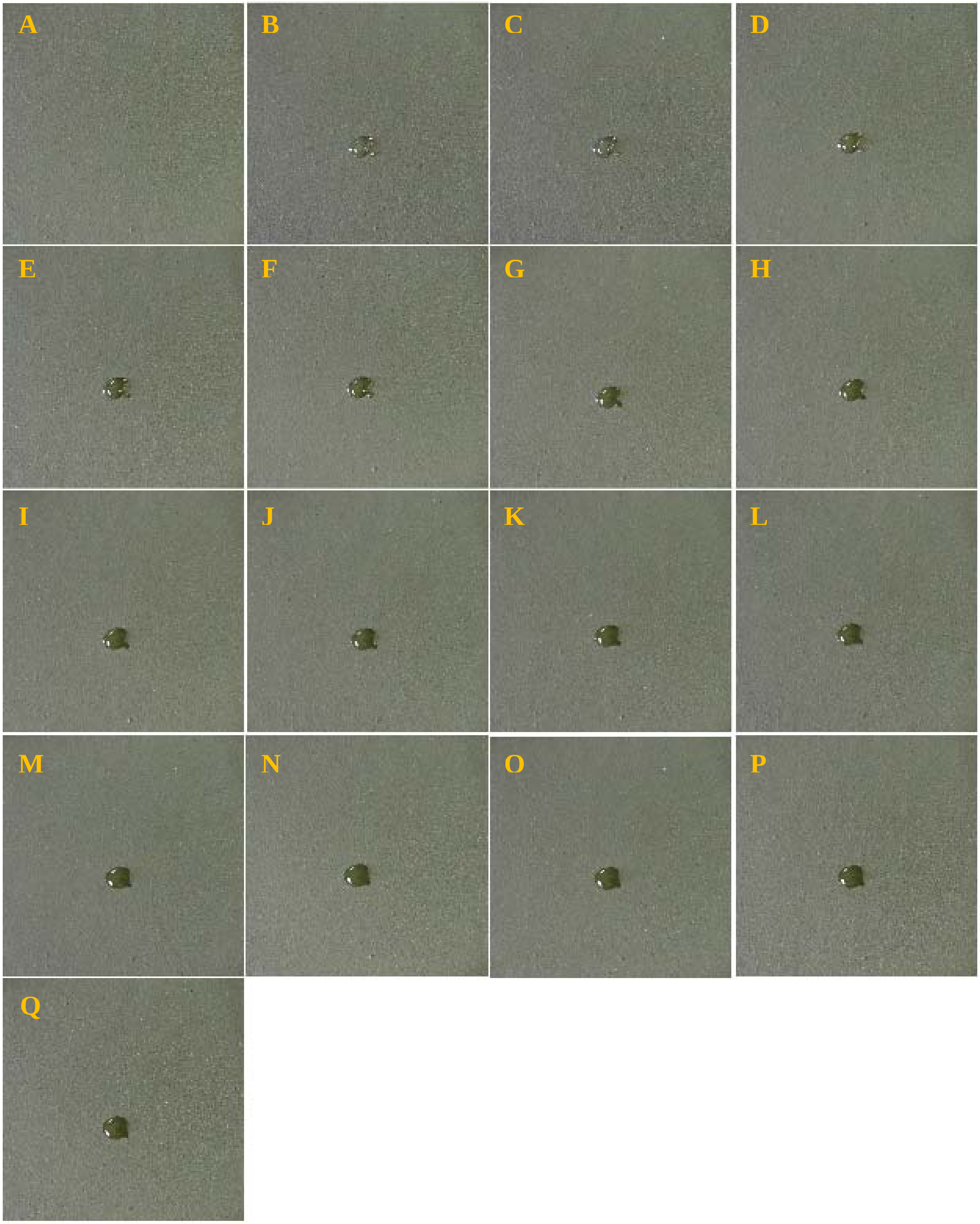
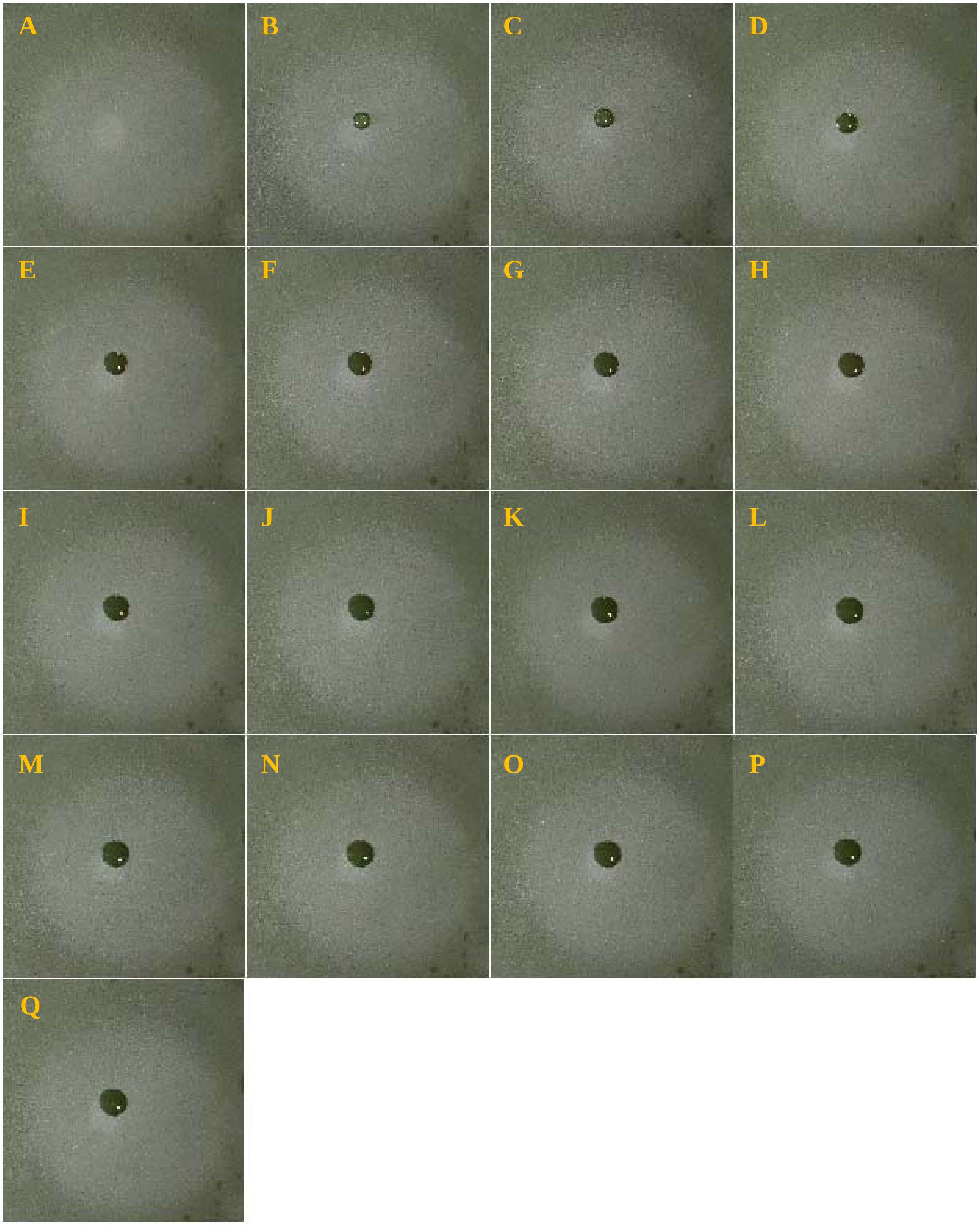


Fig. C3 — DMMP on the fluoropolymer coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix D

IMAGES OF AVIRAL TREATED COUPONS (THICK)

Fig. D1 — DFP on thick AVIRAL 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. (B) No cover at initial application.

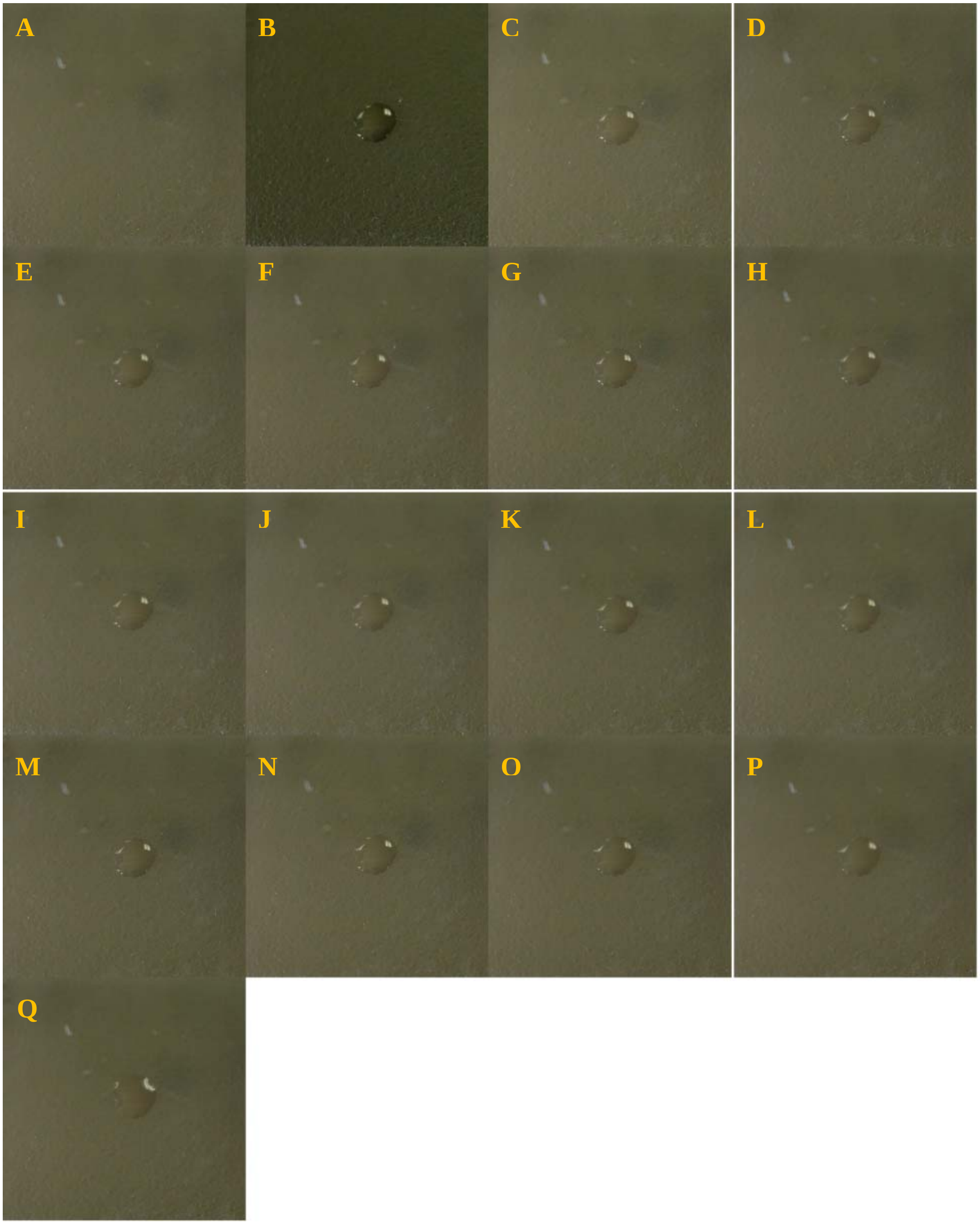


Fig. D2 — MES on thick AVIRAL coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

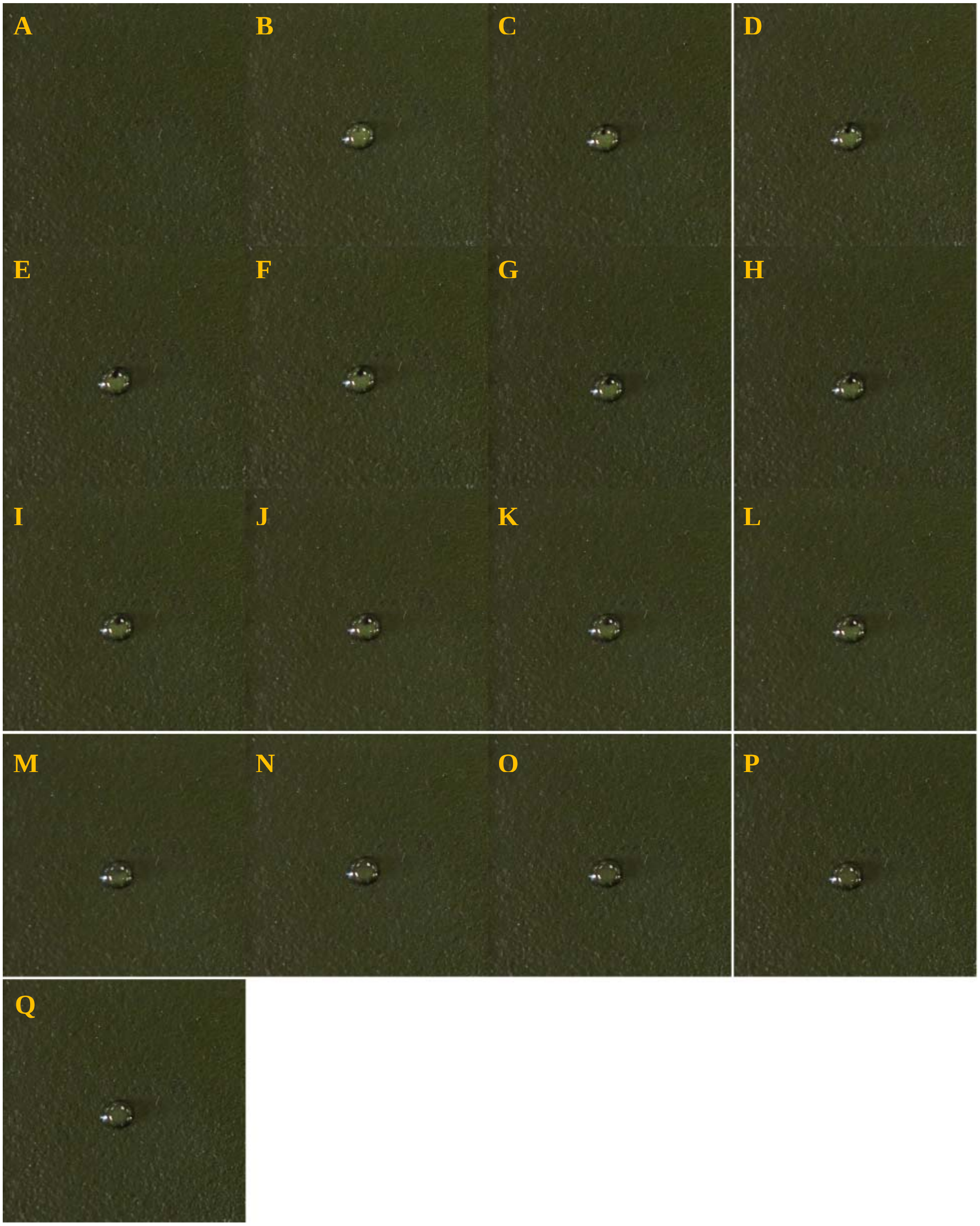


Fig. D3 — DMMP on thick AVIRAL coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

Appendix E

IMAGES OF AVIRAL TREATED COUPONS (THIN)

Fig. E1 — DFP on thin AVIRAL 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.

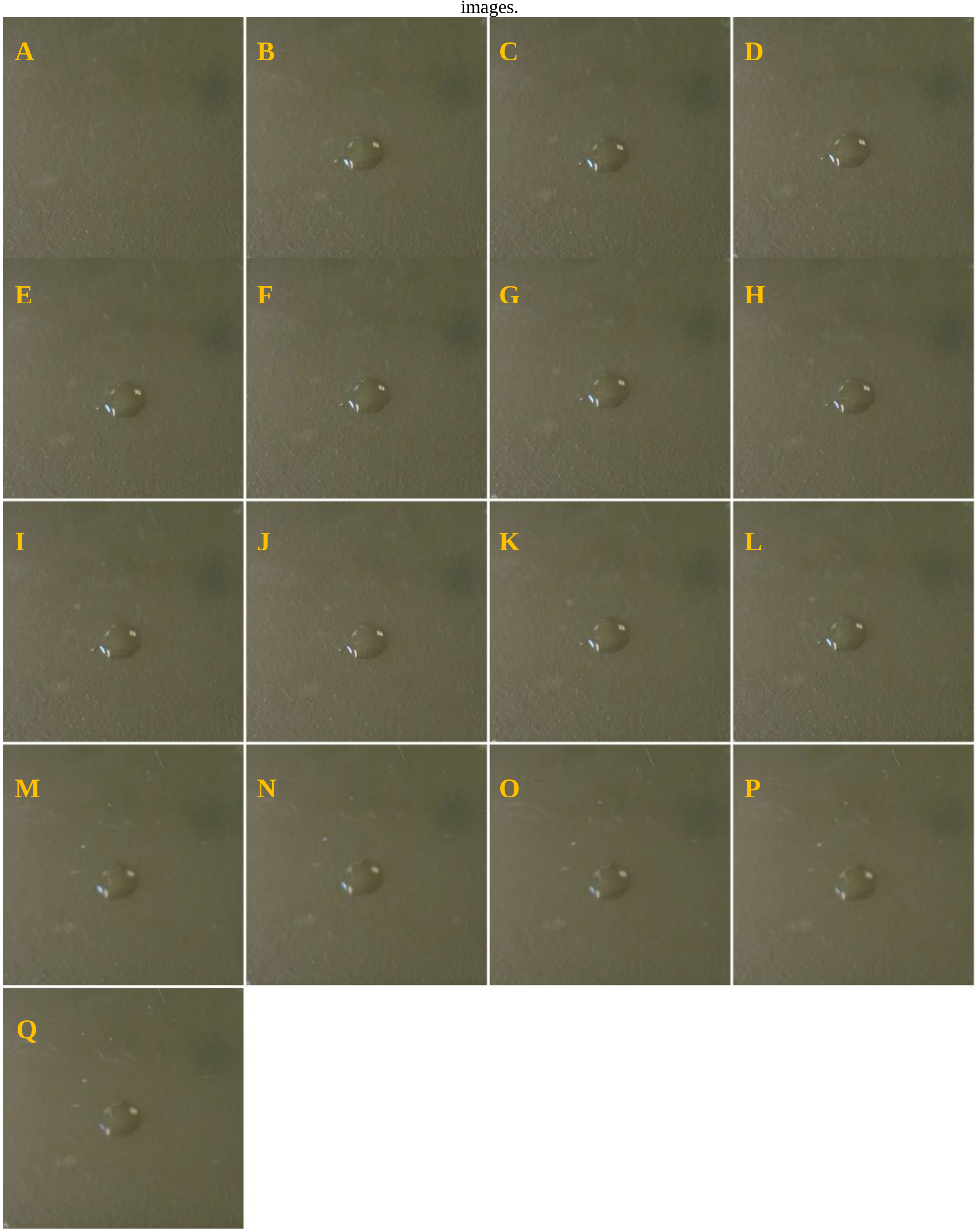


Fig. E2 — MES on thin AVIRAL coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

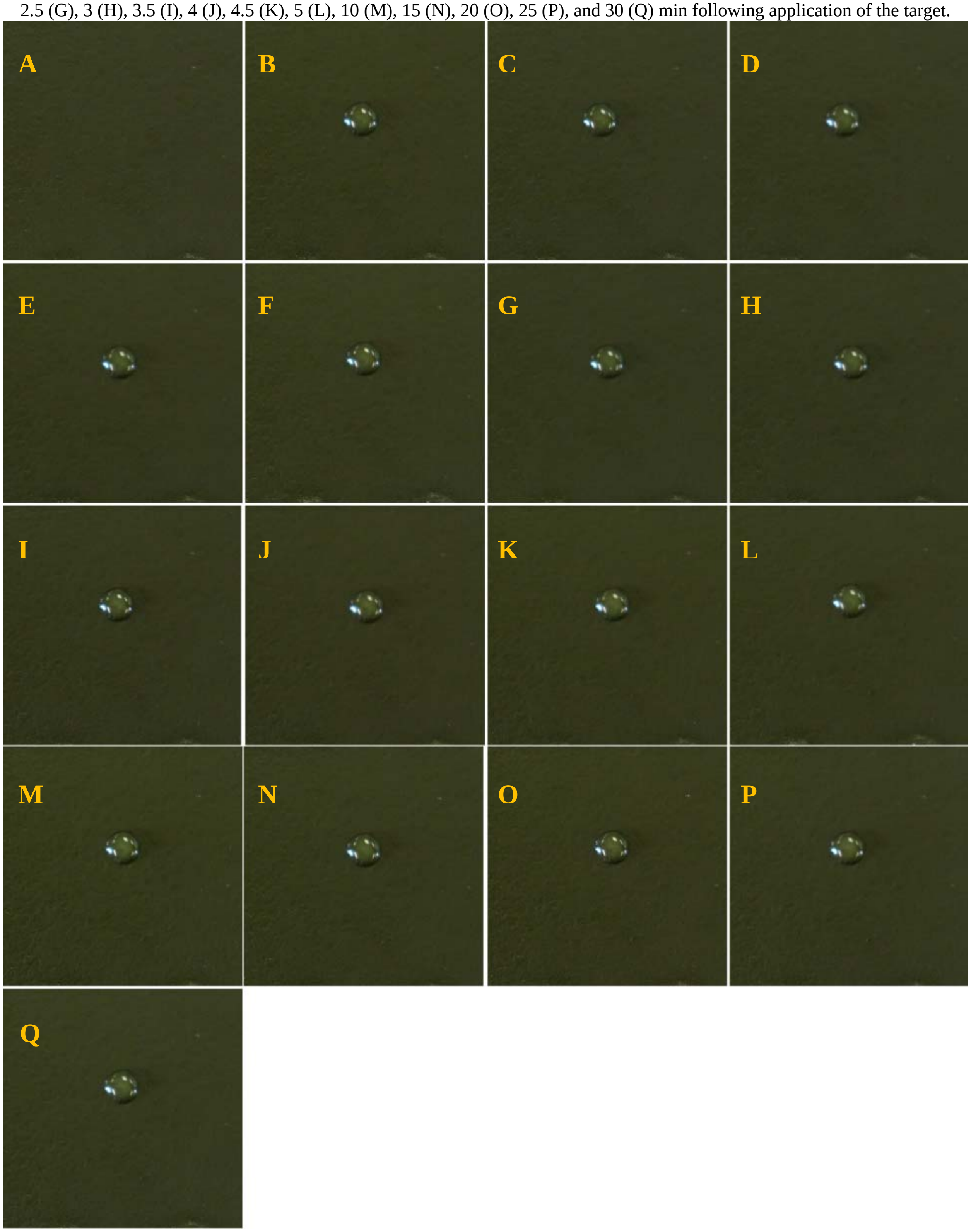


Fig. E3 — DMMP on thin AVIRAL coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.