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Bioinspired Surface Treatments for Improved Decontamination: Ultra-smooth Hybrid Coatings II

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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 surface treatment prepared by attaching liquid-like PDMS chains oriented at the surface using a modified application methodology. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphonate, diisopropyl fluorophosphate, and 2-chloroethyl ethyl sulfide 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 surface treatment prepared by attaching liquid-like PDMS chains oriented at the surface using a modified application methodology. The materials were deposited on polyurethane paint coated aluminum coupons. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphonate, diisopropyl fluorophosphate, and 2-chloroethyl ethyl sulfide 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: ULTRA-SMOOTH HYBRID 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) with a view toward evaluation and development of top-coat type treatments suitable for application to painted surfaces that would reduce retention of chemical threat agents 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 study investigates a recently published coating that has promise as an anti-smudge self-cleaning coating which may also have useful properties for reduced chemical retention.

Slippery omniphobic covalently attached liquid (SOCAL) treatments offer liquid-like characteristics but are based on covalently attached flexible groups, generally on a smooth surface. They are not dissolved or displaced by contacting liquids. Many SOCAL-like treatments involve complex deposition methods or lead to nondurable coatings. Three previous reports covered testing applications of SOCAL based coatings for reduction of target retention.[1-3]. The current report focuses on evaluation of a new SOCAL material identified in the open literature.[4] It had previously been evaluated using literature methods but a modification to the application method was tested in this study.[5] Many potential coatings and the preparation methods are published in the open literature but often use coating techniques such a dip-coating that are not applicable for many application. Investigation of the impact of using more appropriate methods such as squeegee application is an important consideration. The coating considered for this test represented a pretty well performing coating when dip coating was used and could be modified to use the squeegee application methodology.

For the complete system, aluminum coupons painted with a polyurethane paint system were treated with the dimethoxydimethylsilane-tetraethyl orthosilicate (DMDS/TEOS) sol-gel layer by dip-coating or alternate “squeegee” method described later.[4] A range of DMDS/TEOS weight percent solutions were tried with one, 15 wt%, tried with a short aging time and the longer time used for the other samples (Figure 1). The coupons were subjected to standard evaluations including measurement of sessile, sliding, and shedding contact angles and quantification of retention for the simulant compounds.

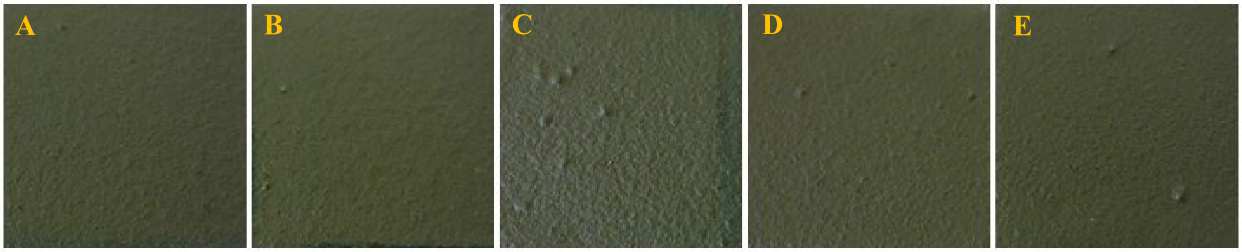

Fig. 1 — Images of painted coupons with (A) 10 wt%; (B) 11 wt%; (C) 12.5 wt%; (D) 13 wt%; (E) 15 wt%.

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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 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) [6]. 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), dimethyl methylphosphonate (DMMP), and 2-Chloroethyl ethyl sulfide (CEES), 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.

Coating Synthesis.

Previous experiments dip-coated sol-gels on painted Al coupons and involved aging steps of multiple days. A simple squeegee-based coating method was used for these experiments, with much shorter aging steps, and a volume of ethanol one-half that present in the dip-coating experiments. Therefore, the sol had increased concentrations of active coating components, which did not result in any notable precipitation or change in viscosity.

Each coating was prepared from an initial sol of molar ratio: 1 TEOS: 0.005 HCl: 5 H2O: 20.5 ethanol (TEOS = tetraethyl orthosilicate). Dimethoxydimethylsilane (DMDS) was added in a determined amount of 10 wt% (1.305 g), 11 wt% (1.44 g), 12.5 wt% (1.63 g), 13 wt% (1.70 g), or 15 wt% (1.96 g) DMDS/TEOS. The approach is that a transparent silicate coating is deposited in which liquid-like PDMS chains orient at the surface.

Specifically, 75 mL ethanol, 13.05 g TEOS, 0.031 g HCl (37% in H2O standard reagent), and 5.63 g H2O were stirred at RT in a closed PFA jar for 1 day. Stirring was stopped and the sol was aged for 1 day at RT. DMDS was added in the determined amount and the mixture was stirred for 1 day at RT, then aged for 1 day at RT. Painted Al coupons were rinsed with 2-propanol and dried at 60 °C prior to coating with DMDS-TEOS. Painted coupon surfaces were coated by dipping a squeegee into the sol and wiping firmly across each surface twice in the same direction (squeegee was turned over after the first wipe). The squeegee was a small silicone wedge, Foshio brand, marketed for "Installing tint, wallpaper, vinyl, decal." Each coating was allowed to dry at RT for 5 minutes, then placed on Fluoroware and cured in an oven at 80 °C for ≥ 30 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 treatments. Each table includes data on the relevant support material, a painted aluminum coupon and for a Fomblin Y lubricated painted aluminum coupon. Results for five variants coated directly on painted coupons were considered. Application of coatings considered here reduced the surface energy of the painted surface (Table 1 and Figure 2) to values similar to what is observed when Fomblin Y is used to coat a coupon.

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)**
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	
15 wt% Dipcoating	water	83.7 ± 1.1	>60	>60	27.3 ± 1.7
	ethylene glycol	79.0 ± 1.0	>60	>60	
	n-heptane	--	--	--	
10 wt% squeegee	water	79.5 ± 0.8	>60	>60	25.9 ± 0.8
	ethylene glycol	70.9 ± 0.57	>60	>60	
	n-heptane	--	--	--	
11 wt% squeegee	water	82.1 ± 1.1	>60	>60	23.6 ± 0.9
	ethylene glycol	70.9 ± 0.26	>60	>60	
	n-heptane	--	--	--	
12.5 wt% squeegee	water	79.5 ± 0.65	>60	>60	25.9 ± 0.8
	ethylene glycol	70.8 ± 0.99	>60	>60	
	n-heptane	--	--	--	
13 wt% squeegee	water	81.4 ± 0.22	>60	>60	24.9± 0.4
	ethylene glycol	74.0 ± 0.81	>60	>60	
	n-heptane	--	--	--	
15 wt% squeegee	water	80.4 ± 0.59	>60	>60	25.3± 0.6
	ethylene glycol	71.9 ± 0.52	>60	>60	
	n-heptane	--	--	--	

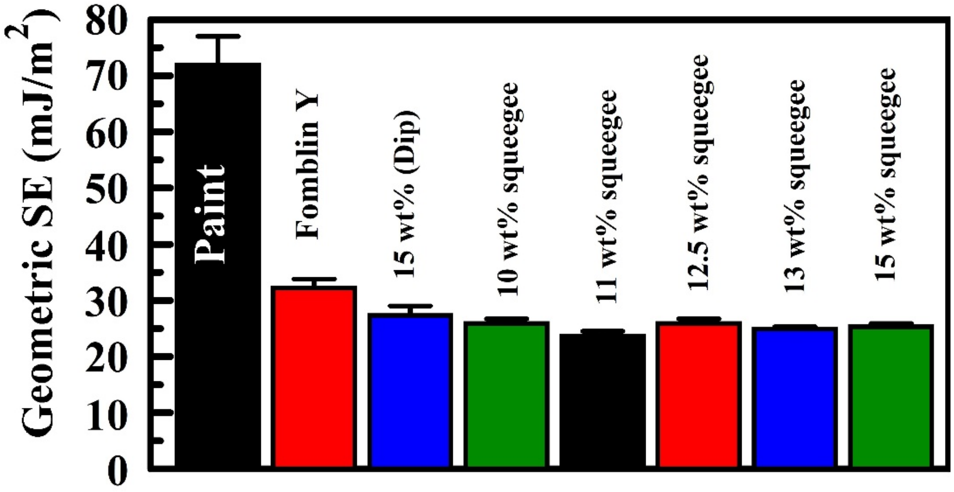

Fig. 2 — Geometric surface energy (mJ/m^2) for the evaluated coatings. Paint and Fomblin Y results provided for comparison.

The 15 wt% DMDS/TEOS variation for dip coating is included for comparison, which had a surface free energy slightly lower than that observed for the Fomblin Y oiled coupon. All of the squeegee applied variants had surface energies similar to each other and only slightly lower than was seen for the dip coated coupon. All of the surfaces were fully wetted by heptane. No sliding on the surfaces was noted below an incline of 60°. No shedding behavior was noted for these surfaces. None of the coating variants induced observable changes in *the* appearance of the painted coupons.

The tendency of droplets to spread across the surfaces was also evaluated (Figure 3; Appendices). 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. The coatings considered here produced similar results to each other and to the formulation when dip coating was used. DMMP spread was negligible for all coatings; application of Fomblin Y had a negative impact on this behavior. DFP spread was negligible for the coatings as well. MES spread was also negligible for all coatings, and all of the surfaces provided reductions larger/equivalent to that noted for the Fomblin Y lubricated surface.

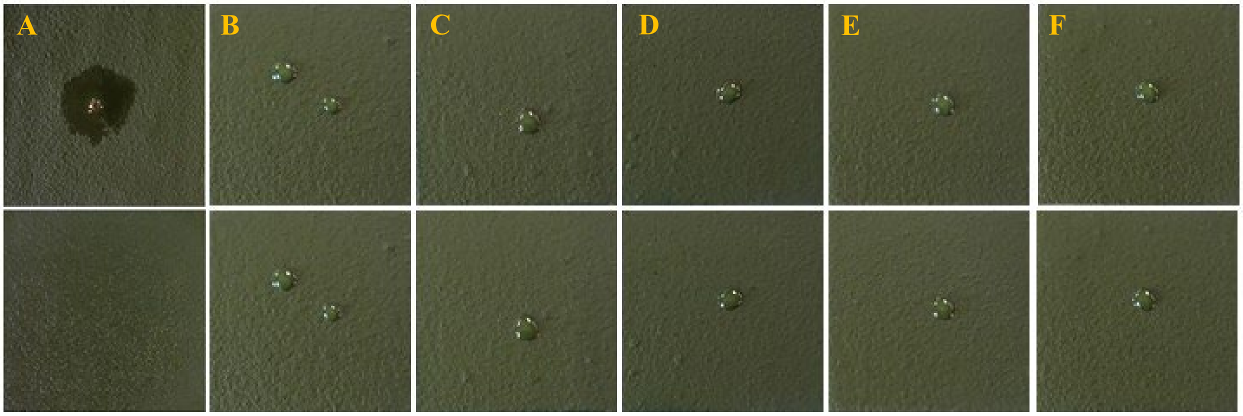

Fig. 3 — Images from initial series of coupons at 0 and 30 min following MES exposure: (A) Paint only; (B) 10 wt%; (C) 11 wt%; (D) 12.5 wt%; (E) 13 wt%; and (F) 15 wt%.

The coupons were subjected to simulant exposure (10 g/m^2), aging, washing, and drying. These materials showed little change in the appearance or wetting characteristics over these processing steps. When the soapy water process was employed (Figure 5 and 6; Table 2), retention of all targets was reduced compared to that observed for the painted coupons or Fomblin Y coated coupons for all chemicals tested.

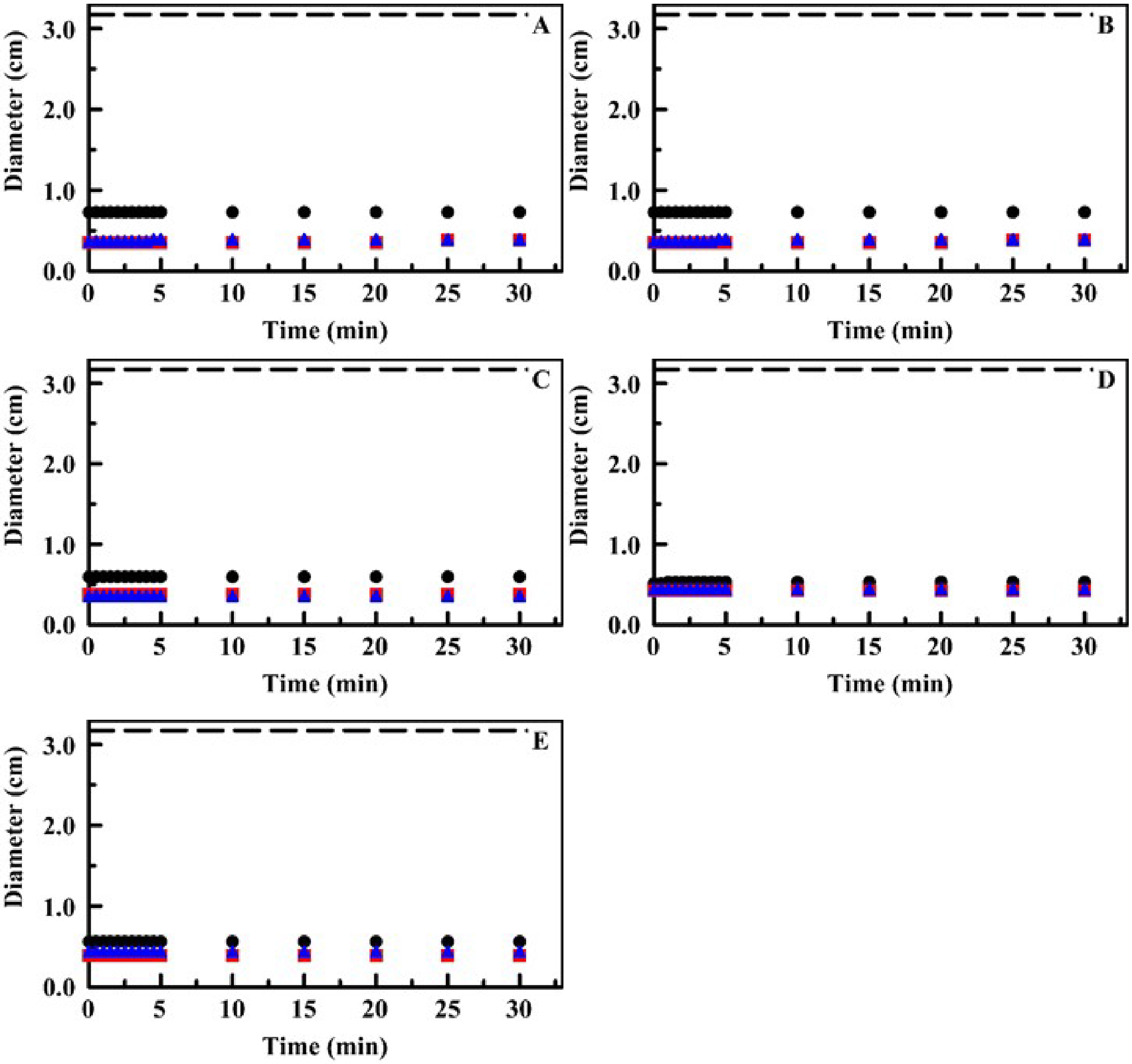

Fig. 4 — Droplet diameters over time following exposure to DFP (black), MES (red), and DMMP (blue) for painted coupons with (A) 10 wt%; (B) 11 wt%; (C) 12.5 wt%; (D) 13 wt%; (E) 15 wt%.

There did not appear to be any correlation in the changes in retention observed and the weight percent of the various formulations. The 15 wt% short aging time sample represented the best reduction across all the chemicals when dip coating was used for application (Figure 5). For all variants applied with squeegee method (Figure 6), significant reductions in retention for all chemicals was observed in comparison to the variant prepared using the literature protocol. The 10 wt% and 11 wt% coated samples performed the worst among the squeegee samples and were only slight improvements over the best dip coating sample. For samples with similar weight percent between dip coating and squeegee clear improvements were always observed. In fact, the variant with 12.5 wt% is one of the best performing materials identified to date and all variants were represented in the list of better performing samples.

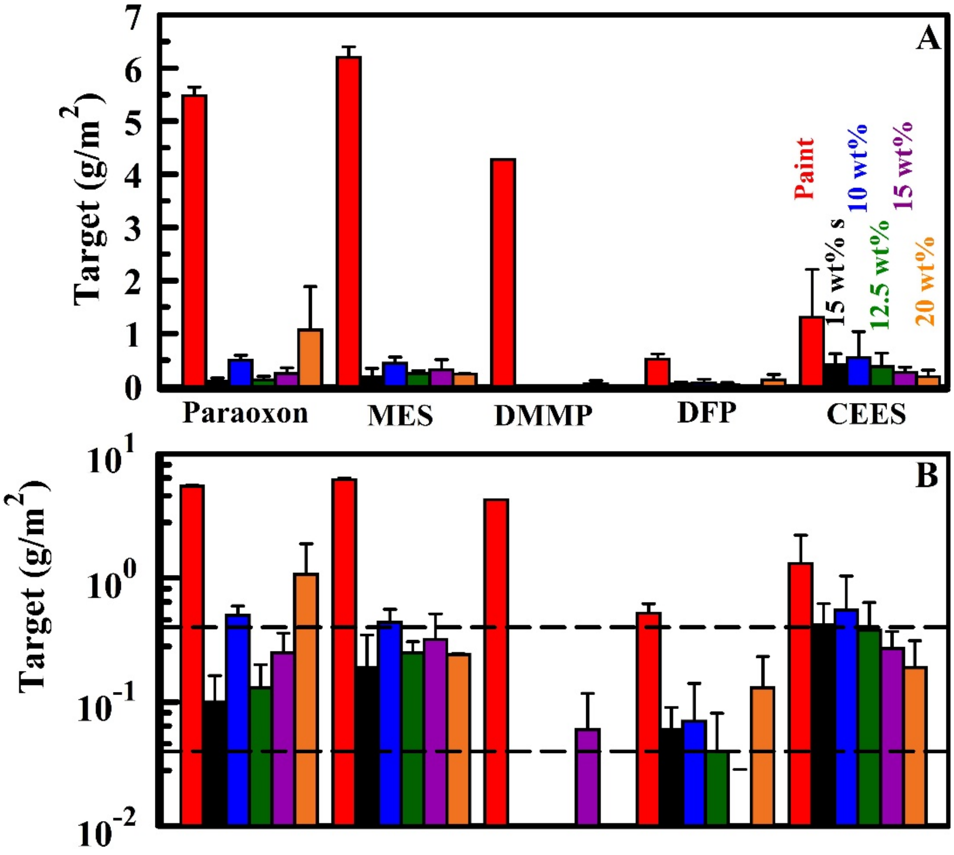

Fig. 5 — Target retention by coupons from previous dip coating series following treatment with an air stream and rinsing with soapy water shown to left on a linear scale (A) and (B) on a log scale: (left to right) painted (red), 15 wt% s (black), 10 wt% (blue), 12.5 wt% (green), 15 wt% (purple), 20 wt% (orange).

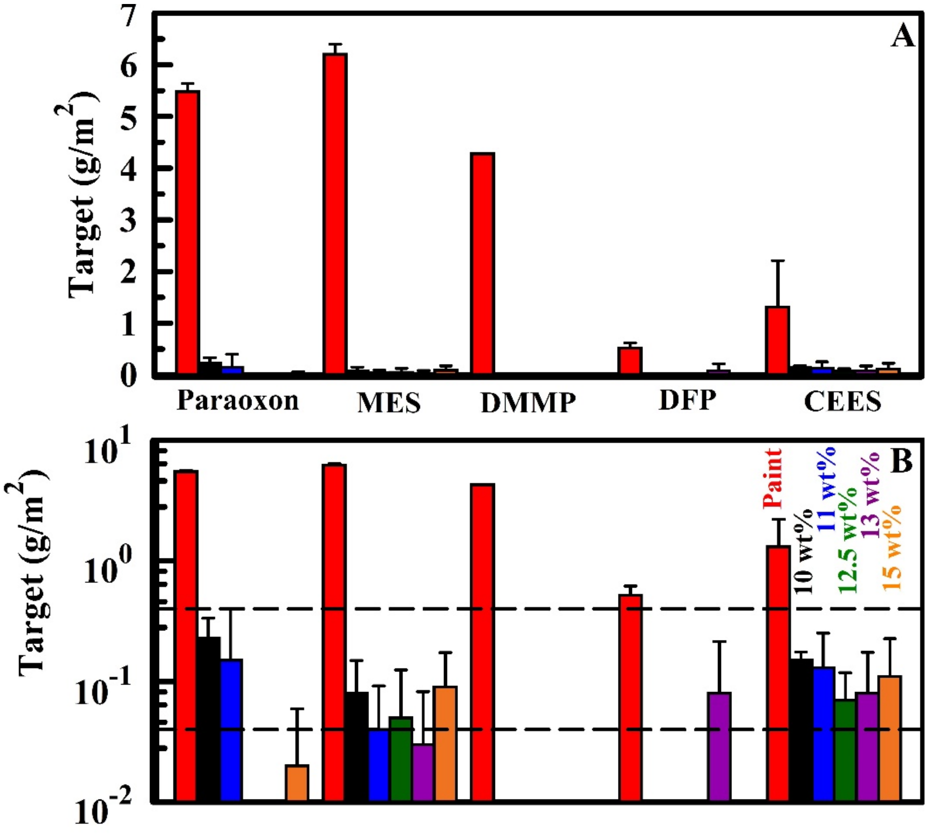

Fig. 6 — Target retention by coupons from current squeegee series following treatment with an air stream and rinsing with soapy water shown to left on a linear scale (A) and (B) on a log scale: (left to right) painted (red), 10 wt% (black), 11 wt% (blue), 12.5 wt% (green), 13 wt% (purple), 15 wt% (orange).

For comparison, paint only coupons retained significant amounts of target at 5.48, 6.20, 4.28, and 0.52 g/m^2. When no rinsing or decontamination steps were used, paint only coupons 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.

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

Coupon	Paraoxon	MES	DMMP	DFP	CEES
Paint Only	5.48	6.20	4.28	0.52	1.31
Fomblin Y Oiled Paint	1.24	2.85	0.59	0.34	1.36
15 wt% dipcoating	0.10	0.19	ND	0.06	0.42
10 wt% squeegee	0.23	0.08	ND	ND	0.15
11 wt% squeege	0.15	0.04	ND	ND	0.13
12.5 wt% squeegee	ND	0.05	ND	ND	0.07
13 wt% squeegee	ND	0.03	ND	0.08	0.08
15 wt% squeegee	0.02	0.09	ND	ND	0.11

ND = not detected

CONCLUSIONS

The coatings generated using dimethoxydimethylsilane to form liquid-like PDMS chains oriented on the surface produced promising results. The materials exhibited lower surface energies than the original painted surface that were similar to what is produced for a Fomblin Y oiled coupon. The droplet spreading behavior was reduced for most coatings by a large amount with only the variation with the lowest weight percent of dimethoxydimethylsilane resulting in DFP still spreading on the surface. Overall retention of all targets was reduced from what was observed for the paint only or Fomblin Y coupons. It may be further modifications to the coating will result in a coating that would further reduce retention of agents. These materials had little to no impact on coupon visual appearance and none showed any visible damage from target application. Spectrophotometric analysis is necessary to determine the overall impact on color and reflectivity. It may also be of interest to consider the impact of outdoor aging on these materials.

As mentioned one of the variants, 12.5 wt% DMDS/TEOS, matched the performance of the best coating tested to date. All the other variants while not matching the performance of this sample still had very low retention numbers for chemical agents. In addition testing for CEES was a relatively late addition to testing protocols and the best to date tested coating was not subjected to CEES retention tests. Since CEES retention had been added many coatings were performing well against other chemicals but would have poor performance for CEES. These coatings demonstrated similar retention characteristics for all chemicals including CEES. This is very promising that the alteration in application method did not reduce the performance of the coating. The fact that the performance in fact increased is useful and further characterizations are being carried out for samples to see if an easily identifiable cause can be found.

ACKNOWLEDGEMENTS

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Appendix A

10 wt% coated COUPON IMAGES

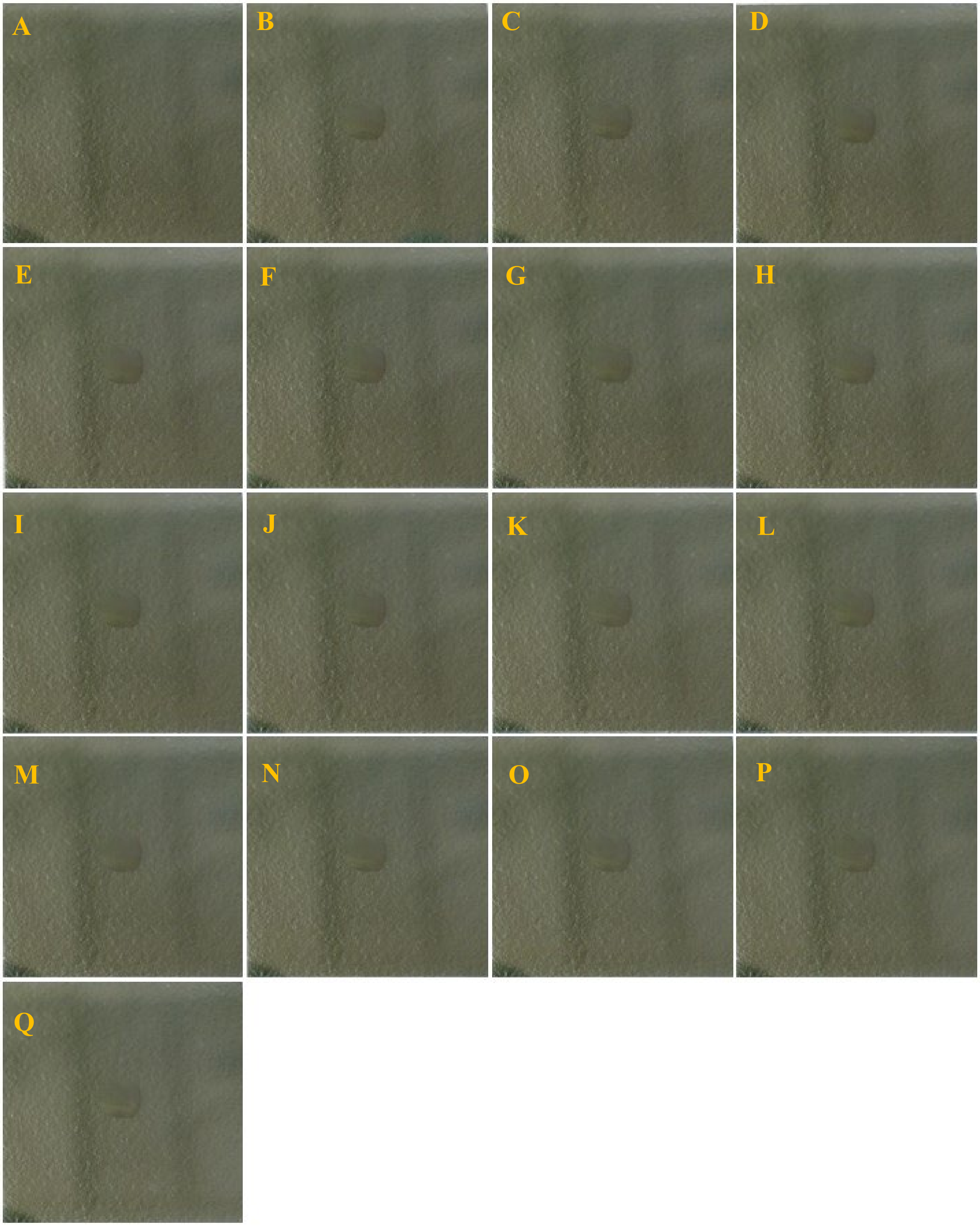


Fig. A1 — DFP on 10 wt% (short) coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images 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 10 wt% (short) coated. Images of a film supported by painted 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.

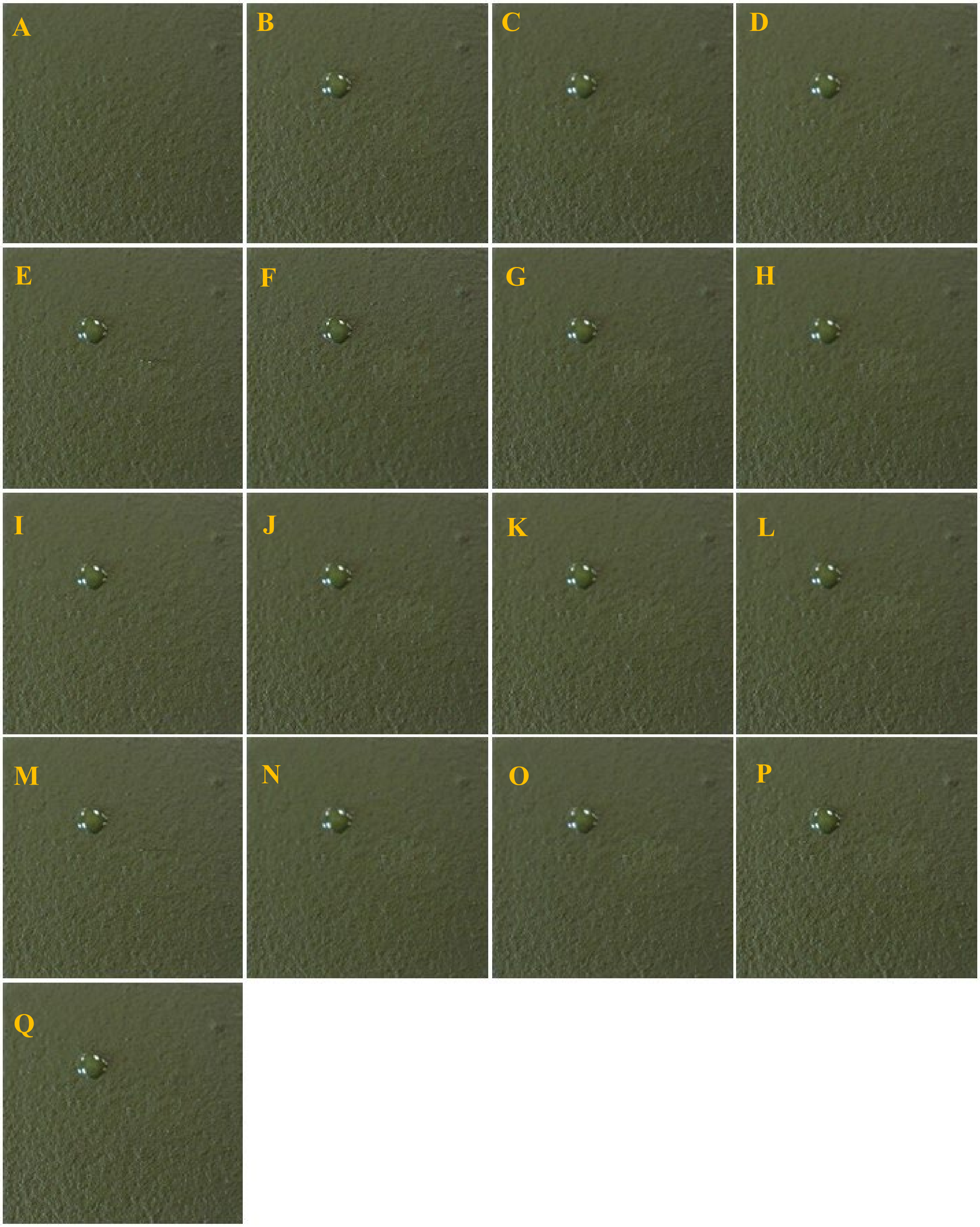
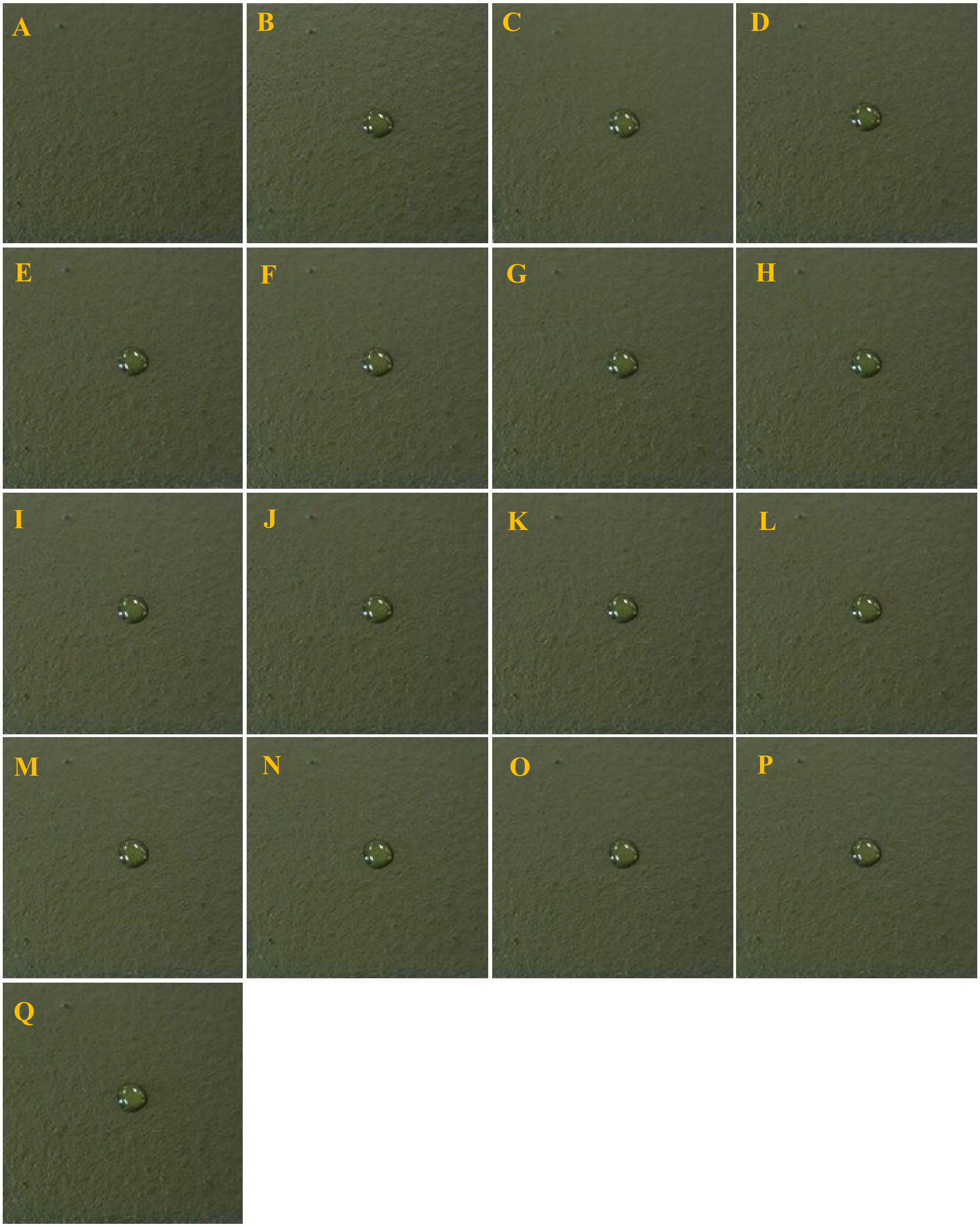


Fig. A3 — DMMP on 10 wt% (short) coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix B

11 wt% coated COUPON IMAGES

Fig. B1 — DFP on 11 wt% coated. Images of a film supported by painted 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), 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.

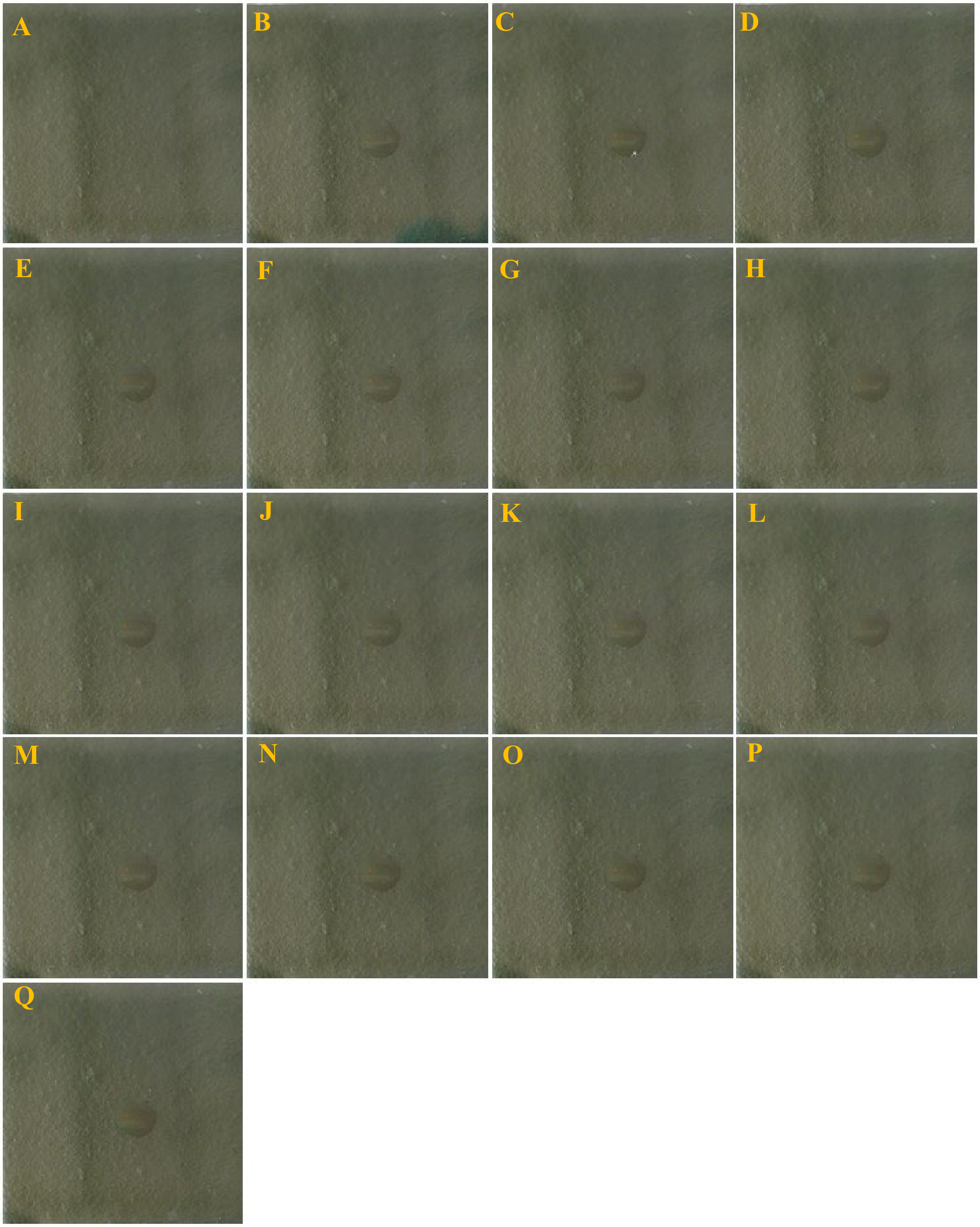


Fig. B2 — MES on 11 wt% coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

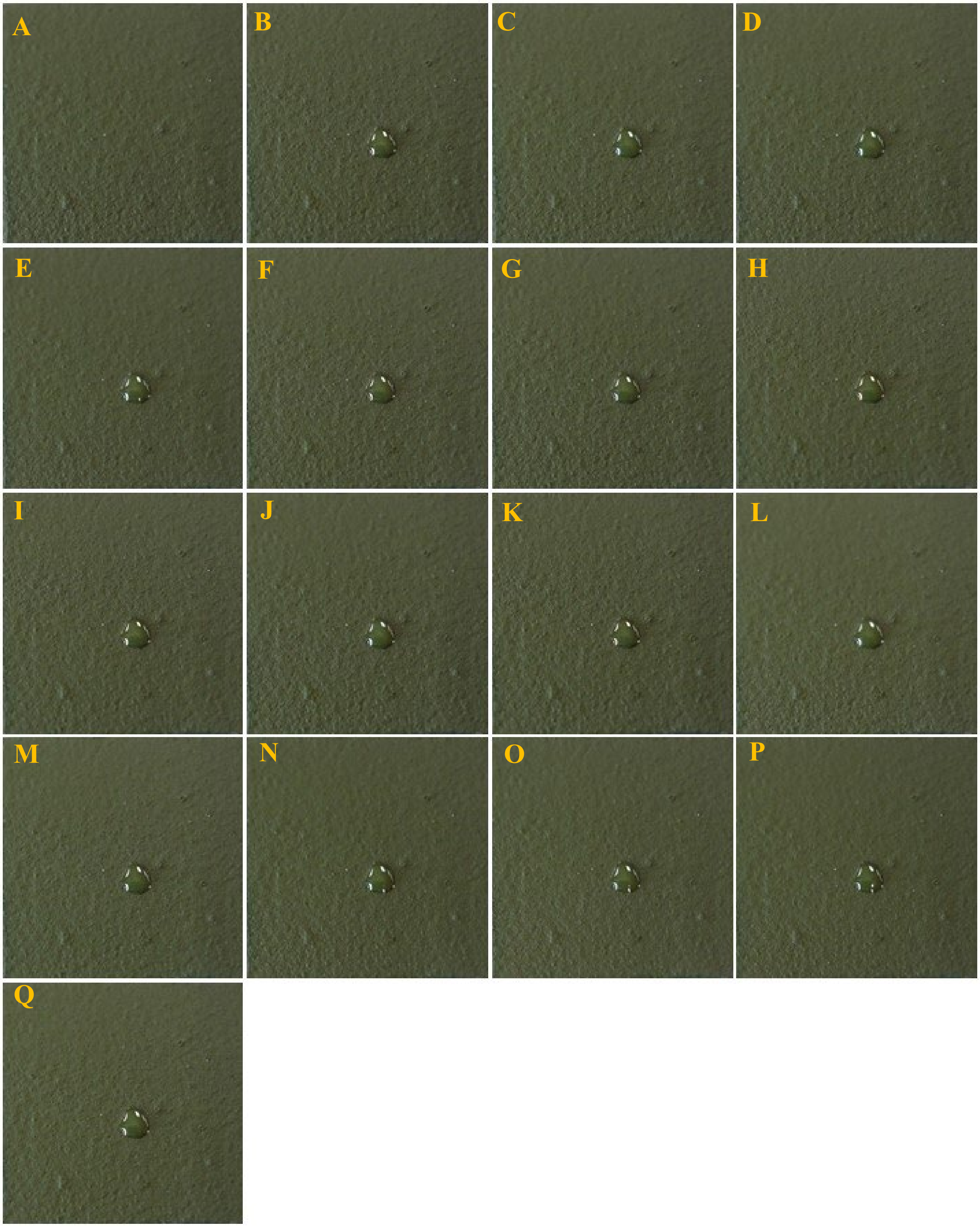
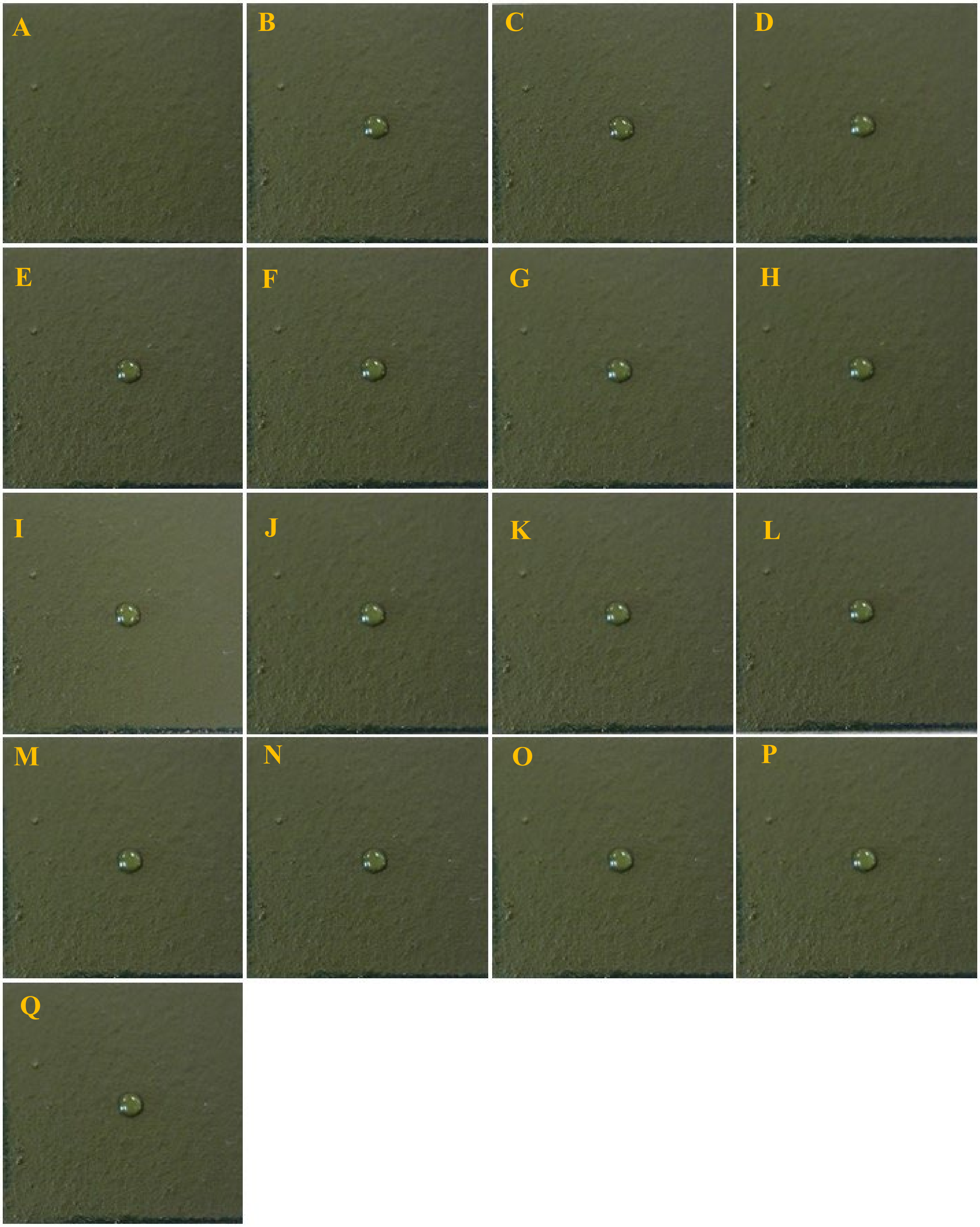


Fig. B3 — DMMP on 11 wt% coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix C

12.5 wt% coated COUPON IMAGES

Fig. C1 — DFP on 12.5 wt% coated. Images of a film supported by painted 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), 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.

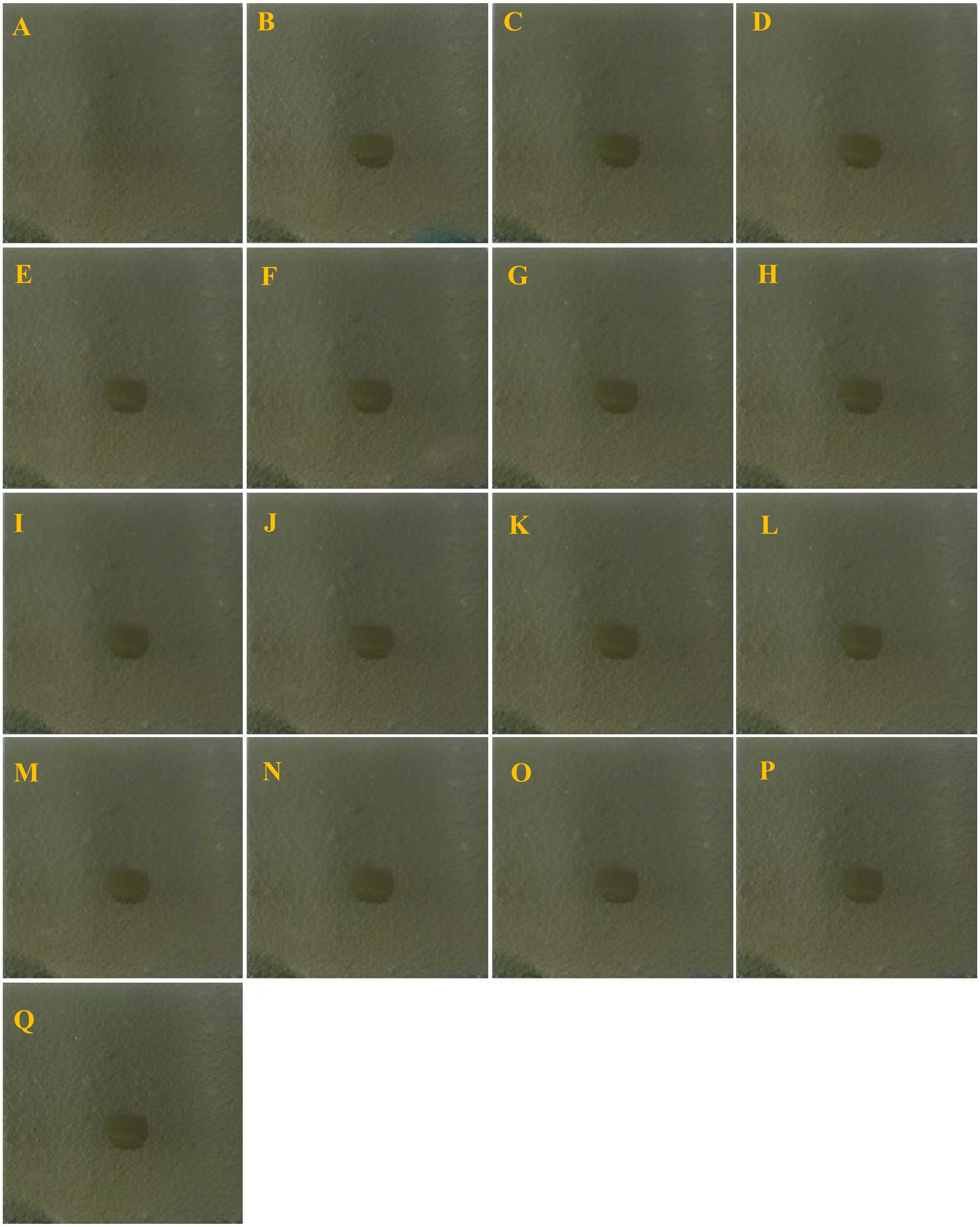


Fig. C2 — MES on 12.5 wt% coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

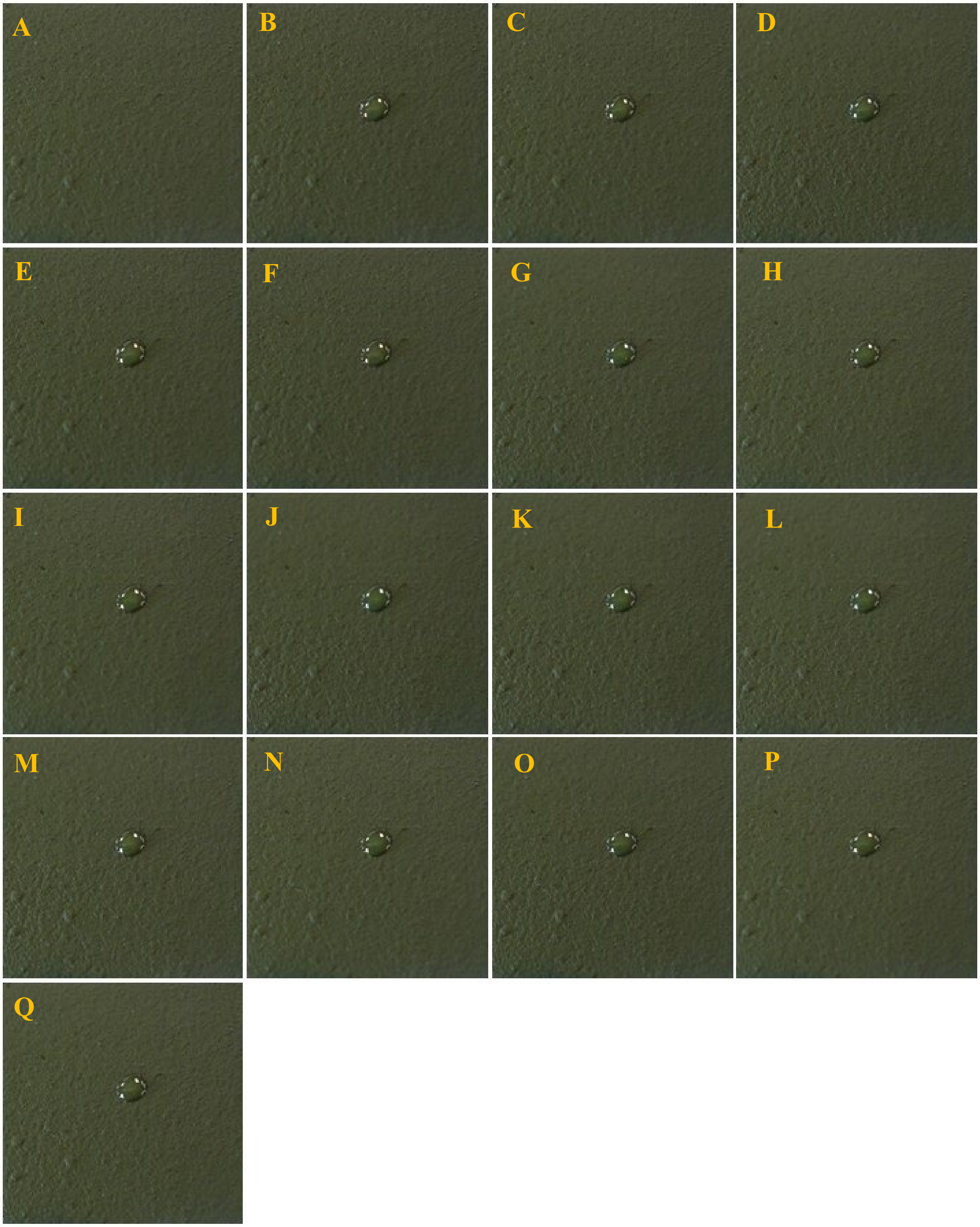
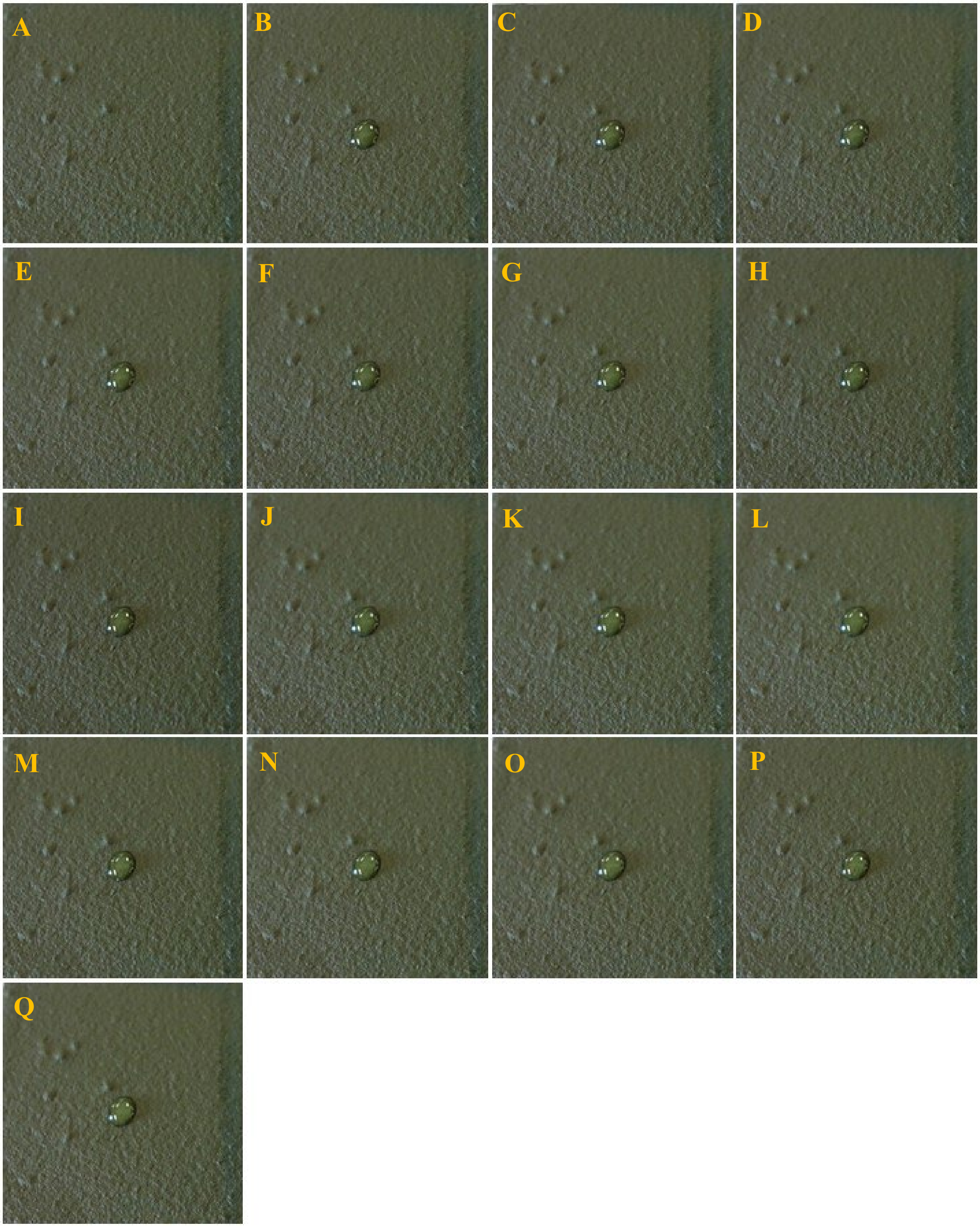


Fig. C3 — DMMP on 12.5 wt% dip coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix D

13 wt% coated COUPON IMAGES

Fig. D1 — DFP on 13 wt% coated. 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), 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.

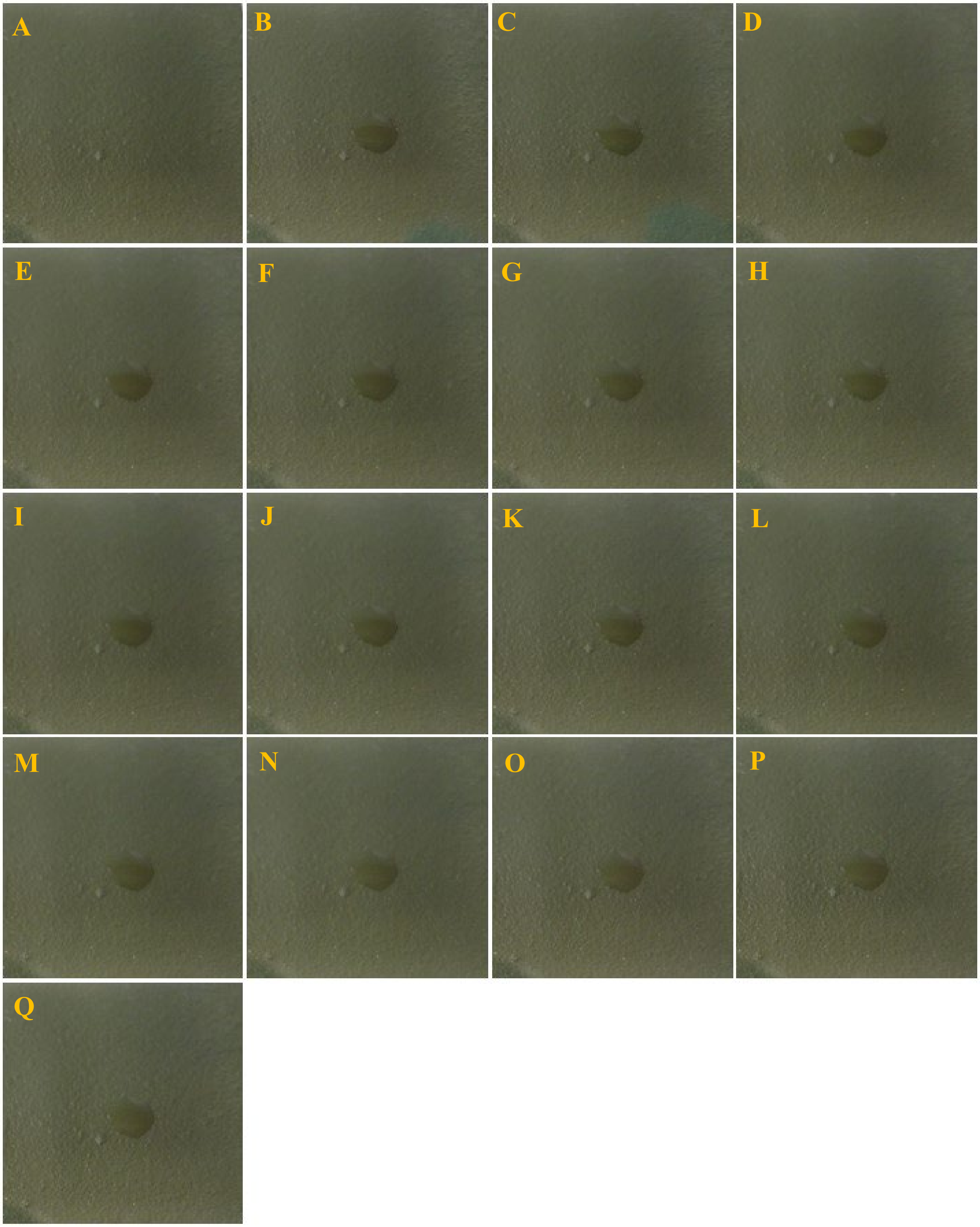


Fig. D2 — MES on 13 wt% coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

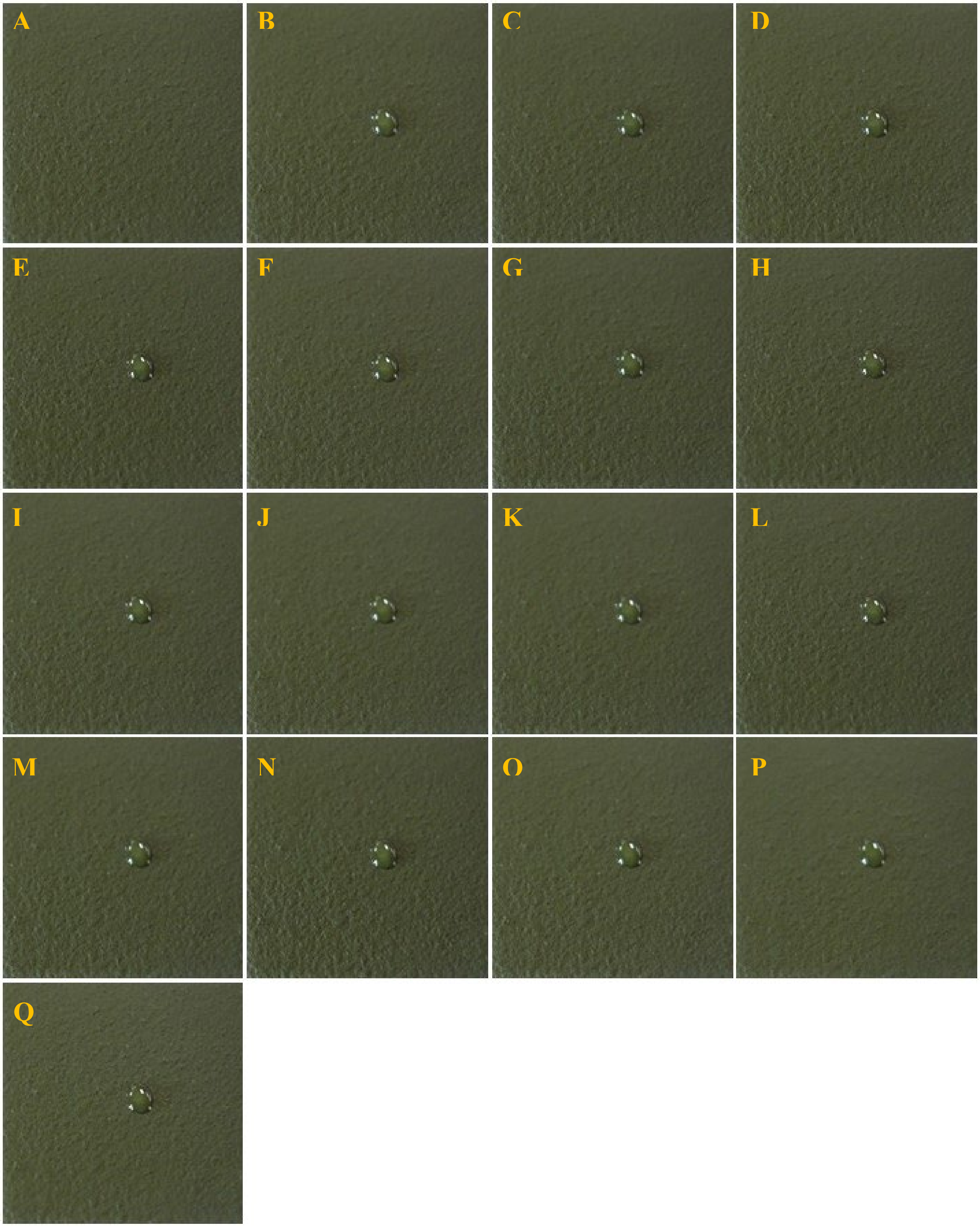
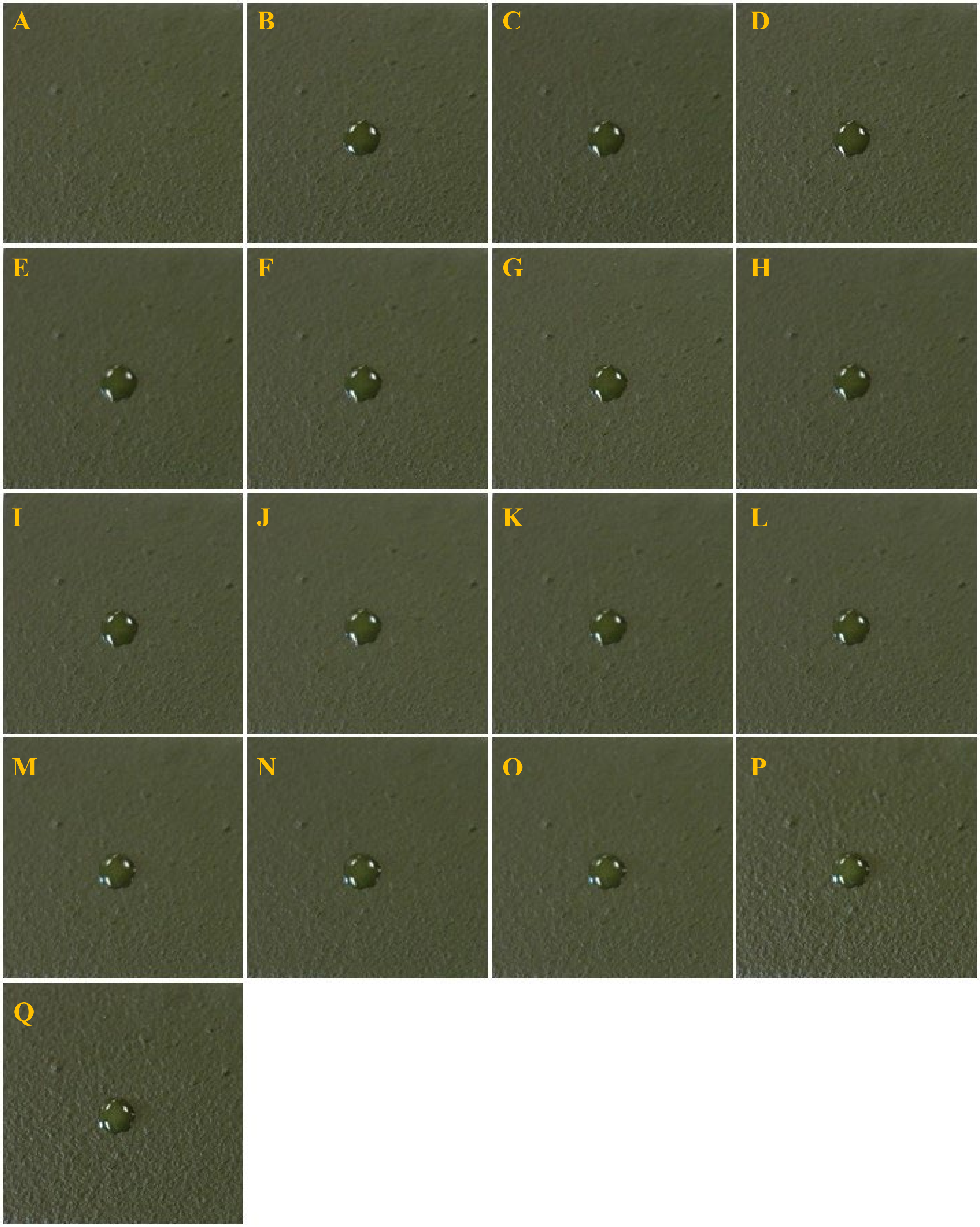


Fig. D3 — DMMP on 13 wt% coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix E

15 wt% coated COUPON IMAGES

Fig. E1 — DFP on 15 wt% coated. 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), 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

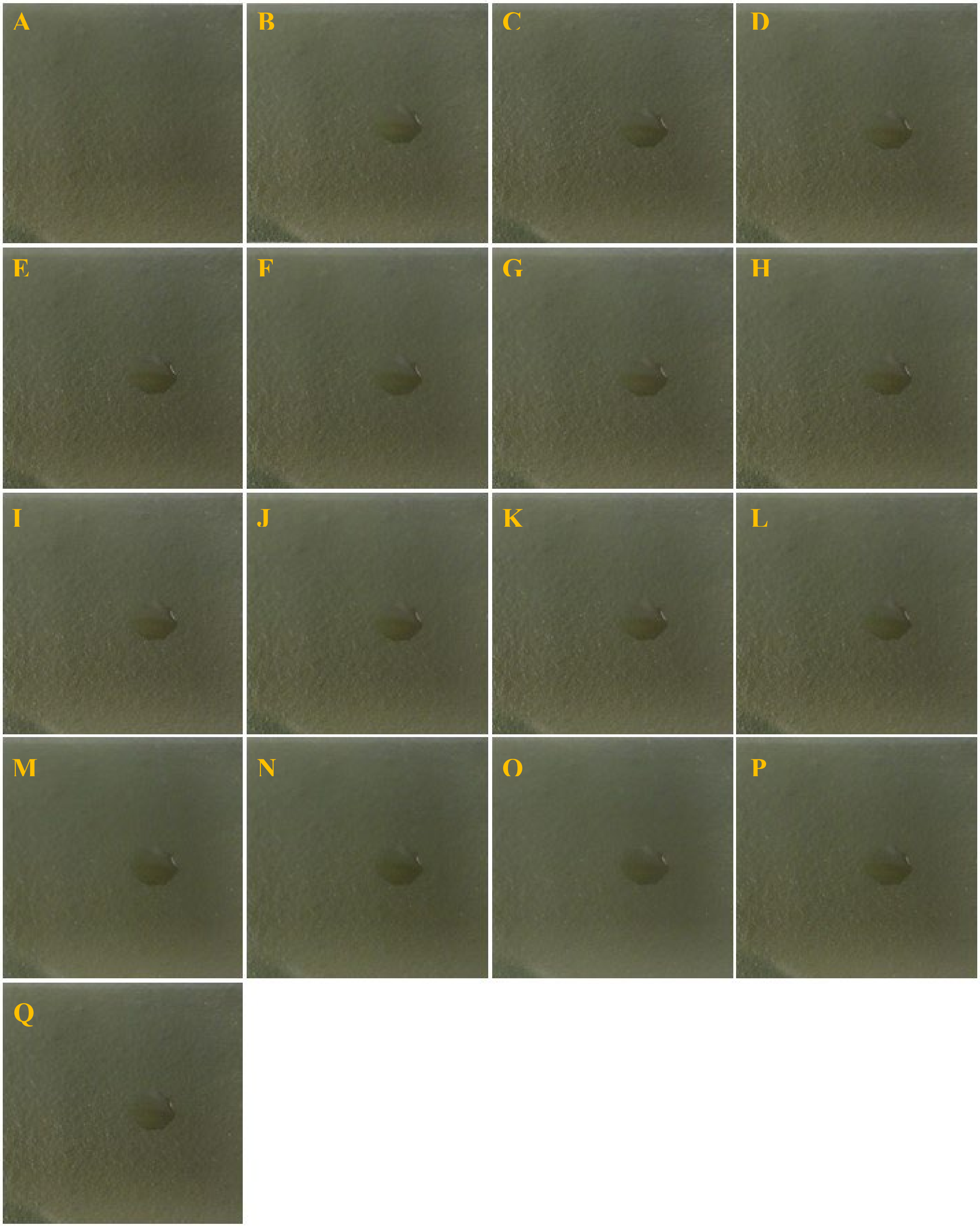


Fig. E2 — MES 15 wt% coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

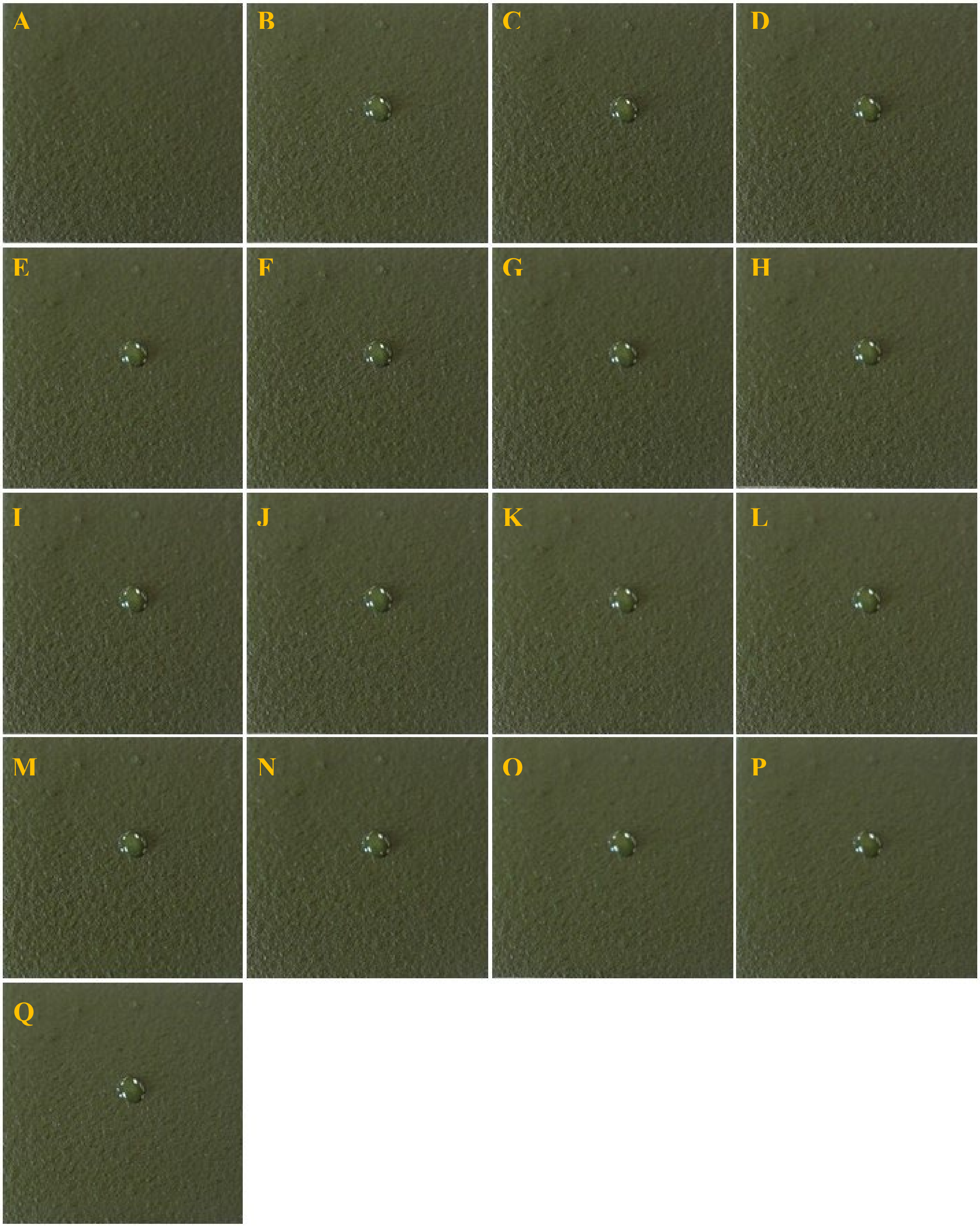


Fig. E3 — DMMP on 15 wt% coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.