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Bioinspired Surface Treatments for Improved Decontamination: Textured Polyurethane for Slippery Liquid-Infused Porous Surfaces (SLIPS)

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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 polymer SLIPS treatment applied over textured polyurethane. This is additional work following the previously published NRL/MR/6930--18-9773 on polymer-based slippery liquid-infused porous surfaces (SLIPS). 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 the potential for use of textured polyurethane in improving the performance of slippery liquid-infused porous surfaces (SLIPS) based on a textured fluoropolymer layer. This approach was intended to provide a surface similar to the textured aluminum of many SLIPS treatments while facilitating the use of a painted surface as the support material. The coatings were evaluated on both glass and polyurethane painted aluminum supports. 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: TEXTURED POLYURETHANE

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.

A previous document summarized results for evaluation of a polymer based slippery liquid-infused porous surface (SLIPS). [1] The current document summarizes results for the use of this SLIPS technology with a textured support layer. Slippery liquid-infused porous surfaces (SLIPS) typically comprise a film of lubricating liquid with a textured substrate (micro/nano or both). [2-7] The textured substrates described often include etched or boiled aluminum. The result of the SLIPS coated surface is one that is effectively smooth on the molecular scale and provides 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 offers a self-healing mechanism for damage to the surfaces, especially damage with a long, narrow surface profile. The liquid lubricant of the SLIPS treatment will 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.

In a previous study, we evaluated a polymer SLIPS treatment based on a poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) layer with texture in the coating driven by the porosity of the polymer layer. [2] Porosity is controlled by incorporating dibutyl phthalate (DBP) during casting of the film; it is subsequently extracted to yield a highly porous film without compromising integrity (bare spots). The coating can be deposited by dip- or spin-coating methods or using a wet squeegee approach. Emersion in ethanol is used to extract the DBP. The surface is infused with an oil; in the original preparation Fomblin® Y, a perfluoropolyether (PFPE), was used. We have also reported on use of the similar Krytox 100 and 103 oils. [1] For the complete system under that study, aluminum coupons, coated with a polyurethane paint system, were treated with the porous PVDF-HFP layer by spin-coating. They were subsequently lubricated with an oil (Figure 1); throughout this report, we will refer to this treatment as the "standard SLIPS".

For the work described here, coupons were first treated using a polyurethane layer that was textured; smooth layers were also used to provide a point of comparison. Based on other work, fluoropolymer SLIPS coatings deposited on a textured surface (aluminum in that case) provided desirable performance characteristics. A textured polyurethane base may enhance the performance of the standard SLIPS treatment used here in a similar way. Texture in the polyurethane layer is achieved using sodium chloride (NaCl) that is later dissolved away from the coating with water; the approach was inspired by a general process for synthesizing porous polyurethane scaffolds. [8, 9] The coupons were subjected to standard evaluations including measurement of sessile, sliding, and shedding contact angles and quantification of retention for the simulant compounds.

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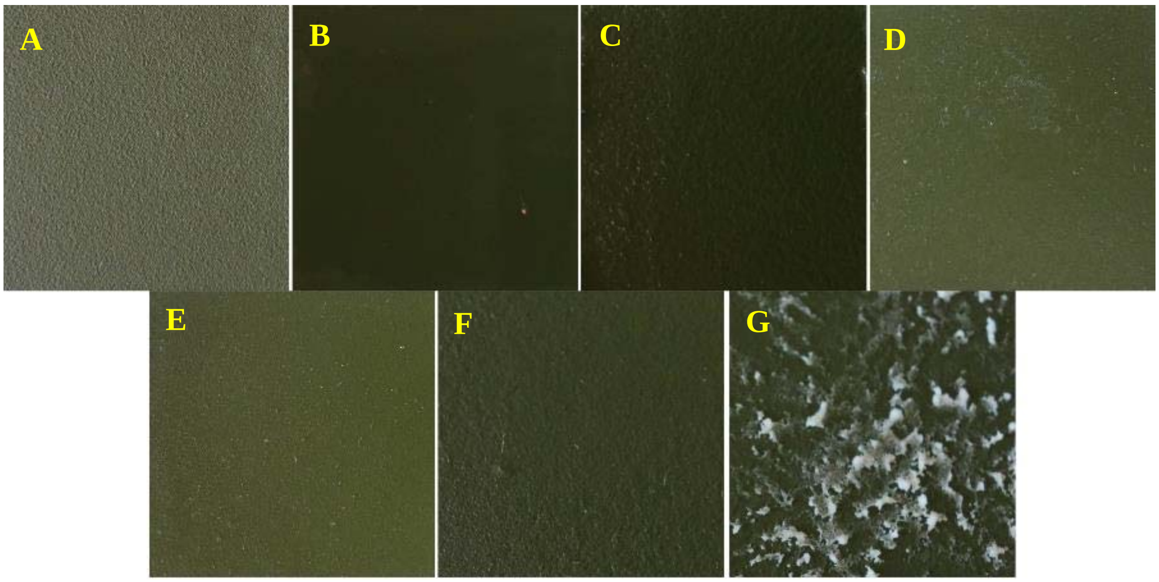

Fig. 1 — Images of a painted coupon (A) and painted coupons treated with Fomblin Y (B), the polymer SLIPS treatment lubricated using Fomblin Y (C), the SLIPS treatment over textured polyurethane (D), the SLIPS treatment over smooth polyurethane (E), the smooth polyurethane (F), and the textured polyurethane (G).

METHODS

Based on application of SLIPS treatments to textured aluminum, it was thought that a textured polyurethane base may enhance the performance of the standard SLIPS treatment used here. While the surface of the painted coupon is not smooth, a surface with increased texture is desired for this study. An NaCl amended polyurethane product can be used to produce a textured result. The textured surfaces prepared here used approximately 2.5 mL Varathane (a commercial polyurethane) added to 10 mL 1:1 dimethylformamide (DMF):tetrahydrofuran (THF). Sieved NaCl (< 425 μm; 1 cm^3) was added, and the mixture was agitated on a vortex shaker immediately before use. For the smooth polyurethane layer, the Varathane and solvent mixture was prepared with no NaCl.

The SLIPS treatment described here is deposited as follows: for the fluoropolymer coating, [1, 7] a 20 weight percent solution of poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP; M_w ~ 400000, M_n ~ 130000, ~ 10 mol% HFP) and di-*n*-butyl phthalate (DBP) in acetone was prepared. A 1:2 mass ratio of PVDF-HFP: DBP was utilized; this ratio of PVDF-HFP: DBP was reported to yield a highly porous film without compromising integrity (bare spots) after extraction of DBP. The solution was stirred at 50°C for 1 h and aged at room temperature >1 d before casting. On glass surfaces, films were spin-cast using 5000 RPM.

Glass Supports. On glass supports, five coatings were compared: a smooth polyurethane layer, a smooth polyurethane layer coated with SLIPS, a textured polyurethane layer, a textured polyurethane layer coated with SLIPs, and an over coated textured polyurethane layer coated with SLIPS. The smooth polyurethane was deposited by spin-coating at 500 RPM and allowed to dry for 1 d. The material was used as synthesized and as a support material for subsequent deposition of the SLIPS coating. For the textured polyurethane surfaces, the smooth coating was first applied and allowed to dry. The textured polyurethane coating (preparation described above) was spin-cast over the smooth layer and allowed to cure for 1 d. NaCl is dissolved out of the coating at this point by submerging the coupon in water for 1 day. This material was used as synthesized or as the basis for subsequent deposition of the PVDF-HFP-based gel-SLIPS. For the over coated polyurethane samples, the smooth coating was first applied, followed by the textured coating, but the salt was not leached out of the surface. The salt-containing layer was over coated using a polyurethane solution (2.5 mL Varathane in 10 mL 1:1 DMF:THF) at 500 RPM and allowed to cure for 24 h. NaCl was dissolved out of the coating at this point by submerging the coupon in water for 1 day. PVDF-HFP-based gel-SLIPS was spin-cast over the resulting textured layer. Following spin-casting of the gel-SLIPS, transparent coatings were aged at room temperature overnight. Immersion in ethanol for approximately 1 min was used to extract DBP.

Painted Aluminum Supports. The textured polyurethane was also applied over a more traditional polyurethane paint system supported by aluminum coupons. The paint system was deposited following manufacturer guidance. Deposition of the smooth or textured polyurethane coatings followed the protocols described above. The smooth polyurethane had little impact on the appearance of the surfaces. The textured coating had a significant impact. The polymer SLIPS coating was also prepared as described above. Deposition speeds in this case were 3000 RPM; higher speeds were not possible due to weight of the square coupons and their size as compared to the available spin platform. The color of the paint is easily visible through transparent as-cast film, slightly obscured after DBP extraction, and clear again after infusion of Fomblin® Y. The coated, lubricated surfaces appear to be wet.

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. Advancing and receding angle measurements utilized initial droplets of 3 μL that were increased in 3 μL increments up to 15 μL and then decreased back to 3 μL. Measurements were collected at each increment on both the increasing and decreasing legs of this process. 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. Droplet diameters were determined using tools provided by Adobe Photoshop CS3. 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). [10] Standard target exposures utilized a challenge level of 10 g/m^2. The glass coupons were 0.00188 m^2; the 10 g/m^2 target challenge was applied to the surfaces as four equally sized neat droplets. The painted coupons were 0.00258 m^2; the 10 g/m^2 target challenge was applied to the surfaces as five 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 surfaces (glass, painted aluminum) 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. Glass only coupons that were rinsed with soapy water prior to extraction retained low levels of all targets, a reflection of the lack of texture on these surfaces. For paint only coupons, retention was significantly higher but was less than that of paint only coupons that were extracted with no rinsing. 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.

Glass Surfaces.

The gel-SLIPS coating was applied over smooth polyurethane, textured polyurethane, and over coated, textured polyurethane using cover glass substrates to support the coatings. Contact angles for the materials were collected. As shown in Table 1, contact angles for water and ethylene glycol are significantly increased for the standard SLIPS material over those observed on glass (Table 1). Contact angles were also increased for the SLIPS materials applied over textured polyurethane. The surface energy for these materials was higher, however, than that observed for the SLIPS treatment alone. Retention of paraoxon was reduced for the SLIPS over textured polyurethane with no overcoat, but retention of DFP was not significantly impacted (Table 2).

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

Coupon	Liquid	Sessile Angle	Sliding Angle	Shedding Angle	Geometric Surface Energy (mJ/m^2)
Glass Support					
Glass Only	water	36.8 ± 0.29	>60	>60	59.1 ± 0.2
	ethylene glycol	26.3 ± 0.10	>60	>60	
	n-heptane	--	>60	>60	
Standard SLIPS	water	108.8 ± 0.60	21 ± 2.0	15 ± 2.0	12.6 ± 0.6
	ethylene glycol	91.5 ± 0.58	>60	39 ± 2.0	
	n-heptane	--	--	--	
SLIPS over textured polyurethane, over coated	water	99.3 ± 1.15	>60	>60	29.2 ± 5.2
	ethylene glycol	70.2 ± 3.34	>60	>60	
	n-heptane	--	>60	>60	
SLIPS over textured polyurethane, no over coat	water	100.3 ± 0.58	>60	>60	38.6 ± 2.5
	ethylene glycol	66.5 ± 1.06	>60	>60	
	n-heptane	--	>60	>60	
SLIPS over smooth polyurethane	water	99.5 ± 2.19	>60	>60	23.4 ± 3.9
	ethylene glycol	74.7 ± 2.00	>60	>60	
	n-heptane	--	>60	>60	

Table 2 – Target Retained (g/m^2) Following 1 h Aging of 10 g/m^2 Challenge on Glass Supports

Coupon	Paraoxon	DFP
Glass	0.17	0.03
Standard SLIPS	2.02	--
SLIPS over textured polyurethane, over coated (Fomblin Y)	7.83	0.13
SLIPS over textured polyurethane, no over coat (Fomblin Y)	0.67	0.64
SLIPS over smooth polyurethane (Fomblin Y)	1.90	0.17
Textured polyurethane (Fomblin Y)	2.04	4.46
Smooth polyurethane (Fomblin Y)	0.42	1.67

Aluminum Surfaces.

The SLIPS coatings were applied to painted aluminum coupons. For this deposition, the maximum spin speed that could be used for deposition was 3k RPM. All samples were lubricated with Fomblin Y, though Krytox 100 and Krytox 103 have been evaluated with the gel-SLIPS treatments previously. As shown in Table 3, application of the previously reported on SLIPS coating lead to significant increases in wetting angles and decreases in surface energy for the coupons. These changes were greater than those noted for lubrication of the coupon with Fomblin Y alone. As noted for the glass supported materials, use of the textured polyurethane support layer resulted in a coating with a higher surface energy (Figure 2; water / ethylene glycol values used for all calculations). Of note in Table 3, however, is the impact on specific wetting behaviors. The standard SLIPS treatment had approximately the same impact on heptane wetting as that observed for direct lubrication of the painted surface. The polyurethane coated materials, on the other hand, yielded contact angels for heptane of over 100° as compared to 35° for SLIPS alone. This was noted regardless of whether the polyurethane layer was textured or smooth.

Table 3 – Sessile, Sliding, and Shedding Contact Angles on Aluminum Supports

Coupon	Liquid	Sessile Angle	Sliding Angle	Shedding Angle	Geometric Surface Energy (mJ/m^2)	Advancing Angle	Receding Angle
Aluminum Support							
Paint Only	water	47.5 ± 1.1	>60	>60	71.9 ± 5.1	67.0 ± 1.7	43.9 ± 11.4
	ethylene glycol	55.7 ± 2.1	>60	>60		59.1 ± 1.7	39.3 ± 10.7
	n-heptane	--	>60	>60			
Oiled Paint	water	73.1 ± 2.1	>60	46.7 ± 3.3	32.2 ± 1.6		
	ethylene glycol	52.5 ± 0.6	>60	49.8 ± 4.9			
	n-heptane	40.1 ± 2.9	>60	36.6 ± 3.3			
Standard SLIPS	water	117.2 ± 1.0	>60	>60	21.6 ± 0.28	108.3 ± 14.2	94.2 ± 7.5
	ethylene glycol	93.2 ± 0.4	>60	>60		94.7 ± 2.3	62.4 ± 17.9
	n-heptane	35.4 ± 1.0	>60	27.0 ± 2.6			
SLIPS over textured polyurethane	water	70.9 ± 1.0	>60	>60	38.1 ± 6.2	105.8 ± 3.4	69.8 ± 10.1
	ethylene glycol	39.1 ± 0.7	>60	>60		81.9 ± 3.1	39.0 ± 12.1
	n-heptane	105.6 ± 1.8	>60	37.0 ± 2.6			
SLIPS over smooth polyurethane	water	87.4 ± 0.7	>60	>60	21.5 ± 1.6	111.5 ± 3.6	73.6 ± 24.6
	ethylene glycol	37.3 ± 1.6	>60	>60		91.8 ± 4.7	55.4 ± 22.4
	n-heptane	114.3 ± 0.9	>60	31.0 ± 2.6			
Textured polyurethane	water	*	>60	>60	*		
	ethylene glycol	*	>60	>60			
	n-heptane	*	>60	>60			
Smooth polyurethane	water	90.5 ± 0.6	>60	46.7 ± 3.3	24.8 ± 0.5		
	ethylene glycol	68.3 ± 0.4	>60	>60			
	n-heptane	--	>60	>60			

* The textured nature of the polyurethane prevented visualization of droplets

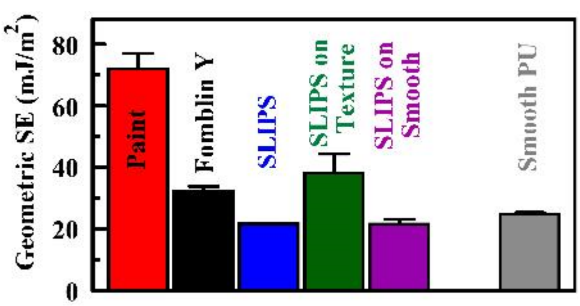

Fig. 2 — Geometric surface energy for the painted coupon and the coupons with the treatments: Fomblin Y (black), standard SLIPS (blue), SLIPS on textured polyurethane (green), SLIPS on smooth polyurethane (purple), the smooth polyurethane (gray). SLIPS and polyurethane surfaces lubricated with Fobmlin Y. *Data not available for the textured polyurethane.

The tendency of droplets to spread across the surfaces was also evaluated (Figure 3; Appendices A through G). 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 (Figures 4, 5, and 6). For the paint only samples, MES and DFP spread quickly reaching the edges of the coupon at 10 and 2 min, respectively (Figure 4). DMMP does not spread on the paint during the course of the 30 min incubation. Droplet spread was slowed on the Fomblin Y oiled surfaces and the total final diameter was reduced for all three targets (Figure 4). The standard SLIPS coating slightly decreased spread of DFP and MES as compared to the oiled surface (Figure 4). The textured polyurethane coating had a negative impact on droplet spread across the surfaces (Figure 5). The smooth polyurethane coating showed similar behavior to the Fomblin Y lubricated coupon. The behavior of MES and DMMP droplets on the polyurethane undercoated SLIPS surfaces was similar to that observed for the SLIPS coating alone whether textured or smooth (Figure 6). DFP spread on these surfaces more closely resembled that observed on the oiled paint.

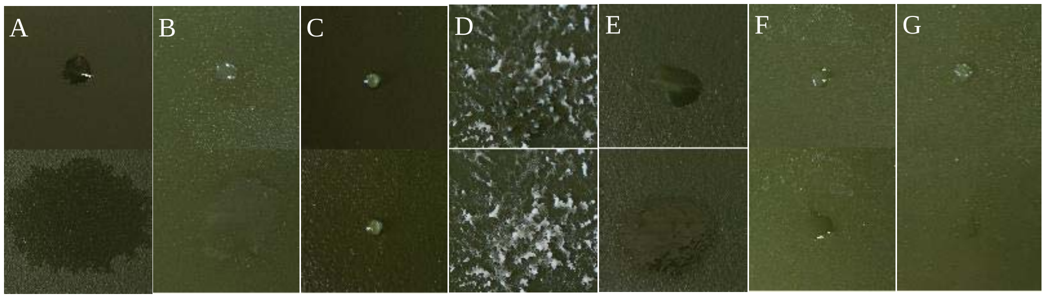

Fig. 3 — Images of a painted coupon and painted coupons treated with SLIPS formulations shown with standing droplets of MES immediately following application (top) and at 30 min (bottom): (A) paint only; Fomblin Y oiled paint (B); the standard SLIPS treatment with Fomblin Y on painted aluminum (C); textured polyurethane with Fomblin Y (D); smooth polyurethane with Fomblin Y (E); the SLIPS treatment with Fomblin Y over textured polyurethane (F); and the SLIPS treatment with Fomblyin Y over smooth polyurethane (G).

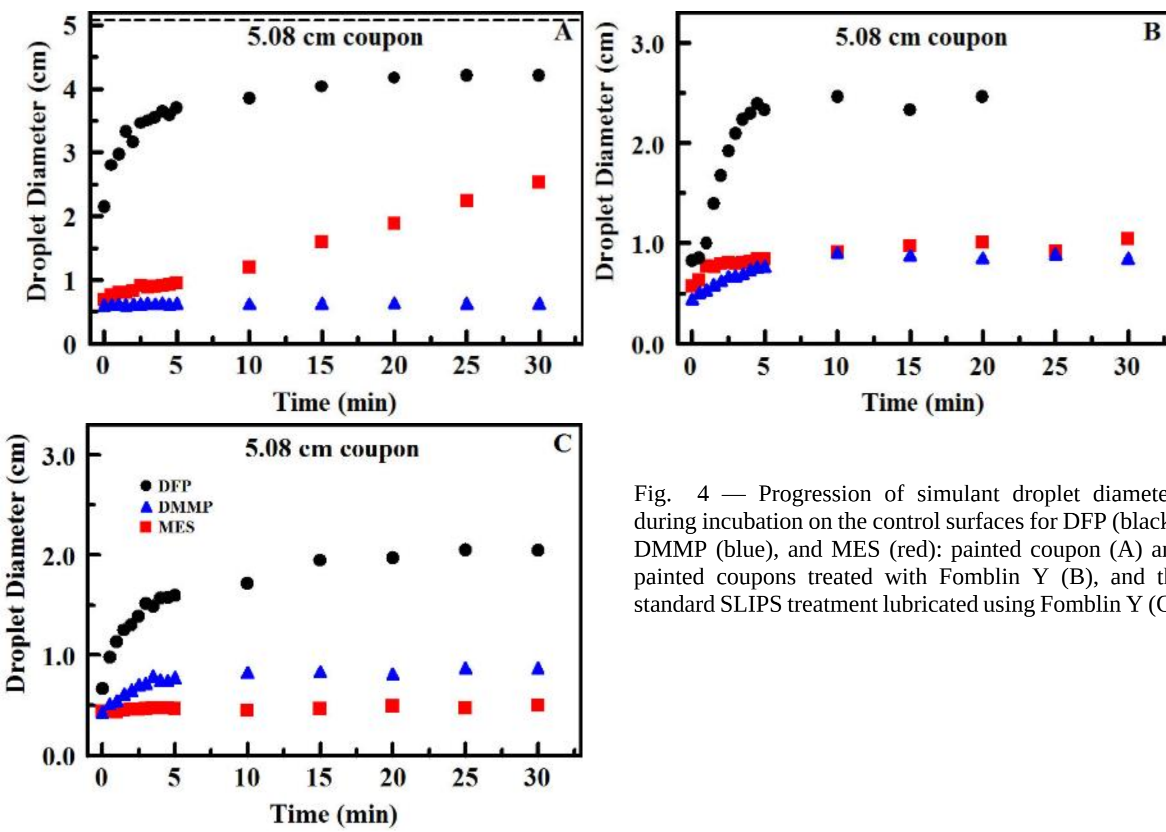

Fig. 4 — Progression of simulant droplet diameters during incubation on the control surfaces for DFP (black), DMMP (blue), and MES (red): painted coupon (A) and painted coupons treated with Fomblin Y (B), and the standard SLIPS treatment lubricated using Fomblin Y (C).

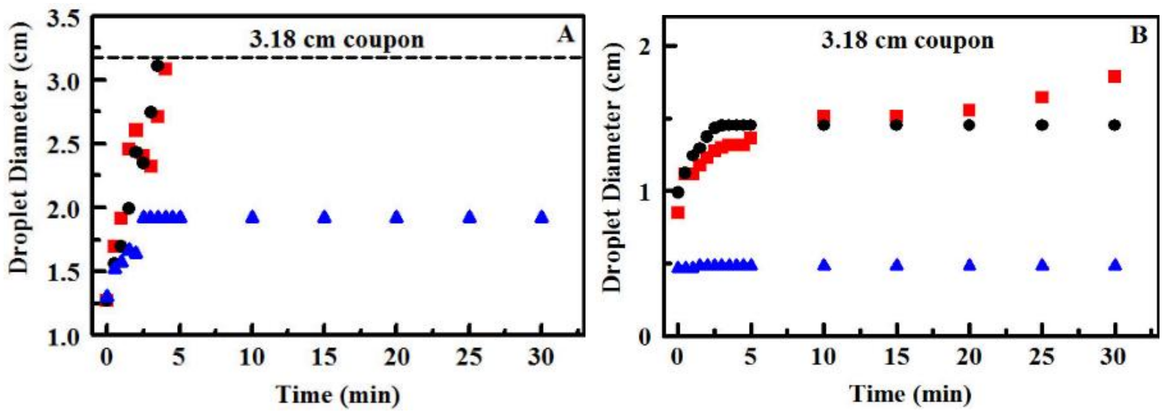

Fig. 5 — Progression of simulant droplet diameters during incubation on the control surfaces for DFP (black), DMMP (blue), and MES (red): textured polyurethane (A) and smooth polyurethane (B) lubricated with Fomblin Y.

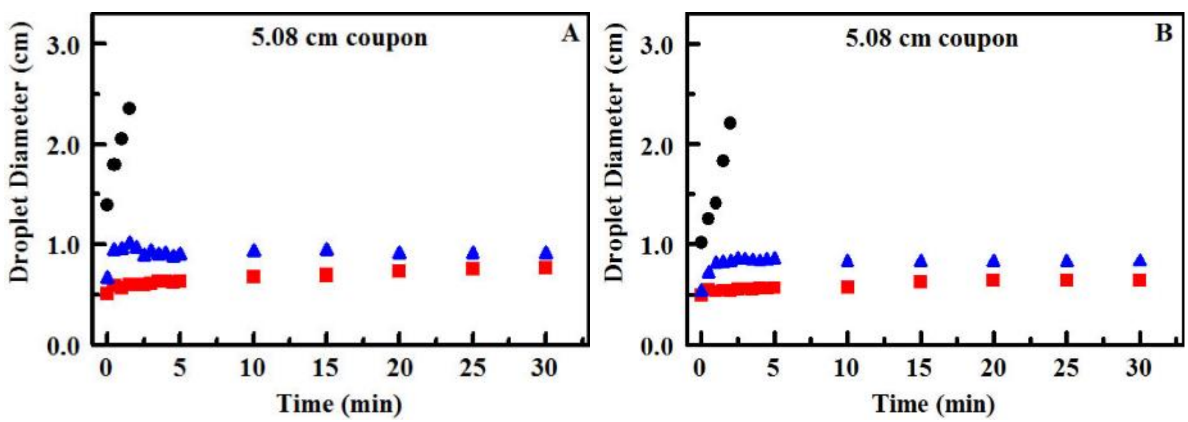

Fig. 6 — Progression of simulant droplet diameters during incubation on the control surfaces for DFP (black), DMMP (blue), and MES (red): SLIPS on textured polyurethane (A) and SLIPS smooth polyurethane (B) lubricated with Fomblin Y.

The coupons were subjected to several cycles of simulant exposure (10 g/m^2), aging, washing, drying, and lubrication over a period of several weeks. No significant changes in the appearance or wetting characteristics were noted for the SLIPS or polyurethane SLIPS surfaces during these evaluations. While, the polyurethane only coatings were not rugged on the glass surfaces, they were rugged when used as a topcoat over the painted surface. Coupons were processed using a stream of air to remove excess target followed by a soapy water rinse, a soak in the soapy water solution, and a water rinse. Retained target was determined by extracting the processed coupon in isopropanol. Figure 7 and Table 4 summarize the results for the polyurethane coatings. The surfaces were evaluated with Fomblin Y and dimethylpolysiloxane (20 cST) used as the lubricating oils. They were also evaluated with no lubricant. With the exception of DMMP, application of the polyurethane increased retention of targets regardless of whether it was smooth or textured. Application of the dimethylpolysiloxane lubricating oil reduced retention by the polyurethane coatings. Dimethylpolysiloxane oiled paint is provided for comparison purposes; this surface retains more paraoxon and DMMP than either of the lubricated polyurethane coatings. Fomblin Y lubrication of these surfaces produced results similar to the Fomblin Y lubricated paint.

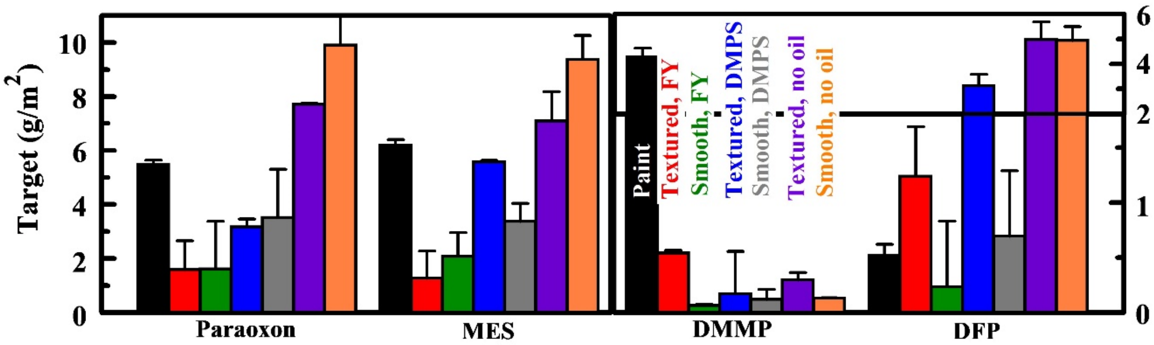

Fig. 7 — Target retained (10 g/m^2 challenge) by coupons following treatment with an air stream and rinsing with soapy water: paint only (black); Fomblin Y oiled, textured polyurethane (red); Fomblin Y oiled, smooth polyurethane (green); dimethylpolysiloxane (20 cST) oiled, textured polyurethane (blue); dimethylpolysiloxane (20 cST) oiled, smooth polyurethane (gray); textured polyurethane with no lubricant (purple), smooth polyurethane with no lubricant (orange). Error bars represent standard deviation.

Table 4 – Target Retained (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
Paint with Fomblin Y	1.24	2.85	0.59	0.34
Paint with DMPS	6.35	3.36	0.62	
Textured polyurethane (Fomblin Y)	1.59	1.27	0.54	1.24
Smooth polyurethane (Fomblin Y)	1.60	2.08	0.06	0.24
Textured polyurethane (DMPS)	3.17	5.58	0.17	3.12
Smooth polyurethane (DMPS)	3.52	3.37	0.12	0.70
Textured polyurethane (no oil)	7.71	7.09	0.30	4.98
Smooth polyurethane (no oil)	9.91	9.37	0.13	4.94

The lubrication of a painted surface using Fomblin Y results in significant reduction in the retention of the simulants by the surface. The SLIPS treatment of our previous report retained slightly more paraoxon and slightly less MES than this oiled paint. The polyurethane undercoat did not improve the performance of the SLIPS treatment (Figure 8 and Table 5). In fact, the textured polyurethane undercoat resulted in significantly greater retention of MES and DFP.

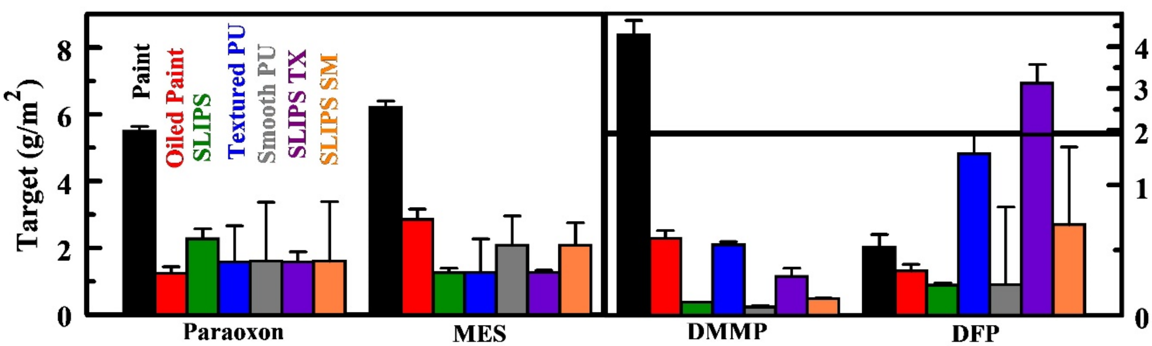

Fig. 8 — Target retained (10 g/m^2 challenge) by coupons following treatment with an air stream and rinsing with soapy water: paint only (black), Fomblin Y oiled paint (red), the SLIPS treatment on paint (green), textured polyurethane with Fomblin Y (blue), smooth polyurethane with Fomblin Y (gray), the SLIPS treatment over textured polyurethane (purple), the SLIPS treatment over smooth polyurethane (orange). Error bars represent standard deviation.

Table 5 – Target Retained (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
Standard SLIPS	2.27	1.26	0.10	0.23
Textured polyurethane	3.17	7.09	0.30	4.98
Smooth polyurethane	1.60	3.37	0.13	4.94
SLIPS over textured polyurethane	1.63	5.34	0.63	2.98
SLIPS over smooth polyurethane	2.22	3.60	0.72	0.55

CONCLUSIONS

The gel-SLIPS coating offered low surface energy and reduced spreading of target droplets on the surfaces. The samples provided promising results with reduced retention of simulants observed through the NRL studies. Other work with SLIPS coatings have used fluoropolymer deposited on a textured surface (aluminum in that case), resulting in desirable performance characteristics. Here, a textured polyurethane base was used to simulate the textured base of those treatments. While the surface of the painted coupon is not smooth, the polyurethane was significantly more textured. The polyurethane undercoat would also be expected to increase the resilience of the coatings. The simplicity of the approach, using sodium chloride and water to achieve this texture, also provides opportunities for scaling. The polyurethane coating alone did not offer a significant advantage over the paint only surface, regardless of whether it was lubricated or not. While some interesting impact on wetting behavior was noted for the SLIPS over polyurethane, the polyurethane undercoat did not provide the benefits desired in reduction of target retained.

ACKNOWLEDGEMENTS

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Appendix A

COUPON IMAGES: SLIPS ON TEXTURED POLYURETHANE

Fig. A1 — DFP on SLIPS over textured polyurethane. 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), 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.

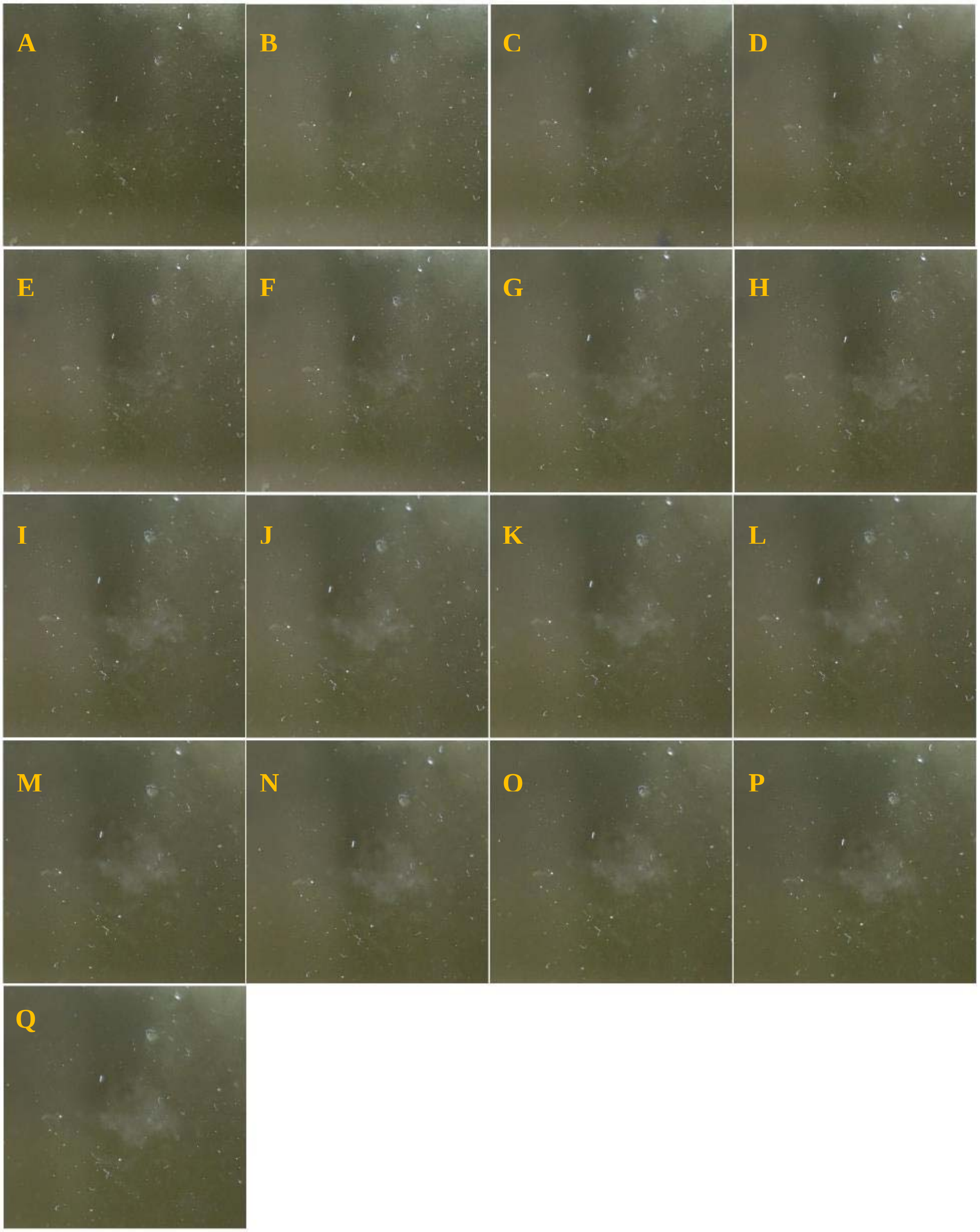


Fig. A2 — MES on SLIPS over textured polyurethane. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

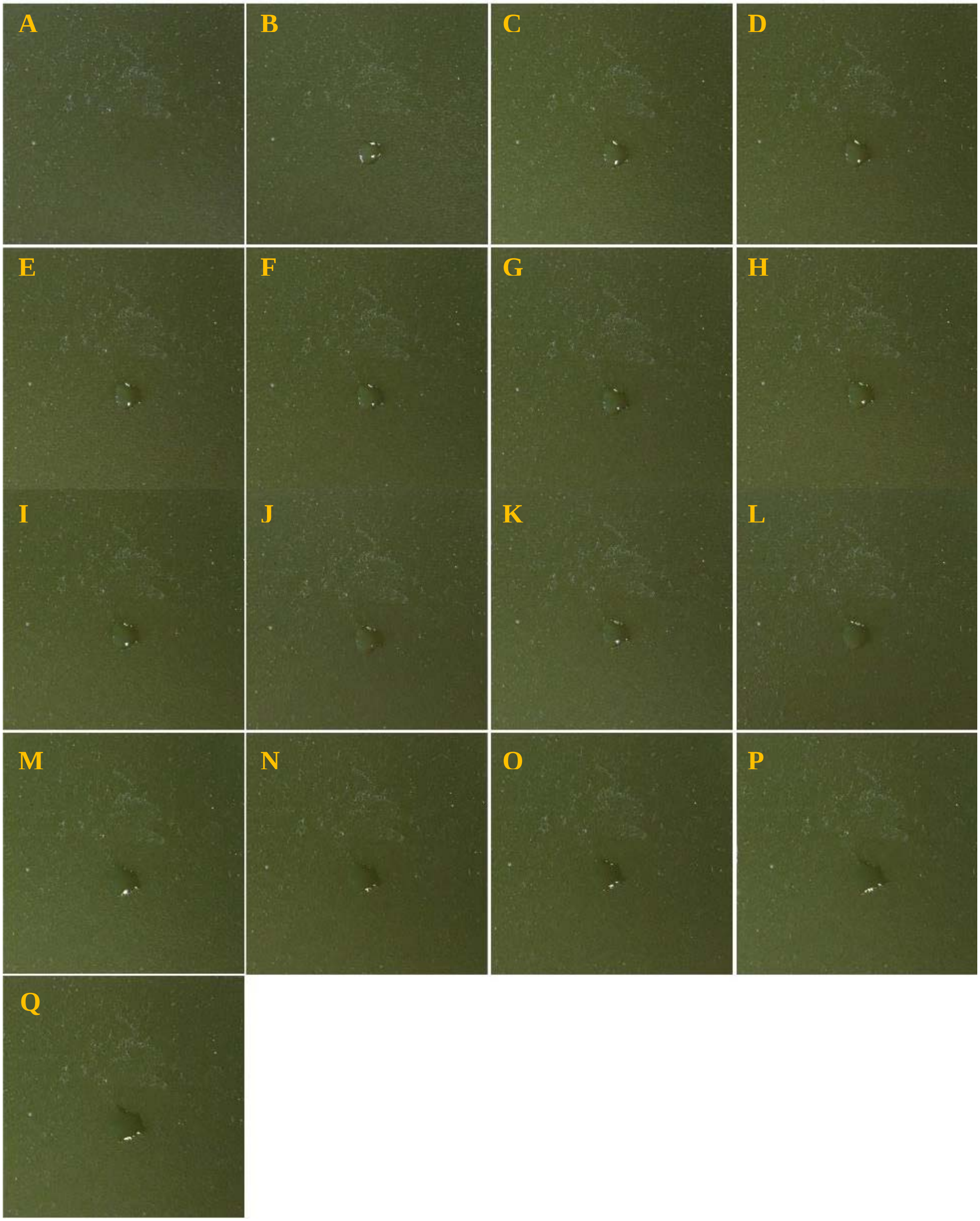
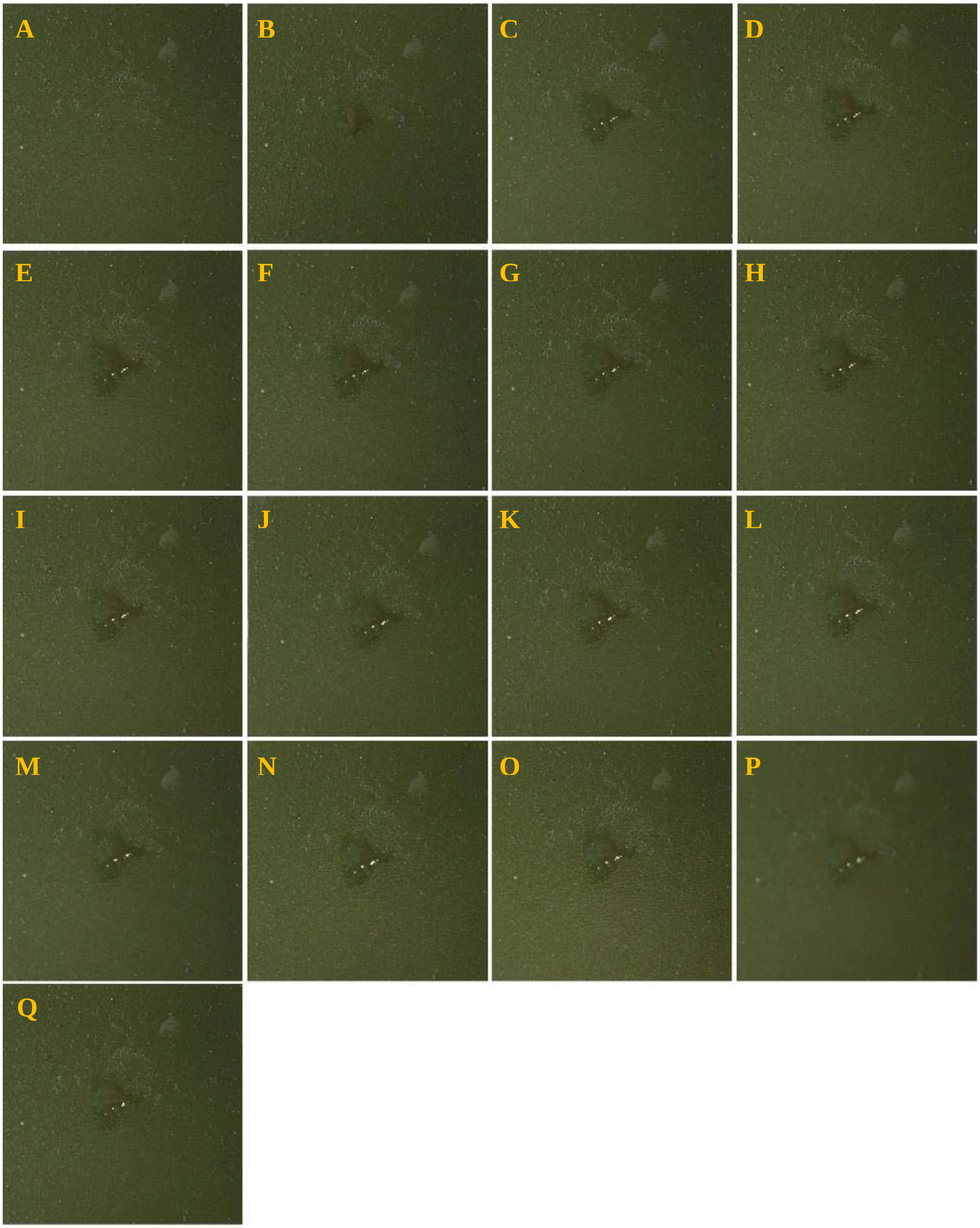


Fig. A3 — DMMP on SLIPS over textured polyurethane. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix B

COUPON IMAGES: SLIPS ON SMOOTH POLYURETHANE

Fig. B1 — DFP on SLIPS over smooth polyurethane. 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 SLIPS over smooth polyurethane. 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.

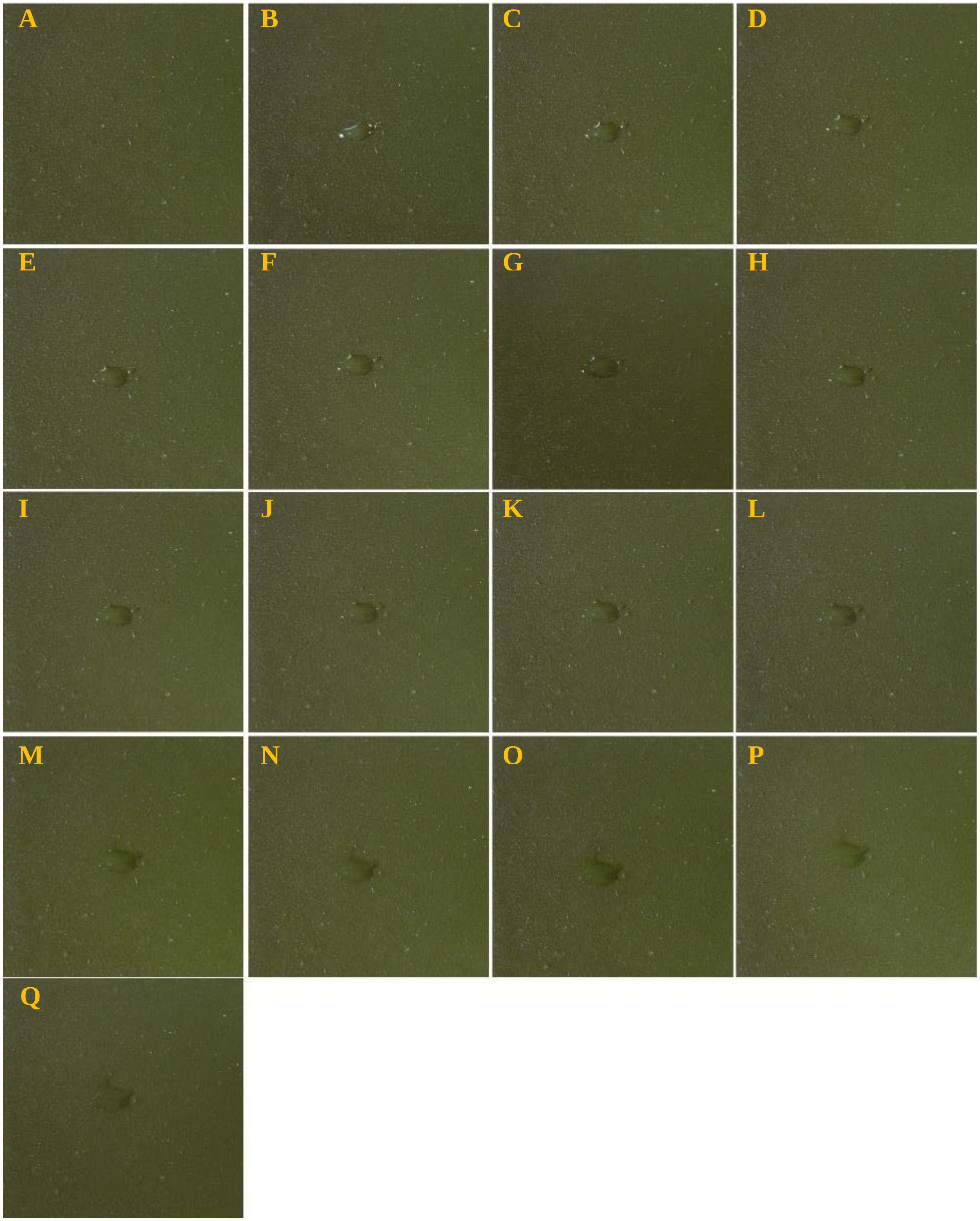
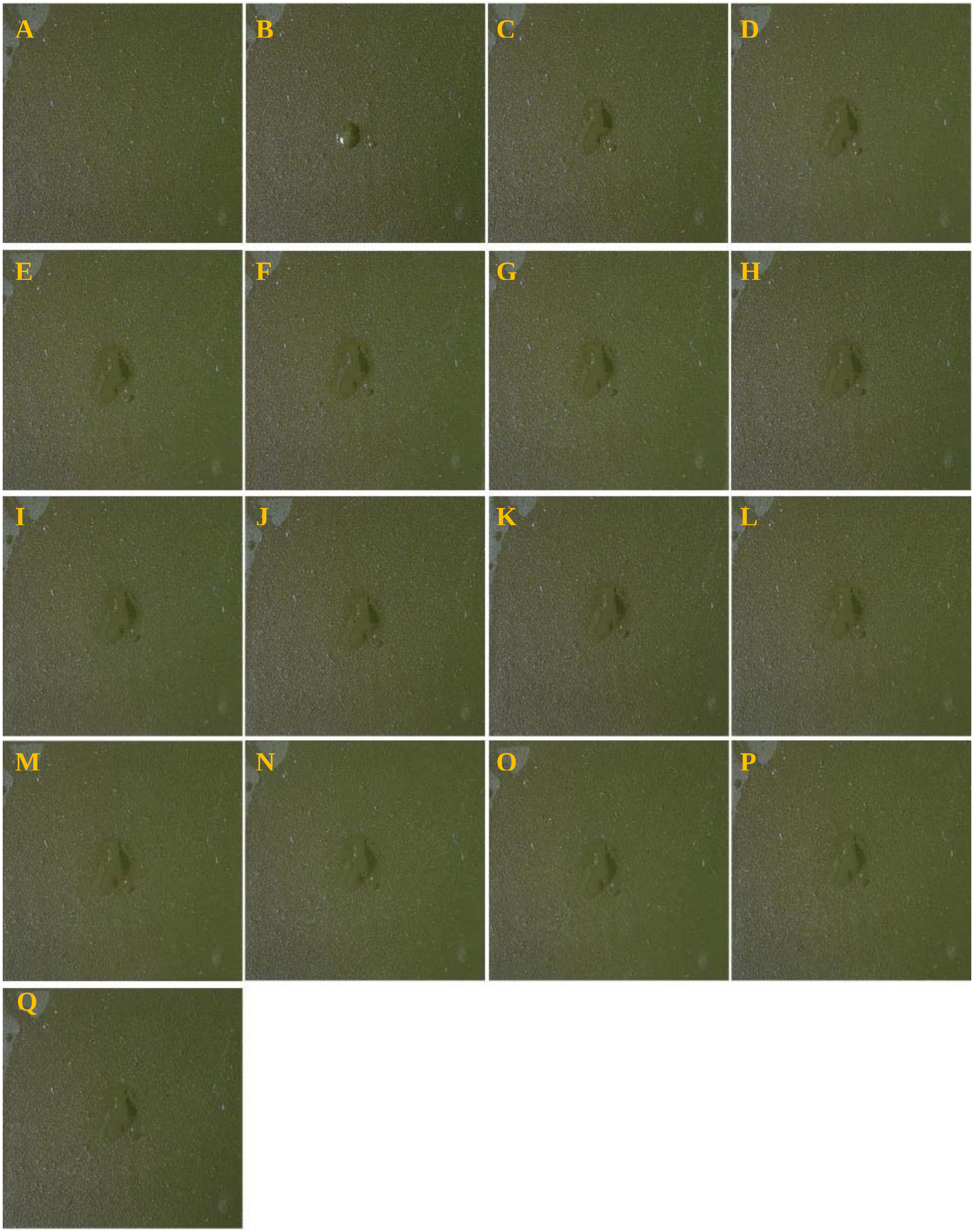


Fig. B3 — DMMP on SLIPS over smooth polyurethane. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix C

COUPON IMAGES: TEXTURED POLYURETHANE

Fig. C1 — DFP on textured polyurethane. 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.

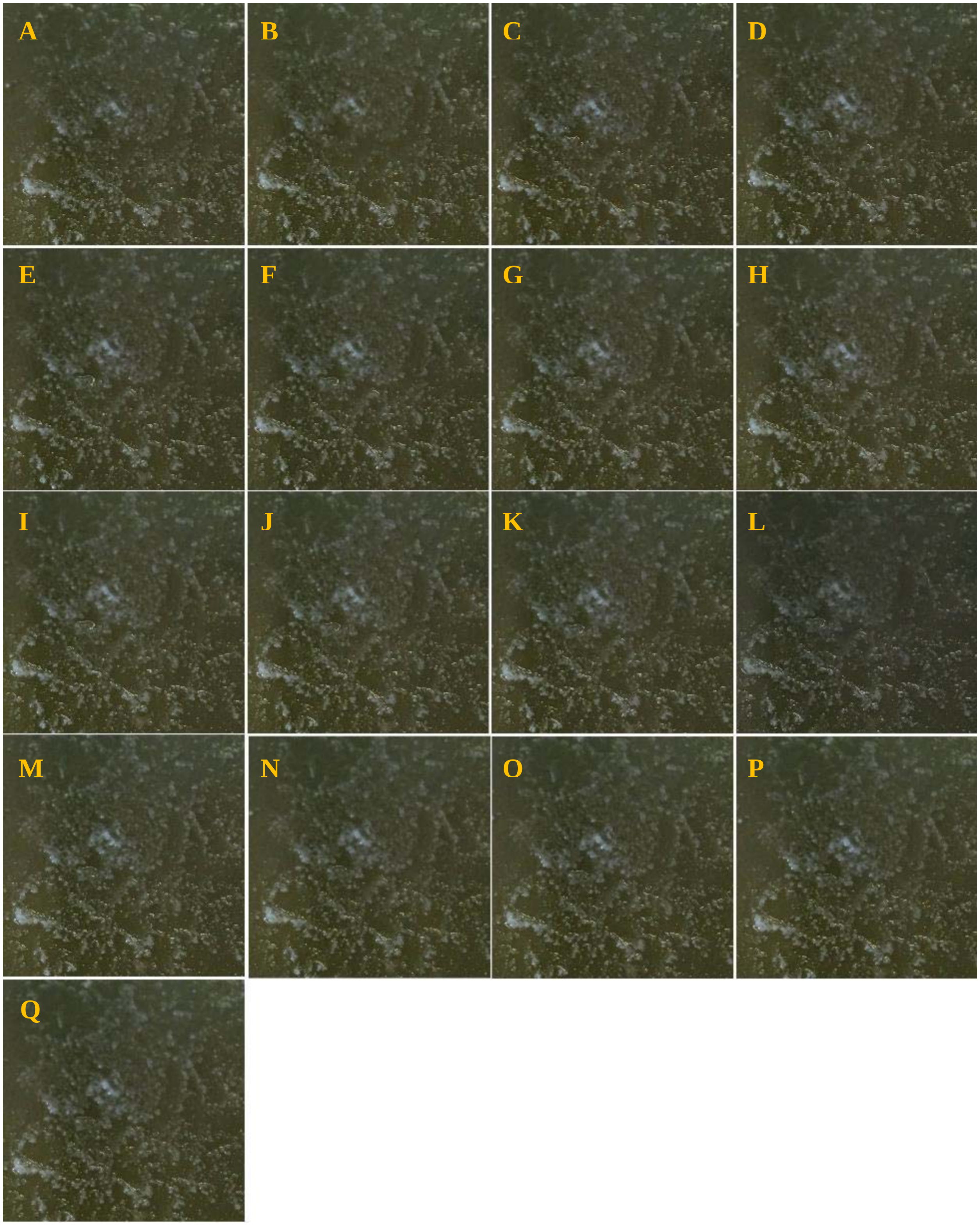


Fig. C2 — MES on textured polyurethane. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

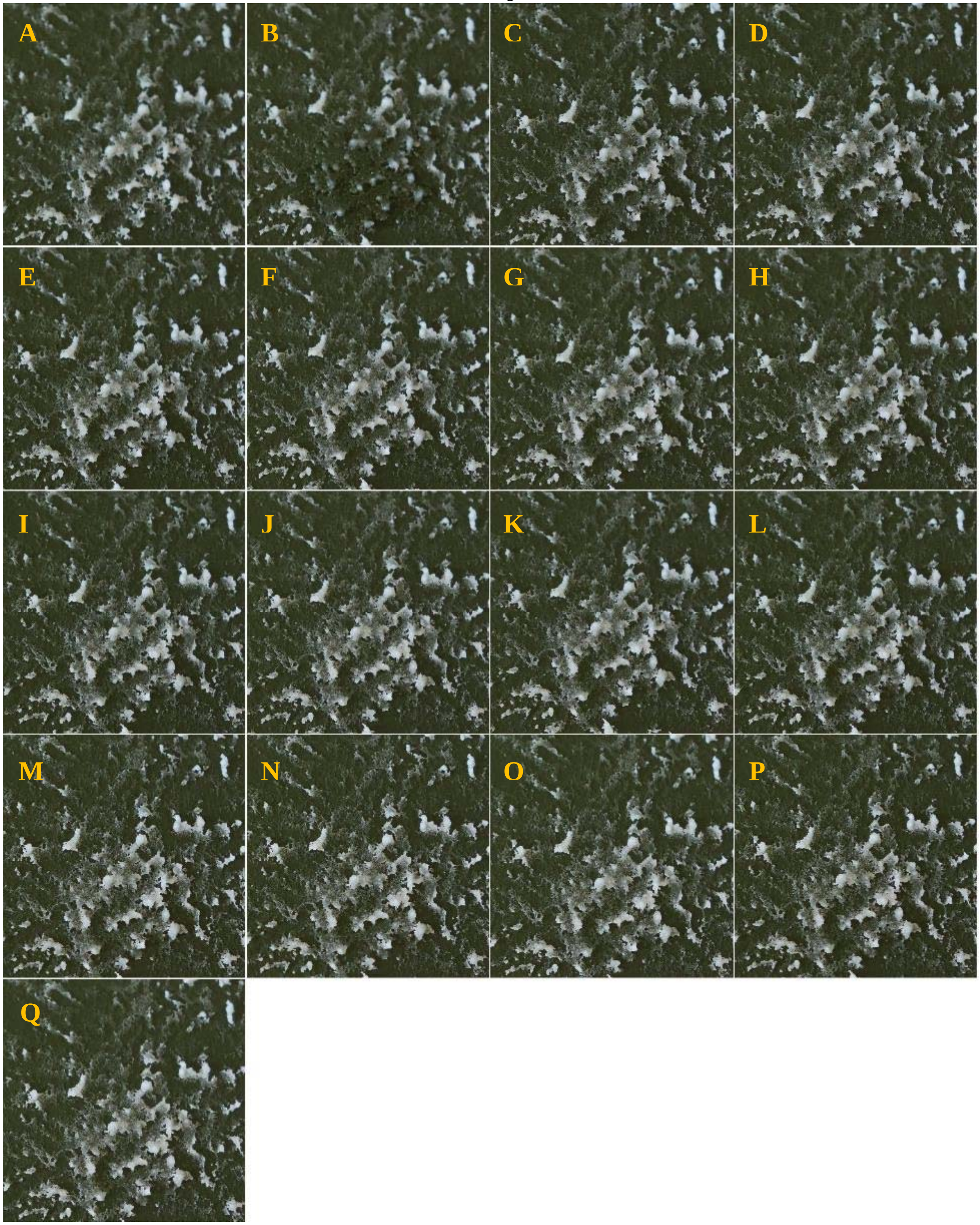
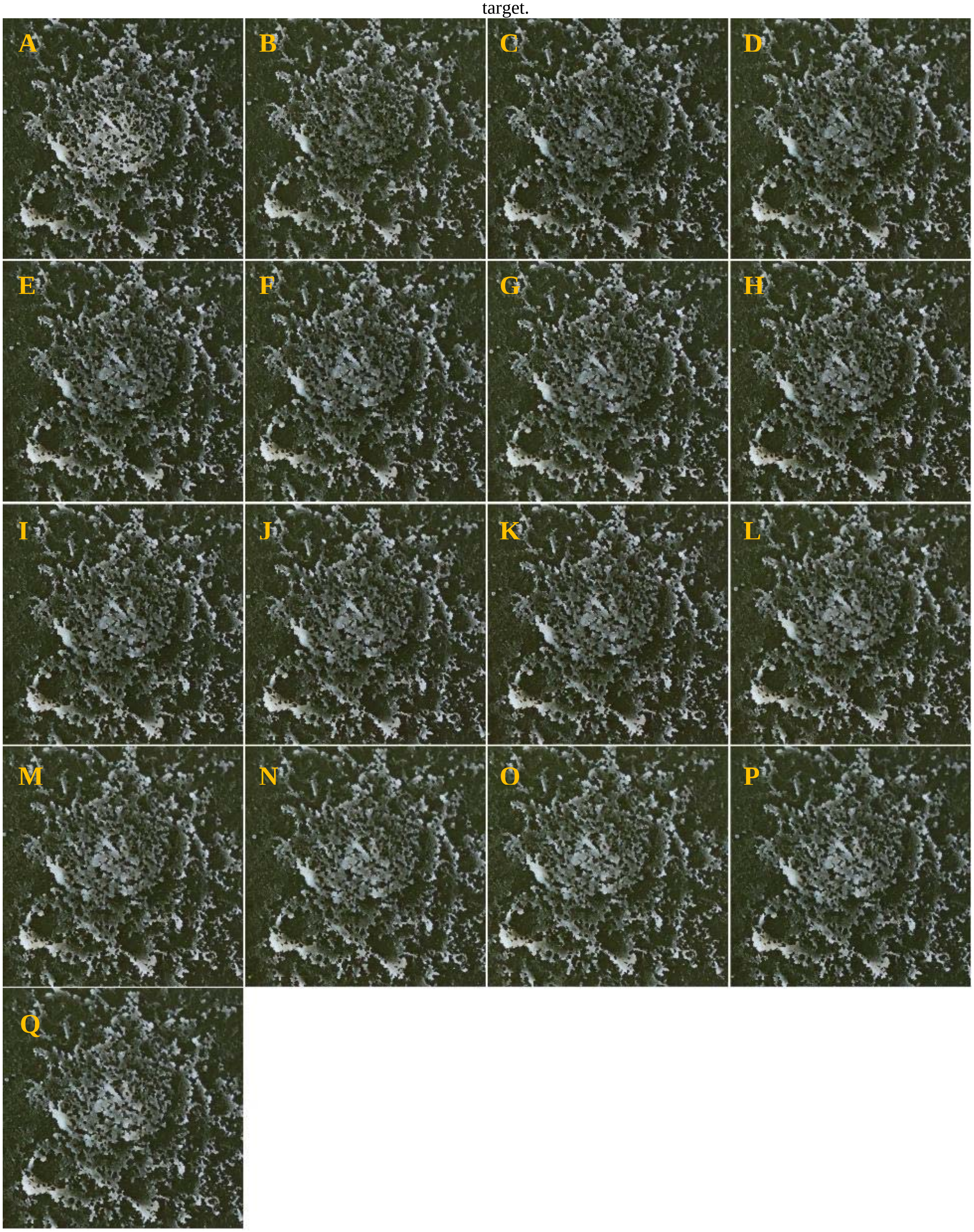


Fig. C3 — DMMP on textured polyurethane. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix D

COUPON IMAGES: SMOOTH POLYURETHANE

Fig. D1 — DFP on smooth polyurethane. 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.

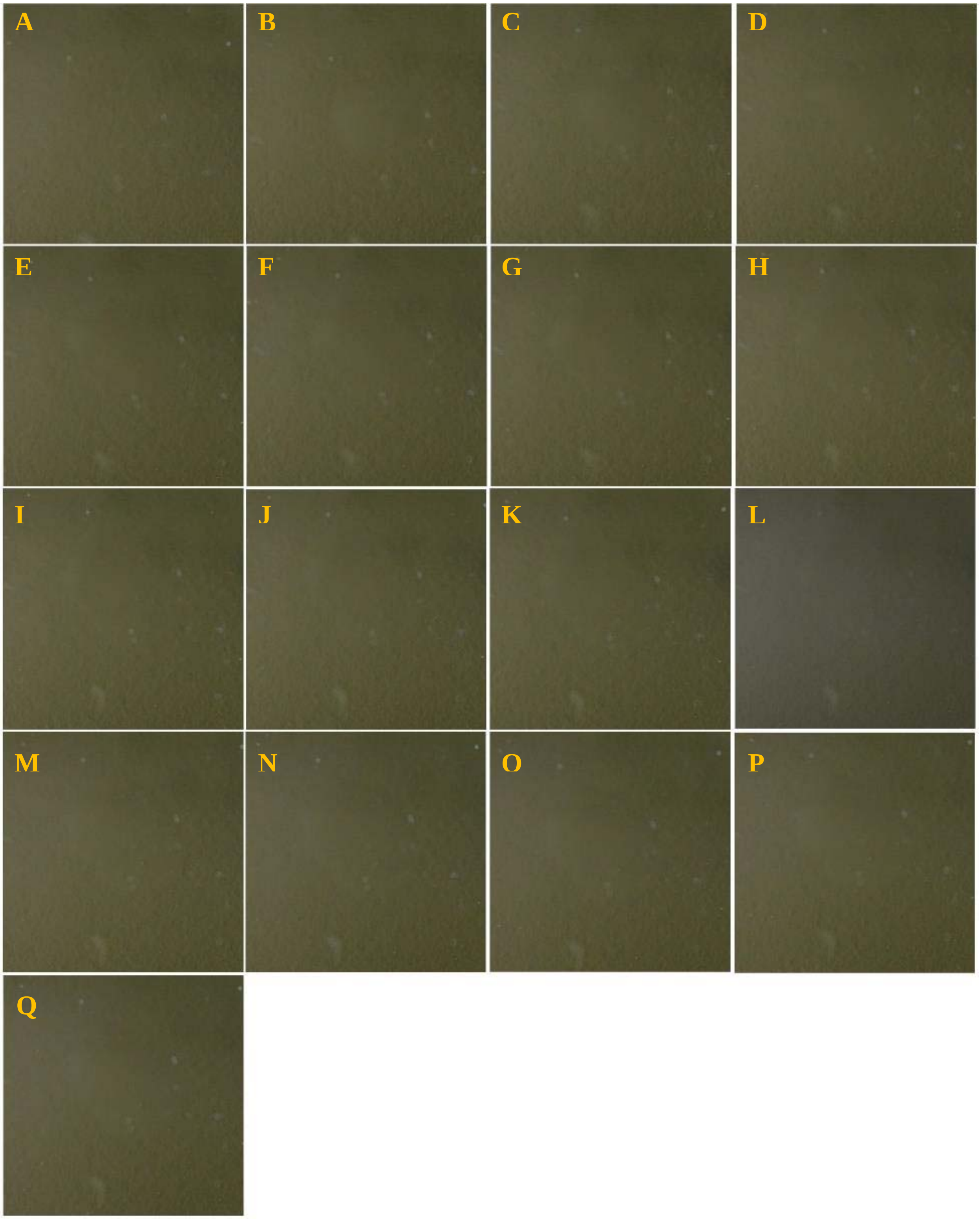


Fig. D2 — MES on smooth polyurethane. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

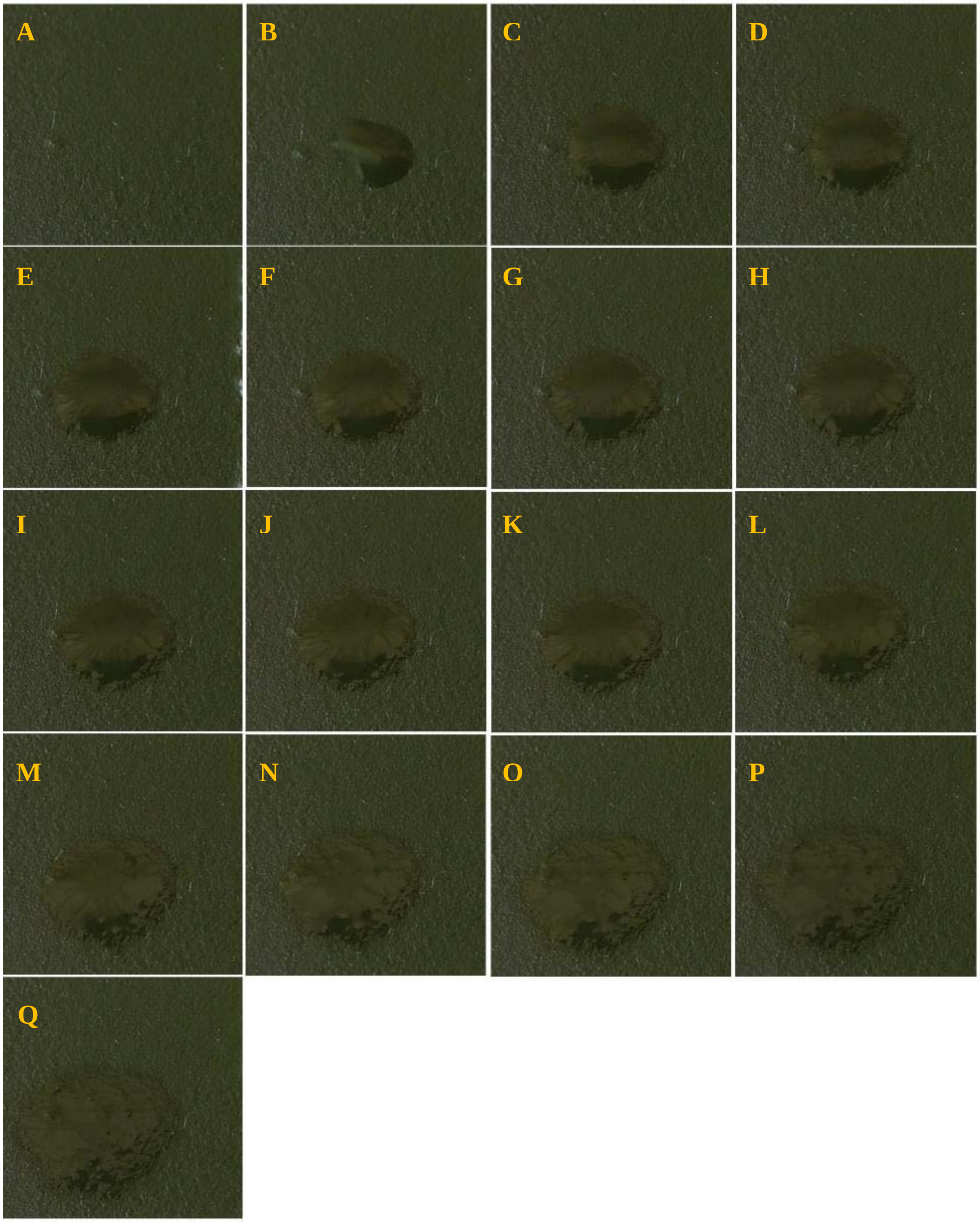
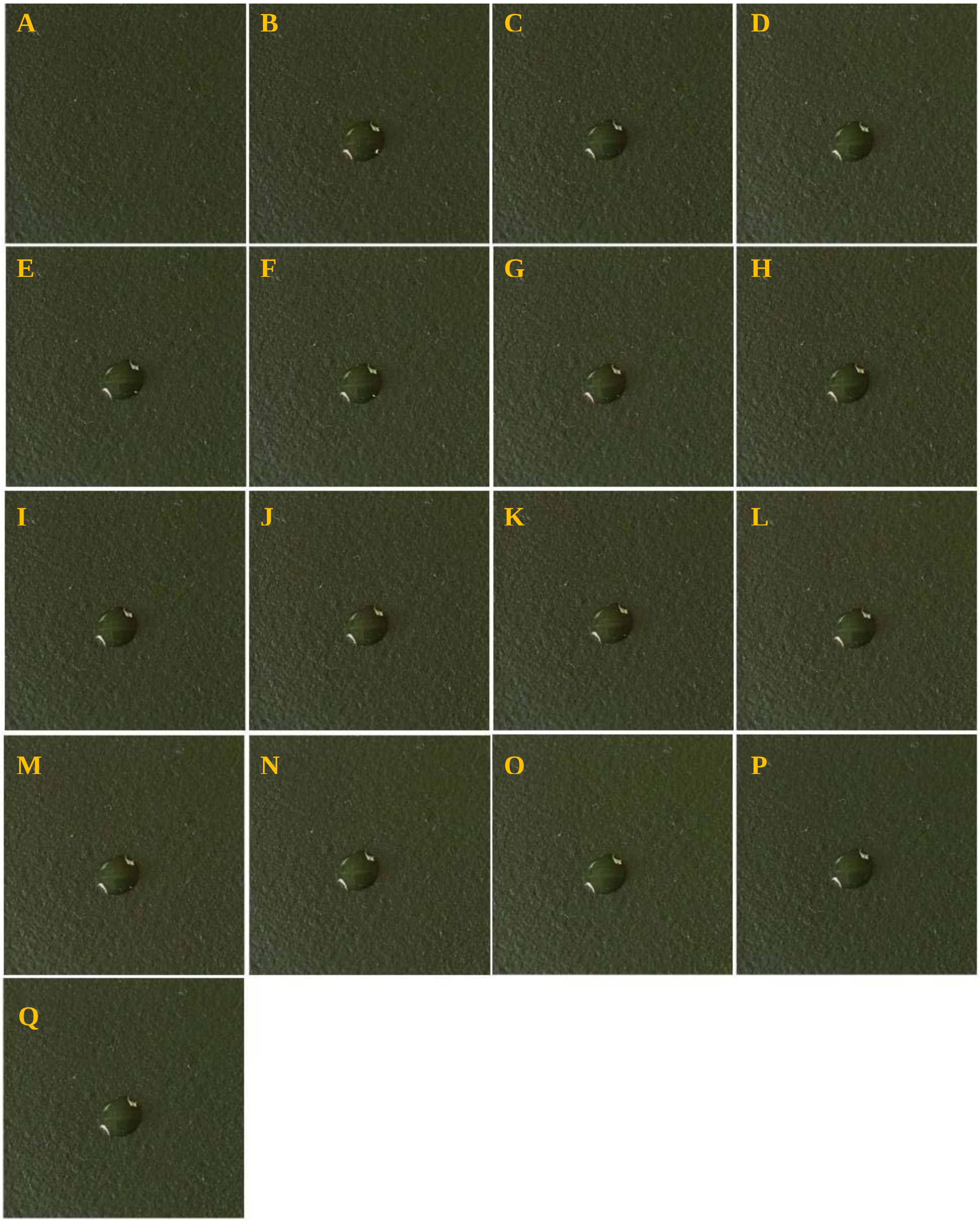


Fig. D3 — DMMP on smooth polyurethane. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix E

COUPON IMAGES: SLIPS ON PAINTED COUPON

Fig. E1 — DFP on SLIPS over painted 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. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

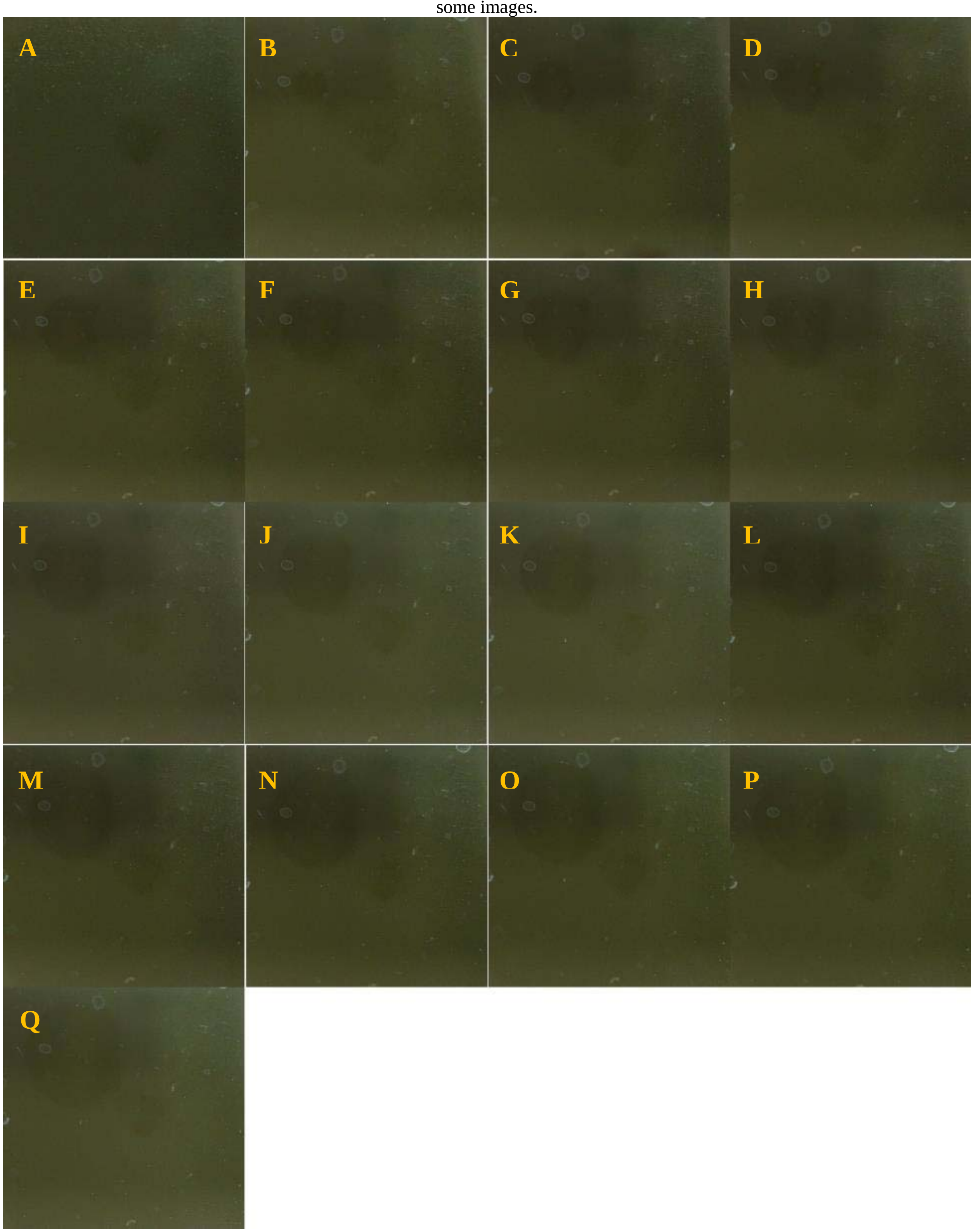
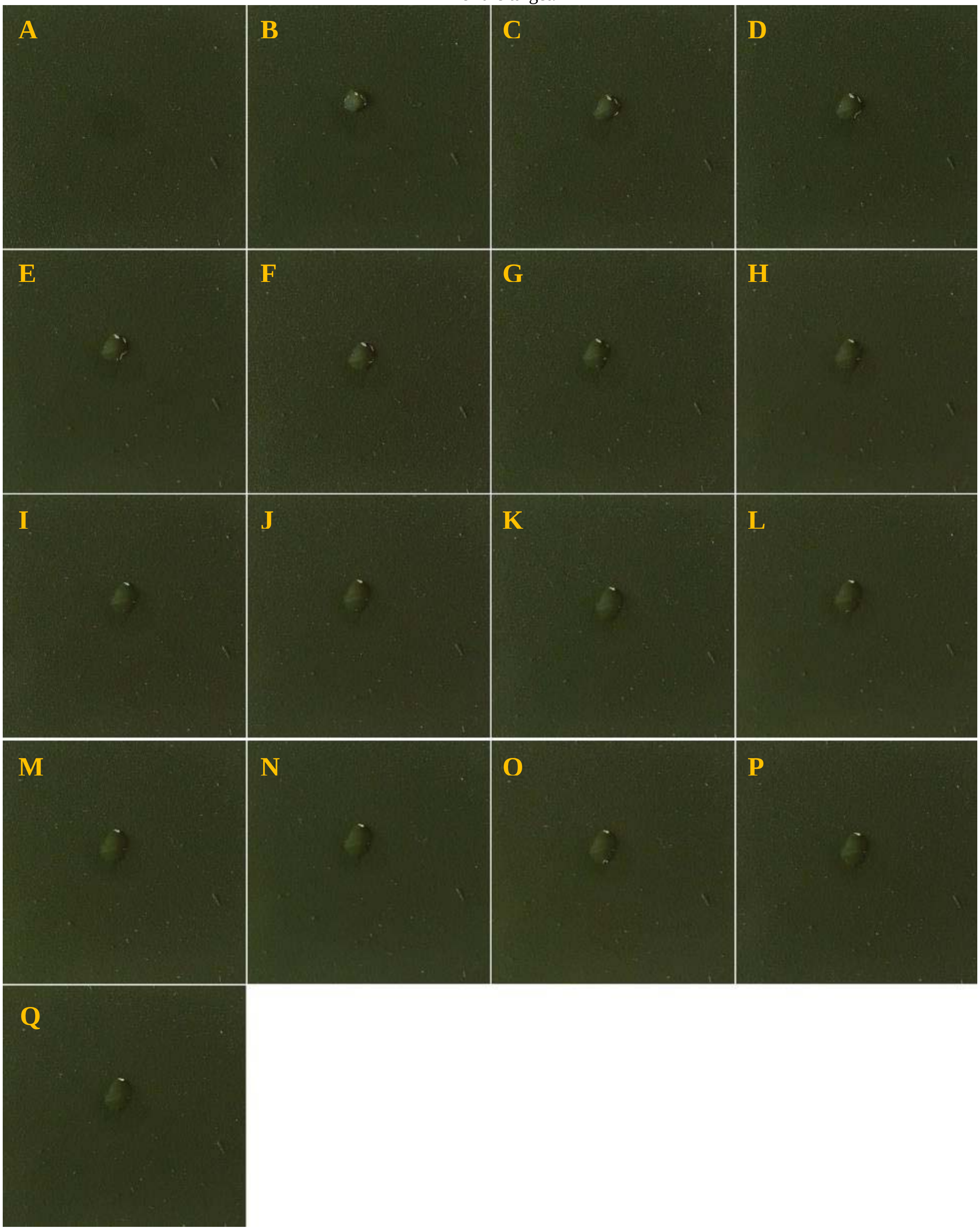


Fig. E2 — MES on SLIPS over painted coupon. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

Fig. E3 — DMMP on SLIPS over painted 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 F

COUPON IMAGES: FOMBLIN Y OILED PAINTED COUPON

Fig. F1 — DFP on Fomblin Y lubricated, painted 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. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

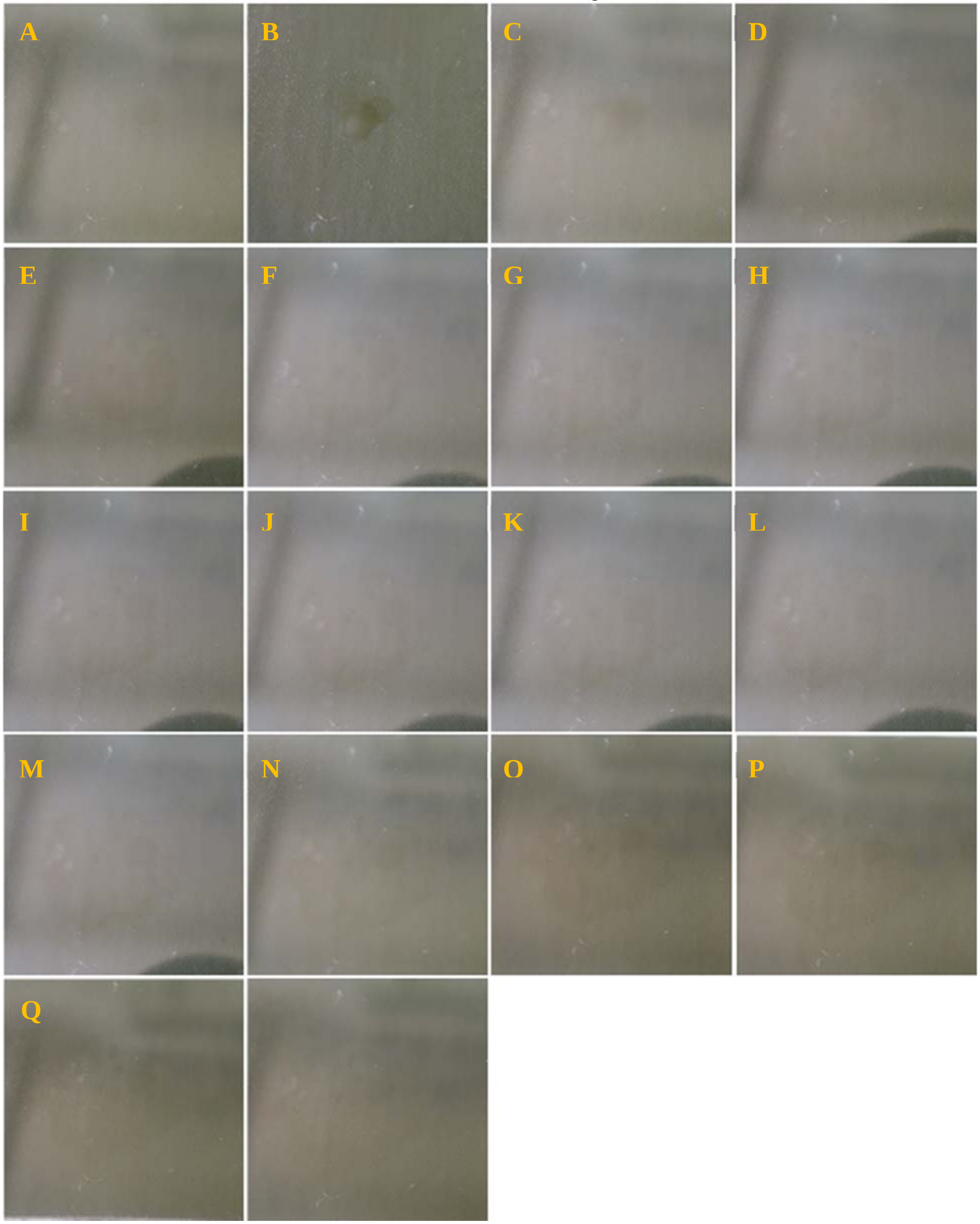
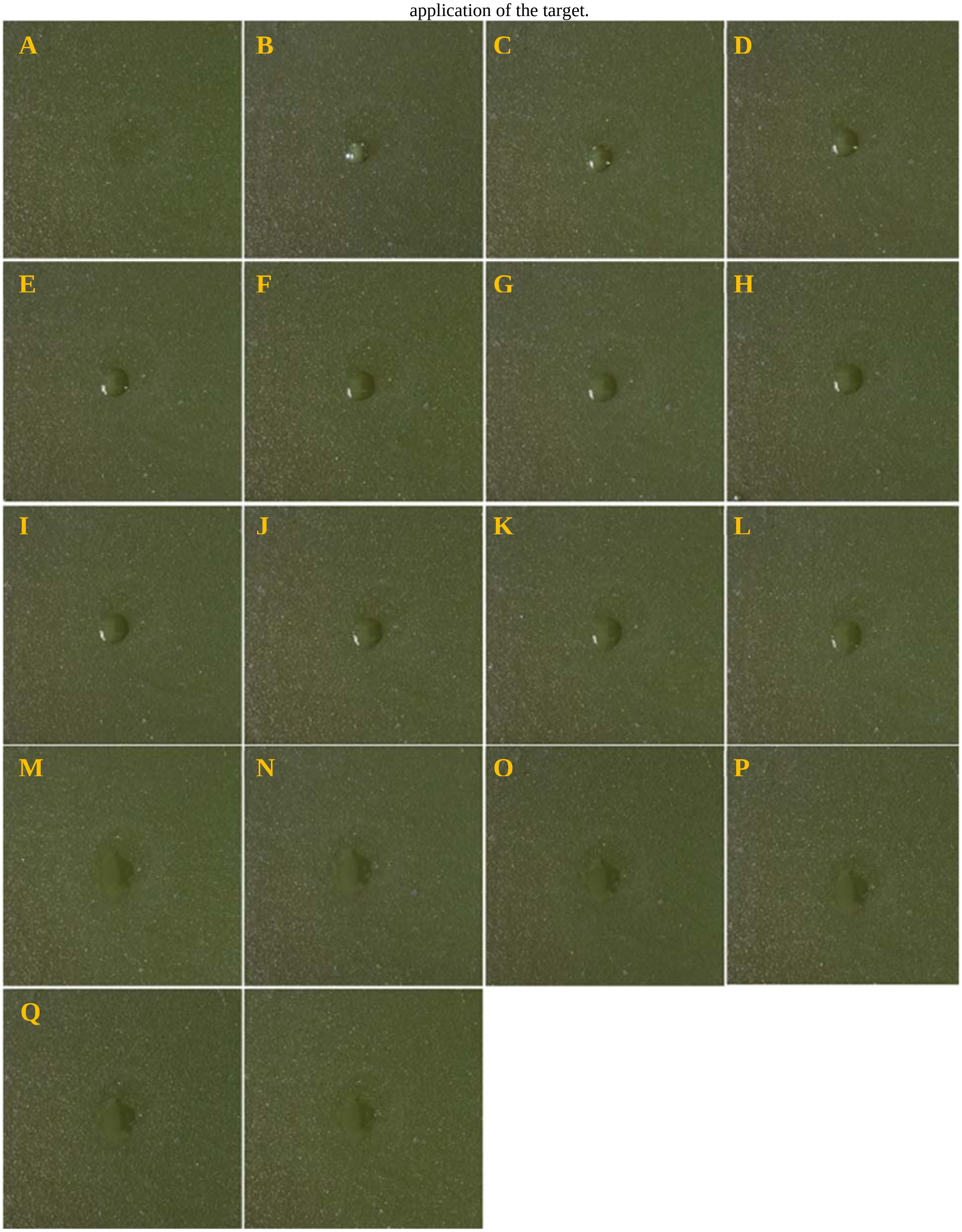


Fig. F2 — MES on Fomblin Y lubricated, painted coupon. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

Fig. F3 — DMMP on Fomblin Y lubricated, painted 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 G

COUPON IMAGES: PAINTED COUPON

Fig. G1 — 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), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), 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.

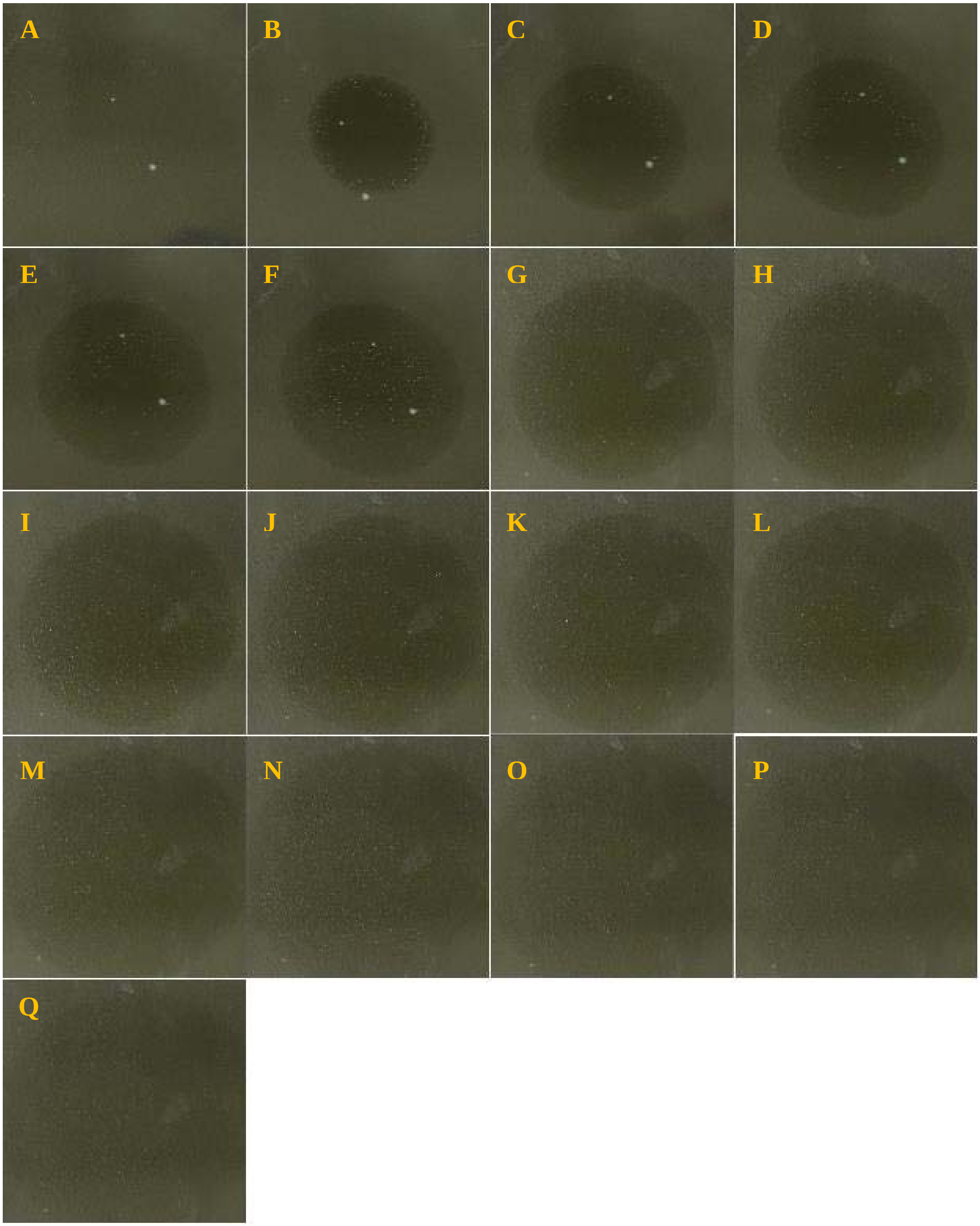


Fig. G2 — MES on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

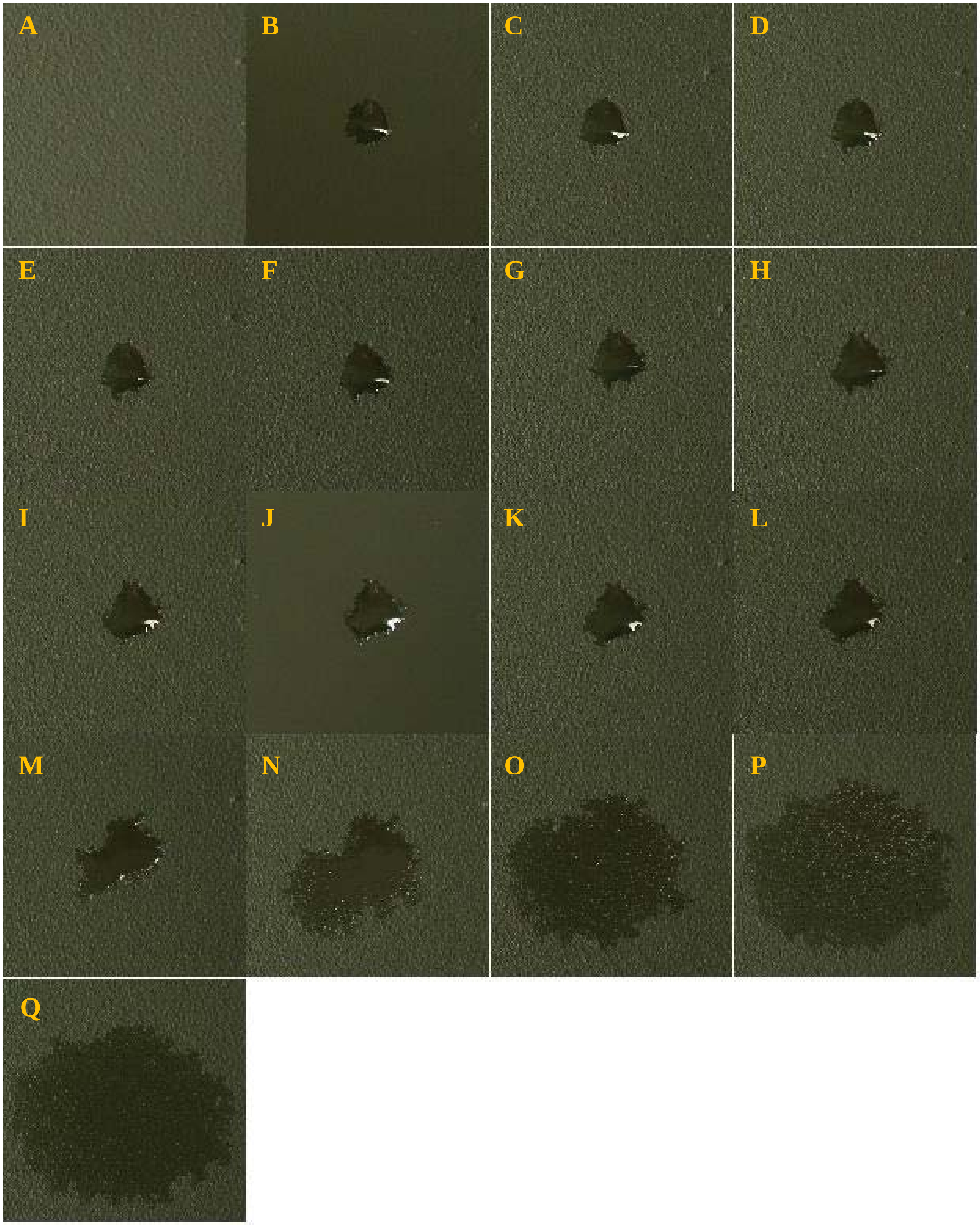


Fig. G3 — DMMP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.