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Bioinspired Surface Treatments for Improved Decontamination: Polymer-Based 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 slippery liquid-infused porous surface (SLIPS) based on a textured fluoropolymer layer. 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. Evaluation of the surface performance following VX, HD, and GD contamination is also reported.

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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 slippery liquid-infused porous surface (SLIPS) based on a textured fluoropolymer layer. The materials 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. Results for analysis of bis-(2-chloroethyl) sulfide (HD), 3,3-dimethyl-2-butyl methylphosphonofluoridate (GD), *O*-ethyl *S*-(2-diisopropylaminoethyl) methyl phosphonothioate (VX), and methyl salicylate retention as determined by the Chemical Agent Resistance Method (CARM) are also presented.

BIOINSPIRED SURFACE TREATMENTS FOR IMPROVED DECONTAMINATION: POLYMER-BASED SLIPPERY LIQUID-INFUSED POROUS SURFACES (SLIPS)

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 document summarizes results for one of the identified technologies. In this case, a slippery liquid-infused porous surface (SLIPS). Slippery liquid-infused porous surfaces (SLIPS) comprise a film of lubricating liquid with a textured substrate (micro/nano or both).[1-6] 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 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.

The polymer-based SLIPS treatment evaluated under this study uses a poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) layer with texture driven by the porosity of the polymer layer.[1] 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 used the similar Krytox 100 and 103 oils. For the complete system, aluminum coupons coated with a polyurethane paint system were treated with the porous polymer layer by spin-coating. They were subsequently lubricated with an oil (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.

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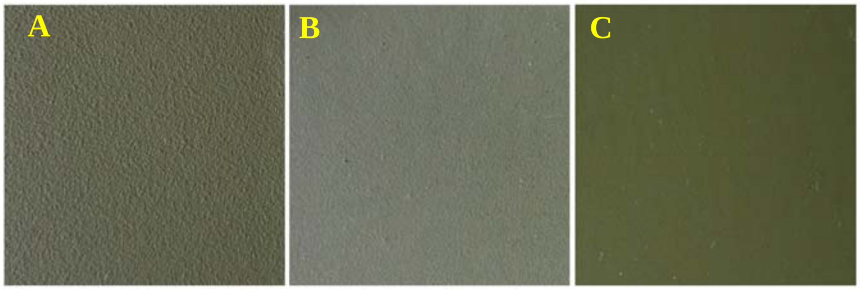

Fig. 1 — Images of a painted coupon (A), a polymer coated coupon (B) and the full SLIPS treatment (C). Presented images are approximately 5 x 5 cm.

METHODS

For the polymer coating,[6] 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 as-cast film can be peeled off the substrate. The solution was stirred at 50°C for 1 h and aged at room temperature >1 d before casting. Films were spin-cast on glass cover slides using speeds of 1000-6000 RPM. The resulting transparent coatings were aged at room temperature overnight. Immersion in ethanol for approximately 1 min was used to extract DBP. When dry, the coatings became more opaque/translucent. Infusion with the fluorinated liquid, Fomblin® Y for example, produces a transparent coating and gives the coated substrate a “slippery” or slightly wet feeling when handled. Qualitatively, drops of water or alkanes flow off the surface easily.

Polymer films were spin-cast onto polyurethane paint coated aluminum coupons. Speeds in this case were between 1000-3000 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. The gel-SLIPS coating on the relatively rough painted substrates is notably less “slippery” to handle. The fluorinated liquid gives the appearance of being absorbed to some extent by the surface. Fomblin® Y similarly applied to paint only coupons does not produce this effect with most of the liquid flowing immediately off the surface.

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. 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).[7] 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 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).[8] 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.

SLIPS coated, Fomblin Y lubricated coupons were also provided to ECBC for analysis of the retention of bis-(2-chloroethyl) sulfide (mustard; HD), 3,3-dimethyl-2-butyl methylphosphonofluoridate (GD), *O*-ethyl *S*-(2-diisopropylaminoethyl) methyl phosphonothioate (VX), and methyl salicylate (MES). Coupons were exposed to targets (2 μL) and aged for 1 h. The coupons were then processed according to the protocol outlined in ECBC-TR-1449, Chemical Agent Resistance Method (CARM). This process includes an initial rinse with deionized water, soapy water (8 mL) immersion for 3 s, and a final rinse in deionized water. The coupon is then extracted using a solvent specific to the target. Analysis is completed using a target appropriate method.

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 synthesized on a cover glass substrate. Contact angles for material were collected. Initially, water, formamide, and heptane were used as wetting liquids. It was found that the formamide damaged the polymer surface when not protected by Fomblin Y. An observation was made that oiled samples were also damaged by formamide when the most recent lubrication had occurred several weeks previous to exposure. This tends to indicate that the oil lubricant is being depleted even during storage of the samples. Based on this result and other reports of formamide damage to polymers, formamide was abandoned, and ethylene glycol was used in measurement of contact angles. As shown in Table 1, contact angles for water and ethylene glycol are significantly increased for the SLIPS materials over those observed on glass (Table 1, SLIPS 5k and 6k). No trends were noted across the spin speeds used for deposition (1k to 6k RPM). Some of these materials were also subjected to simulant exposure, aging, rinsing with water, and extraction. Retention of paraoxon was less on the lubricated SLIPS samples (1.8 g/m^2) as compared with the textured polymer only materials (6.3 m^2/g). The coatings did not reduce paraoxon retention compared to an untreated glass surface.

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	
	formamide	26.3 ± 0.09	>60	>60	
Fomblin Y SLIPS, 1k RPM deposition	water	109.0 ± 1.11	38 ± 2.1	36 ± 2.0	18.0 ± 0.4
	n-heptane	34.3 ± 1.70	>60	>60	
	formamide	107.0 ± 5.41	>60	>60	
Fomblin Y SLIPS, 2k RPM deposition	water	114.4 ± 0.14	28 ± 2.0	19 ± 2.0	16.9 ± 0.2
	n-heptane	35.8 ± 0.72	>60	>60	
	formamide	--	--	--	
Fomblin Y SLIPS, 3k RPM deposition	water	112.3 ± 1.10	24 ± 2.0	18 ± 2.0	16.9 ± 0.2
	n-heptane	36.4 ± 0.72	>60	>60	
	formamide	--	--	--	
Fomblin Y SLIPS, 4k RPM deposition	water	108.9 ± 1.05	28 ± 2.0	15 ± 2.0	17.7 ± 0.3
	n-heptane	34.3 ± 1.07	>60	>60	
	formamide	--	--	--	
Fomblin Y SLIPS, 5k RPM deposition	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	--	--	--	
Fomblin Y SLIPS, 6k RPM deposition	water	114.6 ± 0.77	41 ± 2.0	14 ± 2.0	17.2 ± 2.4
	ethylene glycol	91.37 ± 1.47	>60	19 ± 2.0	
	n-heptane	--	--	--	
SLIPS, no lubrication, 1k RPM deposition	water	123.5 ± 1.23	>60	>60	18.8 ± 1.8
	ethylene glycol	97.5 ± 0.56	>60	>60	
	n-heptane	--	--	--	
SLIPS, no lubrication, 2k RPM deposition	water	129.4 ± 0.90	>60	>60	27.6 ± 2.4
	ethylene glycol	97.5 ± 0.56	>60	>60	
	n-heptane	--	--	--	

SLIPS, no lubrication, 3k RPM deposition	water	128.4 ± 0.82	>60	>60	23.1 ± 1.5
	ethylene glycol	99.1 ± 0.47	>60	>60	
	n-heptane	--	--	--	
SLIPS, no lubrication, 4k RPM deposition	water	127.0 ± 1.24	>60	>60	21.6 ± 2.6
	ethylene glycol	98.8 ± 0.73	>60	>60	
	n-heptane	--	--	--	
SLIPS, no lubrication, 5k RPM deposition	water	117.7 ± 2.28	>60	>60	17.8 ± 3.6
	ethylene glycol	93.4 ± 1.75	>60	>60	
	n-heptane	--	--	--	
SLIPS, no lubrication, 6k RPM deposition	water	120.1 ± 0.48	>60	14	11.5 ± 0.9
	ethylene glycol	100.5 ± 0.73	>60	>60	
	n-heptane	--	--	--	

Table 2 – Paraoxon Retained (g/m^2) Following 1 h Aging on Glass Supports

Coupon	**Paraoxon**
Glass	0.17
2k SLIPS with Fomblin Y	3.34
2k SLIPS with no lubrication	6.09
5k SLIPS with Fomblin Y	2.02
5k SLIPS with no lubrication	6.22
6k SLIPS with Fomblin Y	1.84
6k SLIPS with no lubrication	6.34

Aluminum Surfaces.

The SLIPS coating was applied to painted aluminum coupons. For this deposition, the maximum spin speed that could be used for deposition with these coupons was 3k RPM. Materials were left unlubricated or lubricated with a fluorinated oil, Fomblin Y, Krytox 100, or Krytox 103. These oils are fluorocarbon ether polymers of polyhexafluoropropylene oxide (also known as perfluoropolyether (PFPE), perfluoroalkylether (PFAE) and perfluoropolyalkylether (PFPAE)). The oils are stable, non-flammable, nonvolatile (to >150°F), and insoluble in water, acid, base, and most organic solvents. Fomblin Y has molecular formula $CF_3O(-CF(CF_2)CF_2O-)_x(-CF_2O-)_yCF_3$ and average molecular weight 1800 with density 1.88 g/cm^3 and viscosity 60 cST. The Krytox oils have molecular formula $F-(CF(CF_3)-CF_2-O)_x-CF_2CF_3$. Krytox 100 has density 1.87 g/cm^3 and viscosity 12.4 cST with average molecular weight approximately 1800 while Krytox 103 has density 1.92 g/cm^3 and viscosity 82 cST with average molecular weight approximately 3500. In addition to the SLIPS coatings, the polymer was also cast onto coupons in the absence of DBP to produce a coating without pores. As shown in Table 3 (also Figure 2), application of the coatings lead to significant increases in wetting angles and decreases in surface energy for the coupons. While none of the coatings led to sliding of the solvents on the surfaces, shedding angles were noted for some of the liquids on the SLIPS coated surfaces. Applying oil to the painted coupons in the absence of the polymer treatment did reduce the surface energy of the coupon but not to the extent noted for the polymer coated coupons.

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)
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	--	>60	>60	
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	
2k SLIPS with Fomblin Y	water	114.4 ± 0.58	>60	54.0 ± 1.6	14.4 ± 0.61
	ethylene glycol	87.9 ± 1.1	>60	>60	
	n-heptane	40.3 ± 0.83	>60	32.0 ± 5.9	
3k SLIPS with Fomblin Y	water	117.2 ± 0.96	>60	>60	21.6 ± 0.28
	ethylene glycol	93.2 ± 0.36	>60	>60	
	n-heptane	35.4 ± 1.0	>60	27.0 ± 2.6	
3k SLIPS with Krytox 100	water	114.0 ± 0.53	>60	>60	14.1 ± 0.51
	ethylene glycol	96.0 ± 0.72	>60	>60	
	n-heptane	37.0 ± 1.4	>60	29.5 ± 1.0	
3k SLIPS with Krytox 103	water	116.8 ± 0.82	>60	28.0 ± 1.6	19.5 ± 0.75
	ethylene glycol	90.2 ± 0.49	>60	>60	
	n-heptane	32.4 ± 0.59	>60	28.5 ± 1.9	
3k porous polymer, no lubrication	water	131.1 ± 1.1	>60	36.3 ± 4.7	6.6 ± 0.85
	ethylene glycol	117.2 ± 0.73	>60	>60	
	n-heptane	134.0 ± 1.8	>60	>60	
3k smooth polymer, no lubrication	water	120.6 ± 0.69	>60	>60	18.6 ± 3.1
	ethylene glycol	98.6 ± 2.7	>60	>60	
	n-heptane	21.3 ± 1.2	>60	>60	

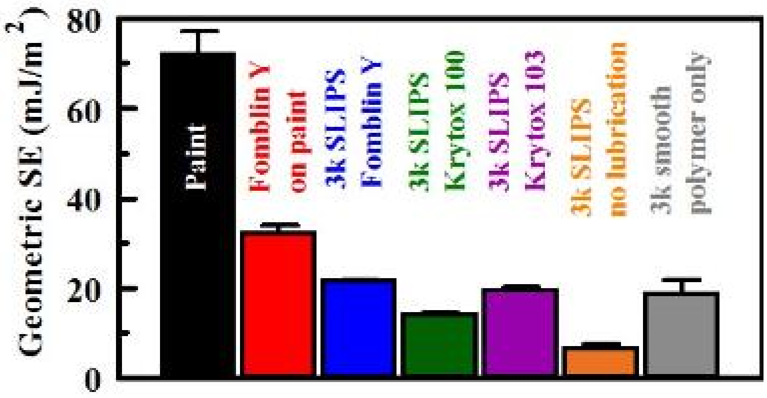

Fig. 2 — Geometric surface energy for the coatings on a painted coupon.

The tendency of droplets to spread across the surfaces was also evaluated (Figure 3; Appendix A). 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 and 5). 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 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. Both the porous and nonporous polymer coatings further reduced spread of the simulant droplets. Lubrication of the nonporous coating with Fomblin Y had minimal impact on the spread of the droplets. Lubrication of the porous polymer coating using any of the three fluorinated oils increased spread of the droplets as compared to the unlubricated polymer coatings. Droplet spread on the SLIPS coatings was similar to that noted for the Fomblin Y lubricated painted surface.

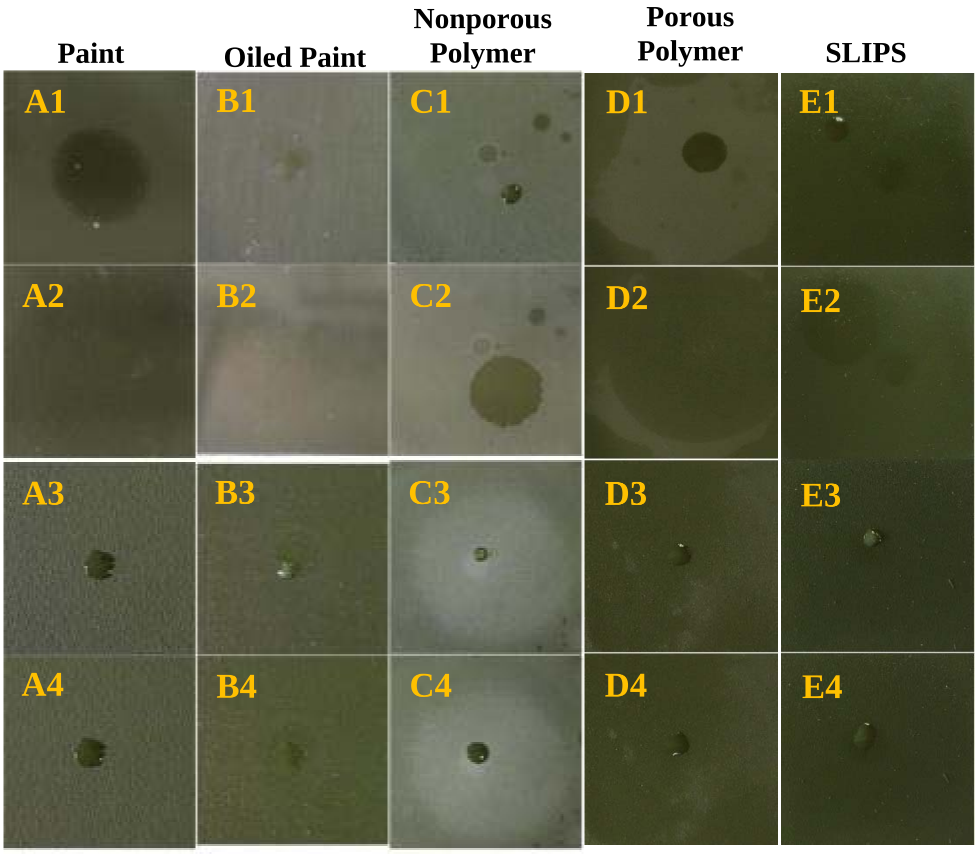

Fig. 3 — Images of a painted coupon and painted coupons treated with components of the SLIPS formulation shown with standing droplets of DFP and DMMP: painted coupon with DFP immediately following application (A); Fomblin Y oiled paint (B); nonporous polymer coated paint (C); porous polymer coated paint (D); and the full SLIPS treatment with polymer coated paint lubricated using Fomblin Y (E). Here, (1) with DFP immediately following application and (2) at 30 min and (3) with DMMP immediately following application and (4) at 30 min.

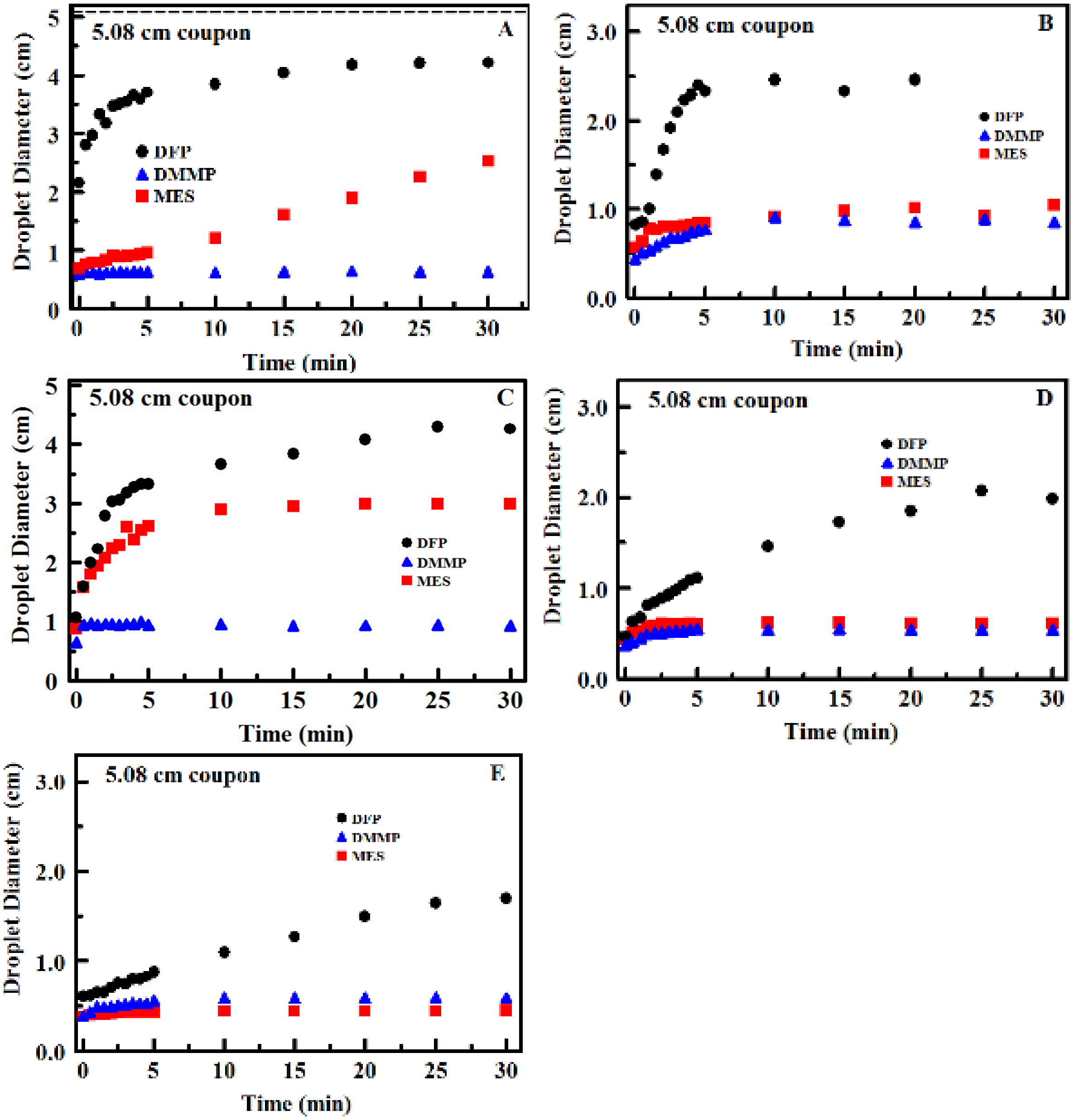

Fig. 4 — Progression of simulant droplet diameters during incubation on the control surfaces for DFP (black), DMMP (blue), and MES (red): paint only (A), paint oiled with Fomblin Y (B), the porous polymer with no lubricant (C), the nonporous polymer with no lubricant (D), and the nonporous polymer lubricated with Fomblin Y (E).

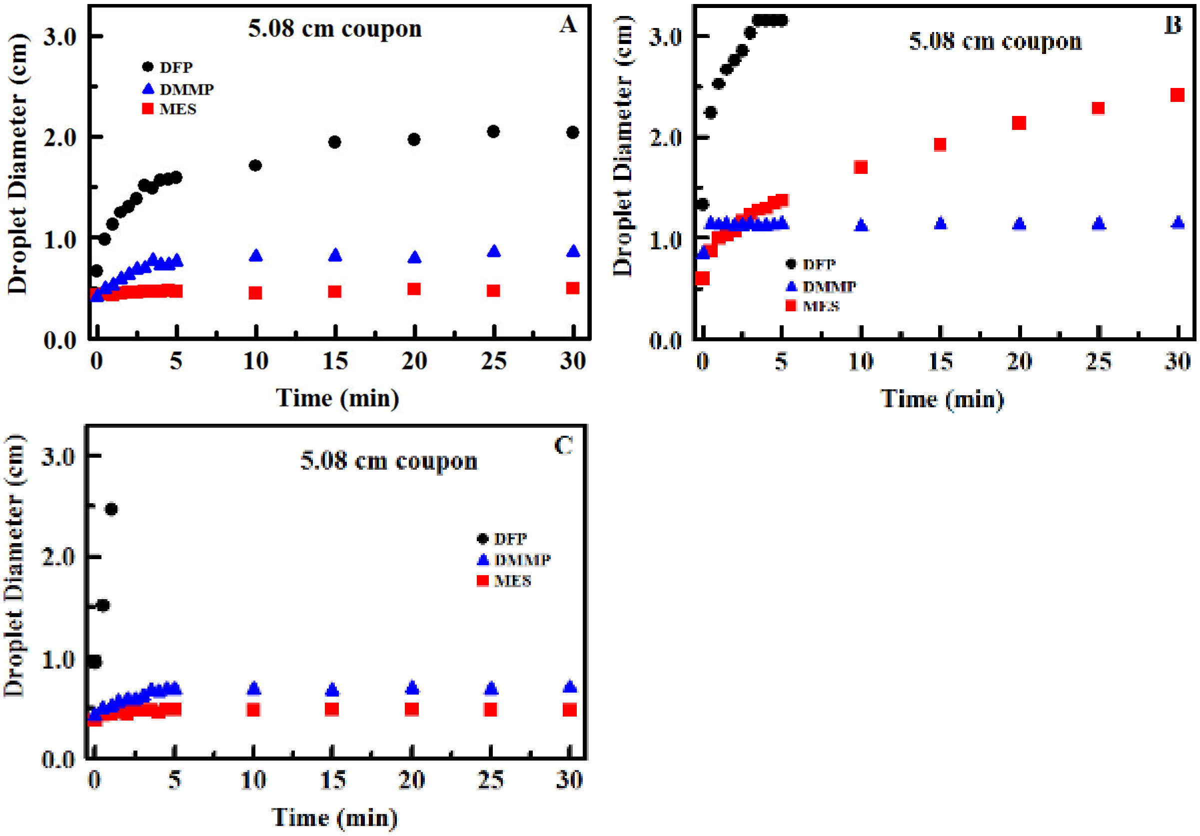

Fig. 5 — Progression of simulant droplet diameters during incubation on the SLIPS surfaces for DFP (black), DMMP (blue), and MES (red): SLIPS lubricated with Fomblin Y (A), SLIPS lubricated with Krytox 100 (B), and SLIPS lubricated with Krytox 103 (C).

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 during this period with one exception. As noted above for the formamide exposures, DFP was found to damage unlubricated polymer coatings. Lubricated surfaces were also damaged by DFP when the most recent lubrication had occurred several weeks previous to exposure. Coupons were decontaminated 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 decontaminated coupon in isopropanol. Figure 6 and Table 4 summarize these results. The lubrication of a painted surface using Fomblin Y results in significant reduction in the retention of the simulants by the surface. The porous polymer surface retains less target than the painted surface, but significantly more paraoxon and methyl salicylate than the oiled surface. The smooth polymer, on the other hand provides performance similar to that of the oiled coupon.

When the Fomblin Y SLIPS variations were compared, retention of all four simulants was less for the 3k samples than for the 2k samples, though differences in paraoxon retention were slight. Neither Krytox 100 nor Krytox 103 was preferable for reduction of all simulants with variations observed across the range of targets. The Fomblin Y lubricated surfaces, however, outperformed both of the Krytox lubricated surfaces. It should be noted that, though the Fomblin Y lubricated SLIPS surfaces outperformed all other surfaces following MES, DMMP, and DFP exposure, the Fomblin Y oiled paint and the smooth polymer surface both retained less paraoxon than this treatment.

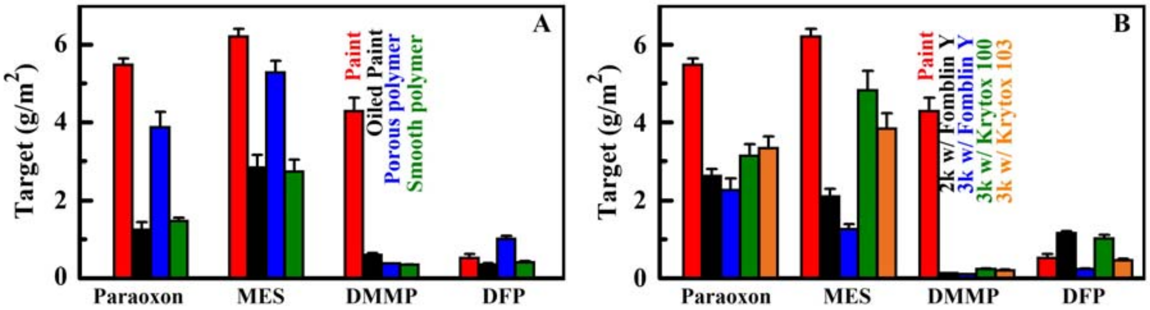

Fig. 6 — Target retained by coupons following treatment with an air stream and rinsing with soapy water. (A) Control surfaces: painted coupon (red); Fomblin Y oiled painted coupon (black); porous polymer only on painted coupon (blue); and smooth polymer only on painted coupon (green). (B) SLIPS samples: Fomblin Y lubricated, 2k SLIPS (black), Fomblin Y lubricated, 3k SLIPS (blue); Krytox 100 lubricated, 3k SLIPS (green); and Kyrtox 103 lubricated, 3k SLIPS (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
Oiled Paint	1.24	2.85	0.59	0.34
2k SLIPS with Fomblin Y	2.63	2.10	0.13	1.16
3k SLIPS with Fomblin Y	2.27	1.26	0.10	0.23
3k SLIPS with Krytox 100	3.13	4.82	0.23	1.02
3k SLIPS with Krytox 103	3.33	3.83	0.20	0.46
3k porous polymer, no lubrication	3.87	5.28	0.38	1.01
3k smooth polymer, no lubrication	1.47	2.74	0.34	0.41

Agent Evaluation.

Painted, SLIPS coated coupons were provided to ECBC. These coupons utilized the 3k deposition and were lubricated with Fomblin Y. The coupons were contaminated with bis(2-chloroethyl) sulfide (HD mustard), O-pinacolyl methylphosphonofluoridate (GD, soman), ethyl *N*-2-diisopropylaminoethyl methylphosphonothiolate (VX), or methyl salicylate (MES) and incubated for 60 minutes. Images of the coupons were collected during exposure to the targets (Appendix B). The SLIPS treatment was observed to reduce the spread of droplets for all of the targets. Figure 7 presents data on droplet spread based on diameter as used above under NRL's evaluation method. The figure also provides the calculated areas obtained by ECBC for the same images.

Following incubation, coupons received the CARM treatment process followed by extraction. No residue or damage was noted for MES, HD, or GD; however, following VX exposure, a mark appearing to be a salt-like residue was noted on the SLIPS coupons (Figure 8). Unlike in the NRL protocol, a fixed mass per surface area was not used in these evaluations. Rather, the CARM analysis used a fixed volume of 2 μL for all targets. For the coupons supplied, this produces contamination levels of 1.64 g/m^2 for HD, 1.37 g/m^2 for GD, 1.45 g/m^2 for VX, and 1.75 g/m^2 for MES. Figure 9 provides a summary of the results for targets retained following the CARM treatment of painted surfaces and the SLIPS coated painted surfaces (Table 5). Analysis based on the approach applied above indicates a slight reduction in GD retention (18%) as well as reduction in VX (82%), and MES (48%) retention. Retention of the ethylmethylphosphonic acid (EMPA) breakdown product of VX was also reduced by 95%.

ECBC bases analysis of samples on log differences in agent mass measured in the coupon extracts (Figure 10). Here, this analysis indicates no significant reduction in retention of GD or HD by the SLIPS treatment (Figure 11). VX retention was reduced by 5.2 times in SLIPS treated coupons as compared to untreated surfaces. This reduction was likely not due to breakdown of VX as the typical breakdown products, EMPA and S-2-diisopropylamino methylphosphonothioate (EA2192), were not observed in the SLIPS coupon extracts. In fact, the amount of EMPA recovered was reduced by 18.5 times for the SLIPS coupons as compared to that observed for the painted coupons.

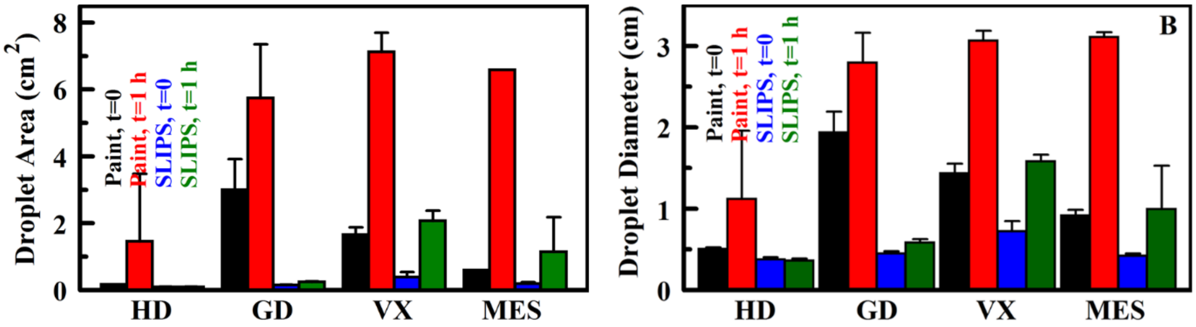

Fig. 7 — Progression of droplet spread on the surfaces during incubation as determined by ECBC (A) paint only and for Fomblin Y lubricated SLIPS on the painted coupons. Also provided are the diameters determined from the same images based on the approach used by NRL (B). Error bars represent standard deviation.

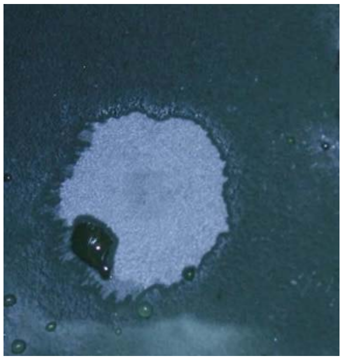

Fig. 8 — Damage or residue on SLIPS coupon following VX exposure and treatment / extraction using CARM.

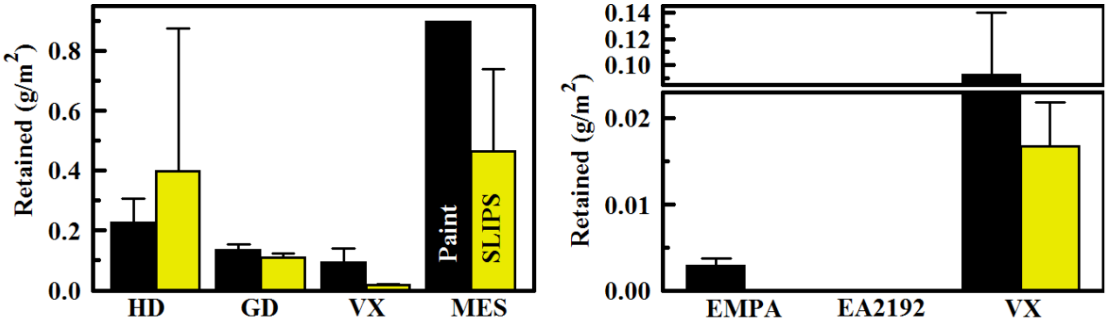

Fig. 9 — Agent retained by painted surfaces (black) and SLIPS coated painted surfaces (yellow): (A) retention of applied targets and (B) VX and related breakdown products determined in extracts. Error bars represent standard deviation.

Table 5 – Agent Retained (g/m^2) Following 1 h Aging on Aluminum Supports

Coupon	**HD**	**GD**	**VX**	**MES**	**EMPA**	**EA2192**
Aluminum Support						
Paint Only	0.22	0.13	0.09	0.90	2.9E-3	0.00
3k SLIPS with Fomblin Y	0.40	0.11	0.02	0.46	0.2E-3	0.00

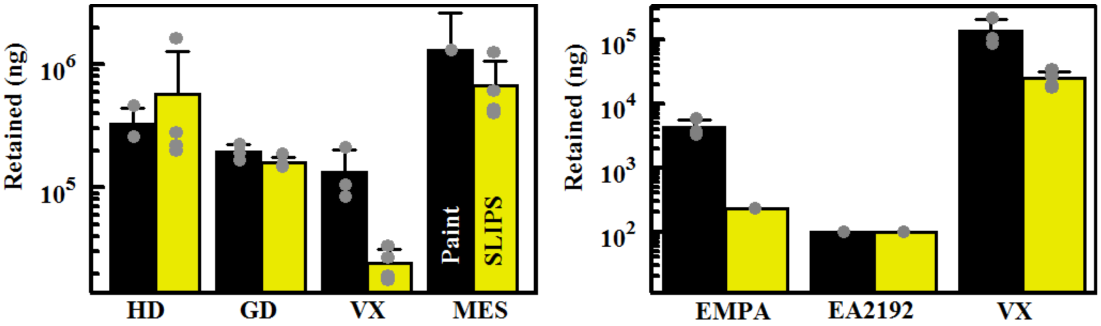

Fig. 10 — Agent retained by painted surfaces (black) and SLIPS coated painted surfaces (yellow): (A) retention of applied targets and (B) VX and related breakdown products determined in extracts. Error bars represent standard deviation; points provide values for individual samples.

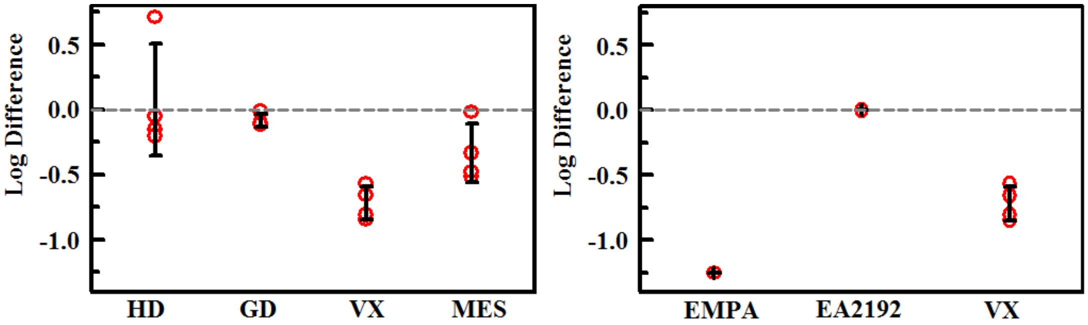

Fig. 11 — Log difference analysis for agent retained data presented in Figure 10. Here, the logarithm (Log_{10}) of the recovered masses for painted surface and for SLIPS treated painted surfaces is calculated. The plot shows the difference between this value for the SLIPs surfaces and the average value for a painted surface: (A) Log difference retention of applied targets and (B) Log difference VX and related breakdown products determined in extracts. Error bars represent standard deviation; points provide values for individual samples.

CONCLUSIONS

The SLIPS samples offer low surface energy, and spreading of target droplets is reduced on the surfaces. These samples provided promising results with reduced retention of simulants observed through the NRL studies. This result was largely not reflected in the results obtained by ECBC. It is important to note that samples were handled differently by NRL and ECBC during the treatment process. The approach at NRL begins with an air stream for removal of excess contaminant before the wash steps. This air stream is not included in the ECBC method. For comparison, when this step is omitted from the NRL protocol, retention of MES by the 3k Fomblin Y lubricated surface increases from 1.26 g/m^2 to 4.91 g/m^2. Similarly, DFP retention increases from 0.23 g/m^2 to 1.89 g/m^2. The result is less pronounced on a paint only surface with

MES retention increased from 6.20 g/m^2 to 6.81 g/m^2. It is possible that this is a result of target partitioning into the lubricating layer. Both MES and DFP have low solubility in water. Other considerations have also been shown to have an impact on the retention of targets by the surfaces.[10]

Application of the lubricated coating produces a slightly wet look on the painted surfaces (Figure 3 and Appendices). The unlubricated polymer coatings tend to have a frosted appearance. Spectrophotometric analysis is necessary to determine the overall impact on color and reflectivity. The long term stability of the coatings should also be more thoroughly evaluated.

This effort is also evaluating the potential of a covalently attached liquid for addressing the ongoing depletion of the lubricating layer faced by all SLIPS coatings.[9] Though the surface functionalization and lubricating liquids are tailored to provide favorable interactions between the surface and liquid, there is slow, continual loss at the edges of a coated region as well as during interactions with other liquids (rinsing, for example). At some point, there is no longer sufficient lubricant remaining on the material to provide the desired liquid-liquid surface interface. These lubricating liquids can also be transferred to clothing and skin, presenting a further problem for implementation as a surface treatment for threat agent resistance. The use of a covalently attached liquid could address this shortfall, though it may also impact the self-healing nature of the SLIPS coating.

ACKNOWLEDGEMENTS

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REFERENCES

1. Okada, I.; Shiratori, S., High-Transparency, Self-Standable Gel-SLIPS Fabricated by a Facile Nanoscale Phase Separation. *ACS Applied Materials & Interfaces* **2014,** 6, (3), 1502-1508.
2. Samaha, M. A.; Gad-el-Hak, M., Polymeric Slippery Coatings: Nature and Applications. *Polymers* **2014,** 6, (5), 1266-1311.
3. Wong, T. S.; Kang, S. H.; Tang, S. K. Y.; Smythe, E. J.; Hatton, B. D.; Grinthal, A.; Aizenberg, J., Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity. *Nature* **2011,** 477, (7365), 443-447.
4. Xiao, L. L.; Li, J. S.; Mieszkin, S.; Di Fino, A.; Clare, A. S.; Callow, M. E.; Callow, J. A.; Grunze, M.; Rosenhahn, A.; Levkin, P. A., Slippery Liquid-Infused Porous Surfaces Showing Marine Antibiofouling Properties. *ACS Applied Materials & Interfaces* **2013,** 5, (20), 10074-10080.
5. White, B.; Moore, M.; Malanoski, A.; Campbell, C. "Bioinspired Surface Treatments for Improved Decontamination: Silicon and Latex Polymer SLIPS Treatments" US Naval Research Laboratory, **2017**, NRL/MR/6930-17-9733.
6. White, B.; Melde, B.; Malanoski, A.; Moore, M. "Bioinspired Surface Treatments for Improved Decontamination: Silicate-Based Slippery Liquid-Infused Porous Surfaces (SLIPS)" US Naval Research Laboraty, **2017**, NRL/MR/6930-17-9734.
7. Lalain, T.; Mantooth, B.; Shue, M.; Pusey, S.; Wylie, D. "Chemical Contaminant and Decontaminant Test Methodology Source Document," US Army RDEC, Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, **2012**; ECBC-TR-980.

8. Gebreegzi, Y. T.; Foster, G. D.; Khan, S. U., Simulltaneous Determination of Carbaryl, Malathion, Fenitrothion, and Diazinon Residues in Sesame Seeds (*Seasmum indicum* L) *J. Agric. Food Chem.* **2000,** 48, 5165-5168.
9. Wang, L.; McCarthy, T. J., Covalently Attached Liquids: Instant Omniphobic Surfaces with Unprecedented Repellency. *Angewandte Chemie International Edition* **2016,** 55, 244-8.
10. White, B.J.; Moore, M.H.; Melde, B.J.; Malanoski, A.P.; Campbell, C. "Bioinspired Surface Treatments for Improved Decontamination: Handling and Decontamination Considerations," US Naval Research Laboratory, **2018**; NRL/MR/ 6930-18-9770.

Appendix A

COUPON IMAGES WITH SIMULANTS

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), 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.

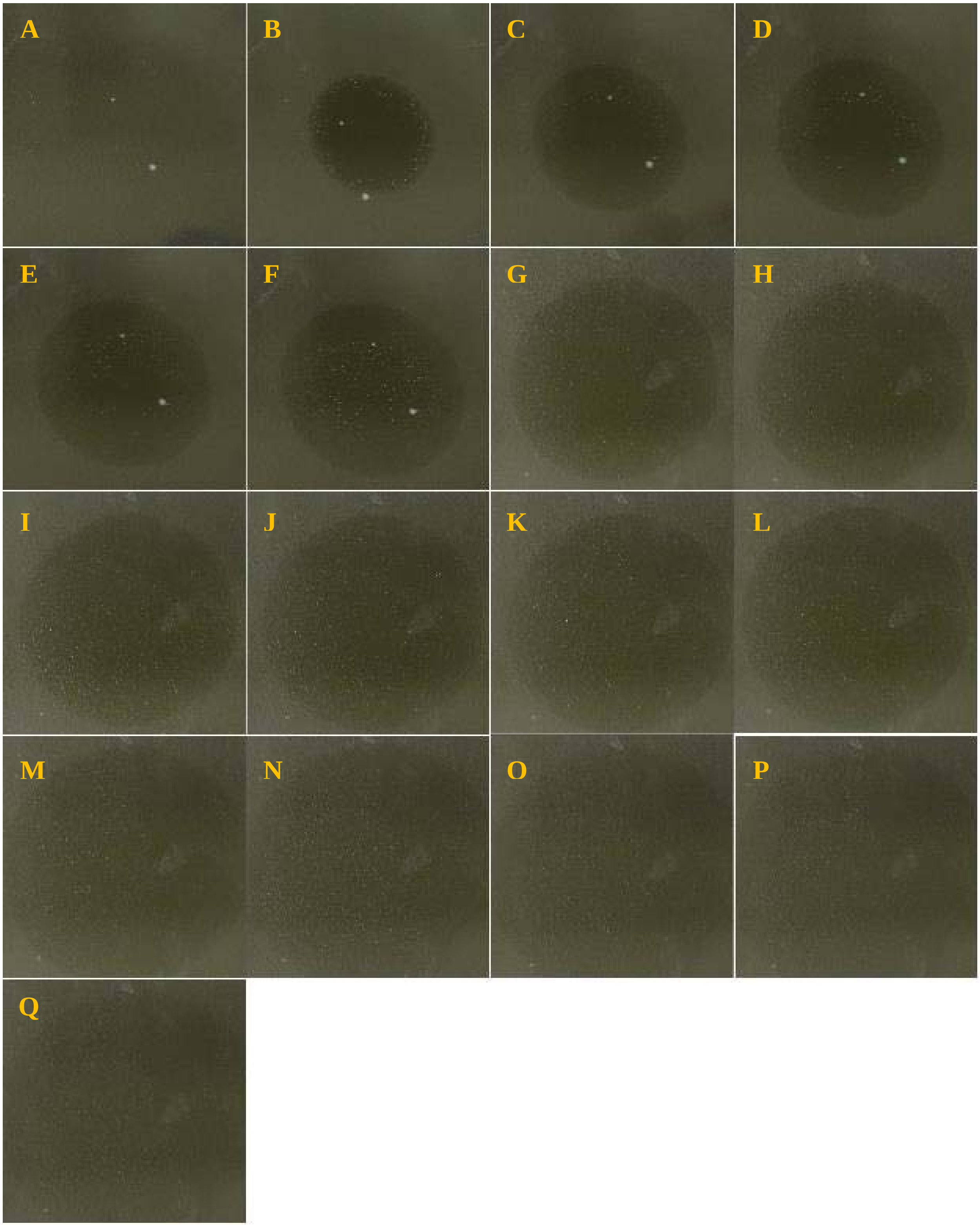


Fig. A2 — MES on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

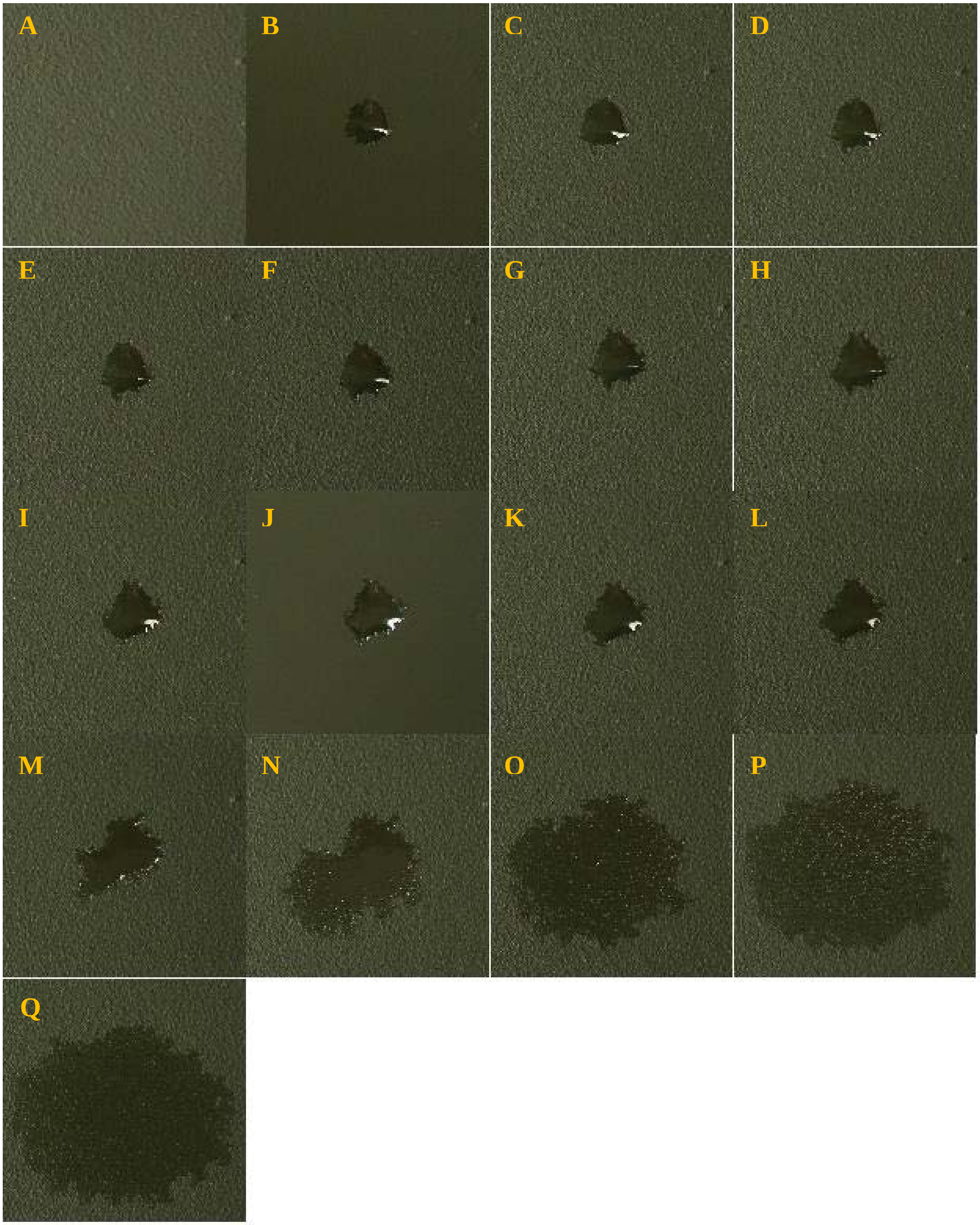


Fig. A3 — DMMP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

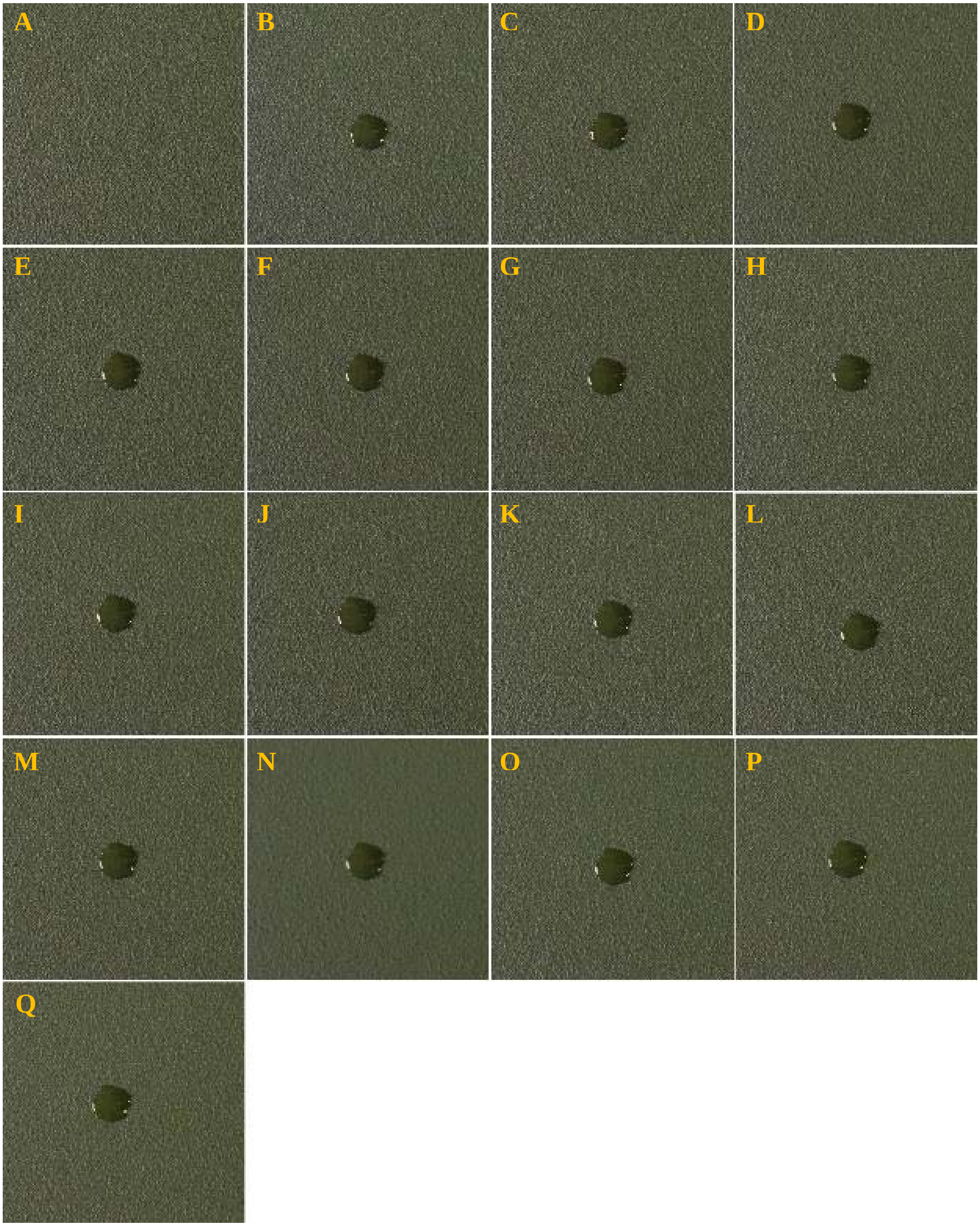


Fig. A4 — DFP on Fomblin Y oiled paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

Fig. A5 — 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. A6 — 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.

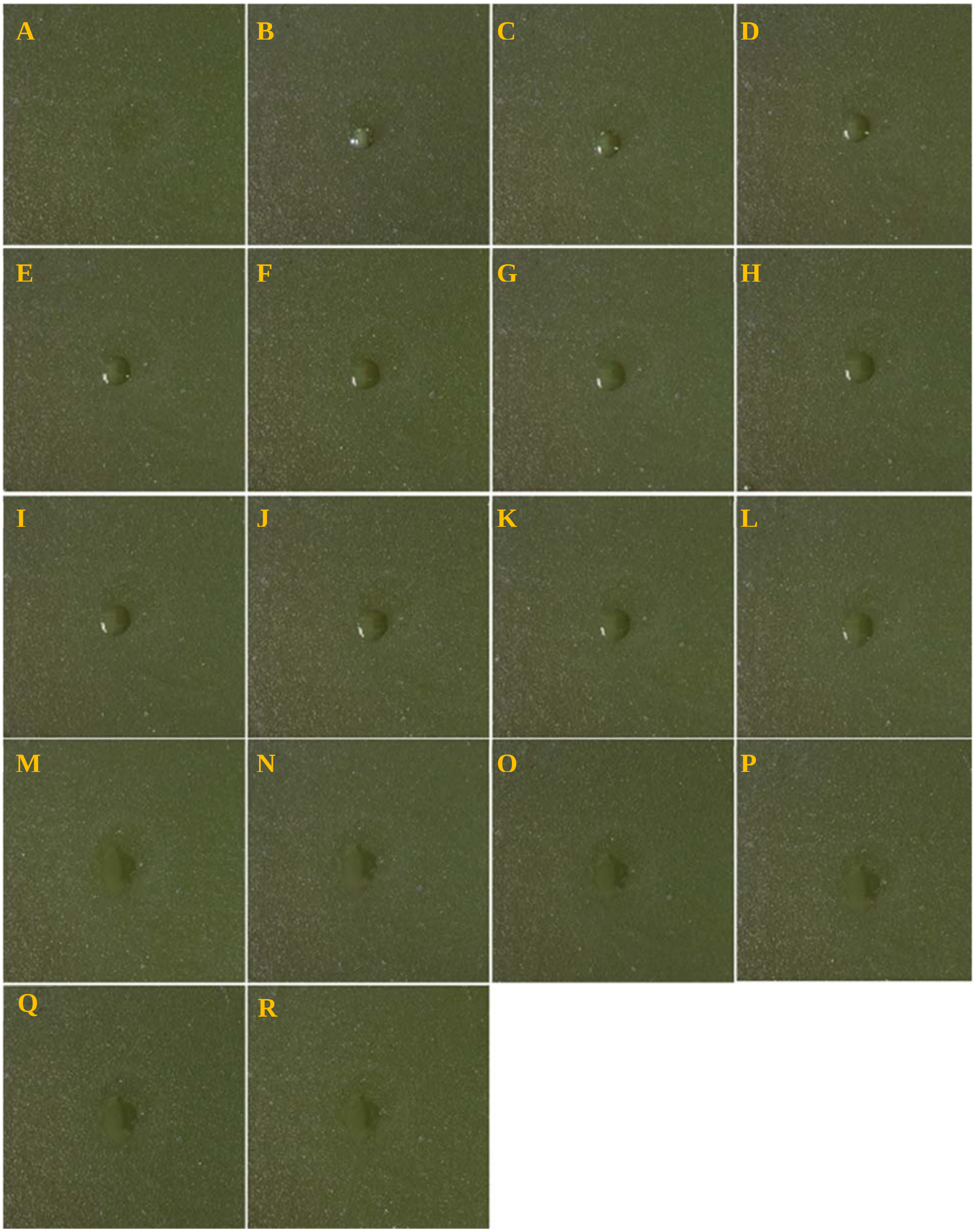


Fig. A7 — DFP on the nonporous polymer with no lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

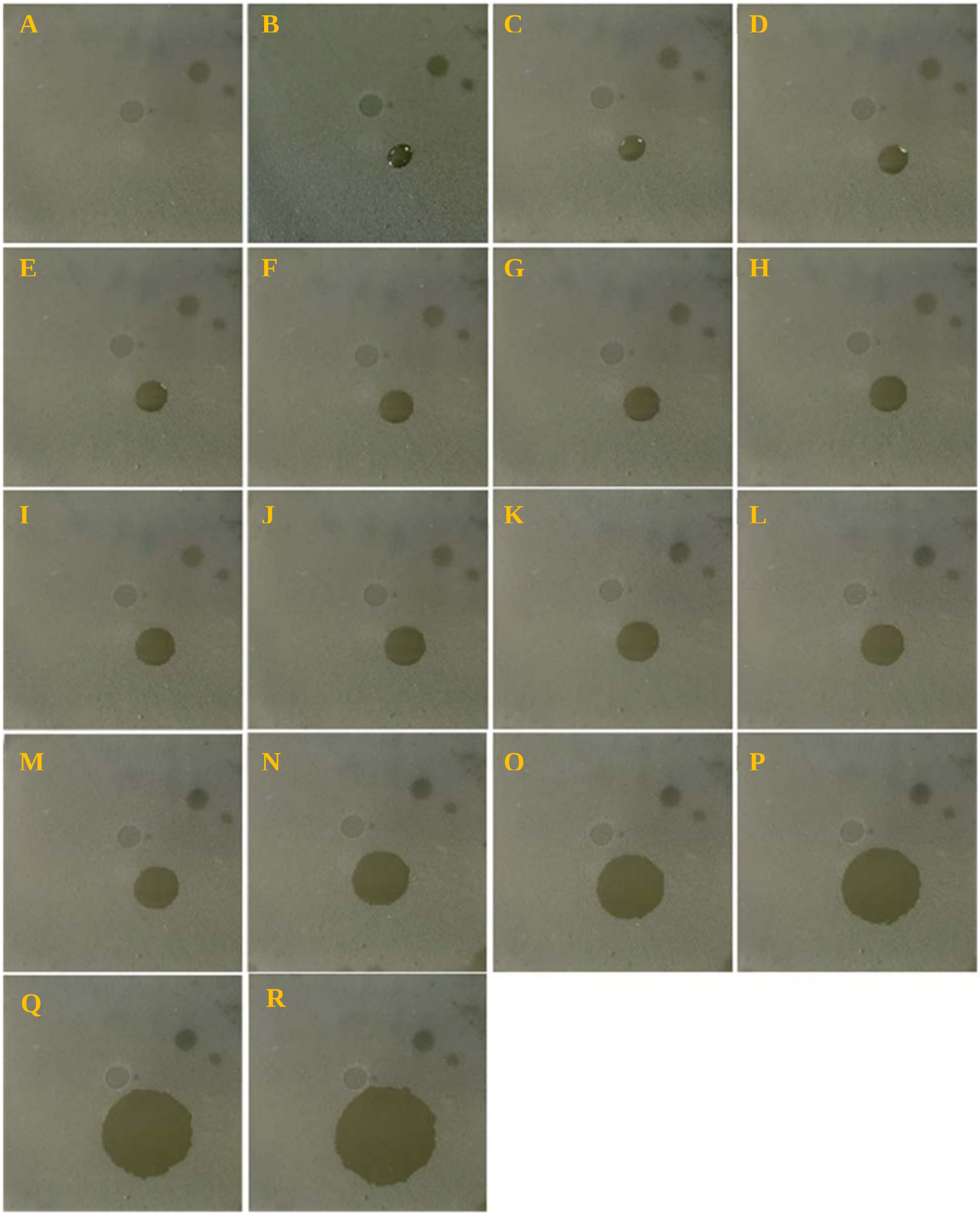


Fig. A8 — MES on the nonporous polymer with no lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

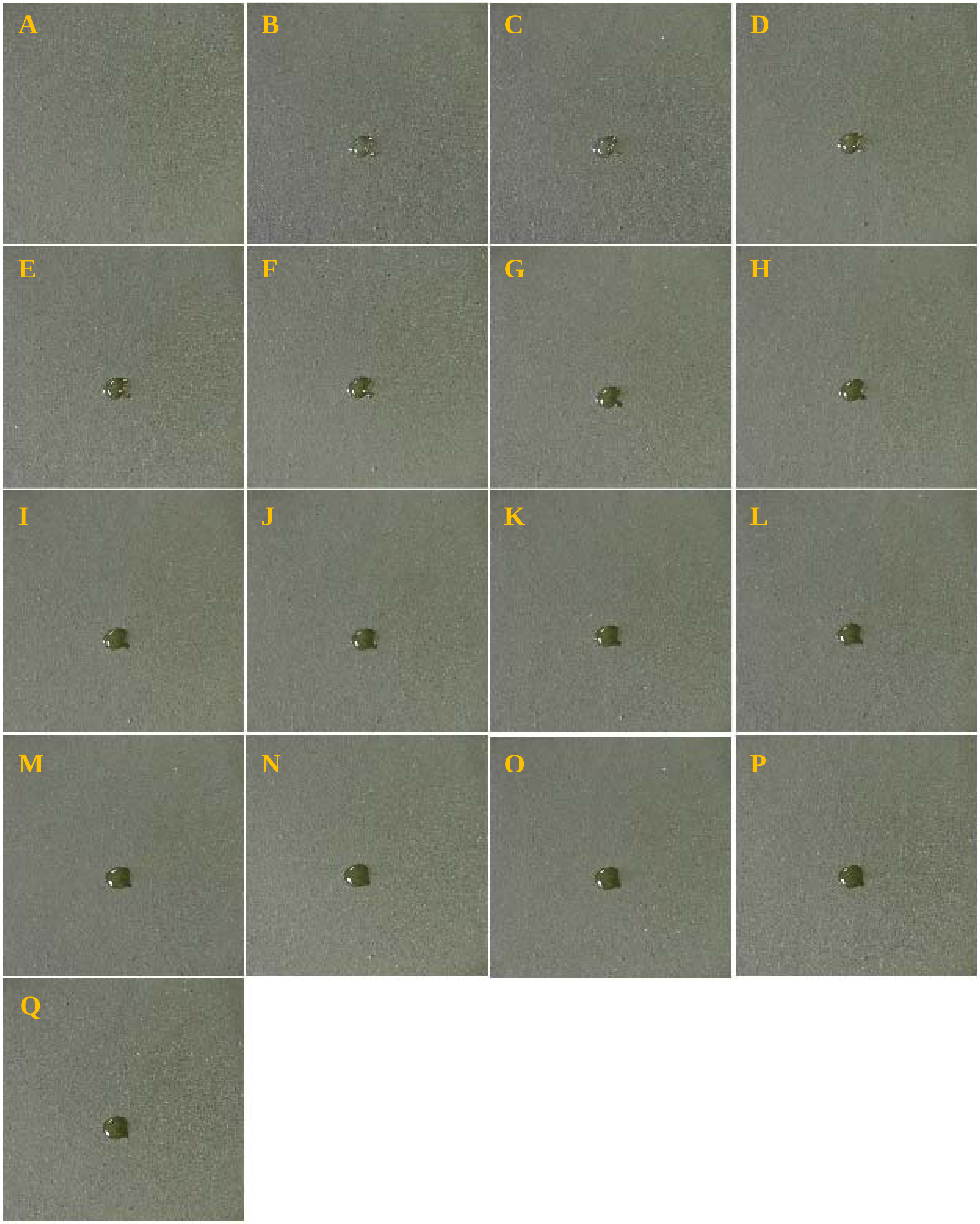


Fig. A9 — DMMP on the nonporous polymer with no lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

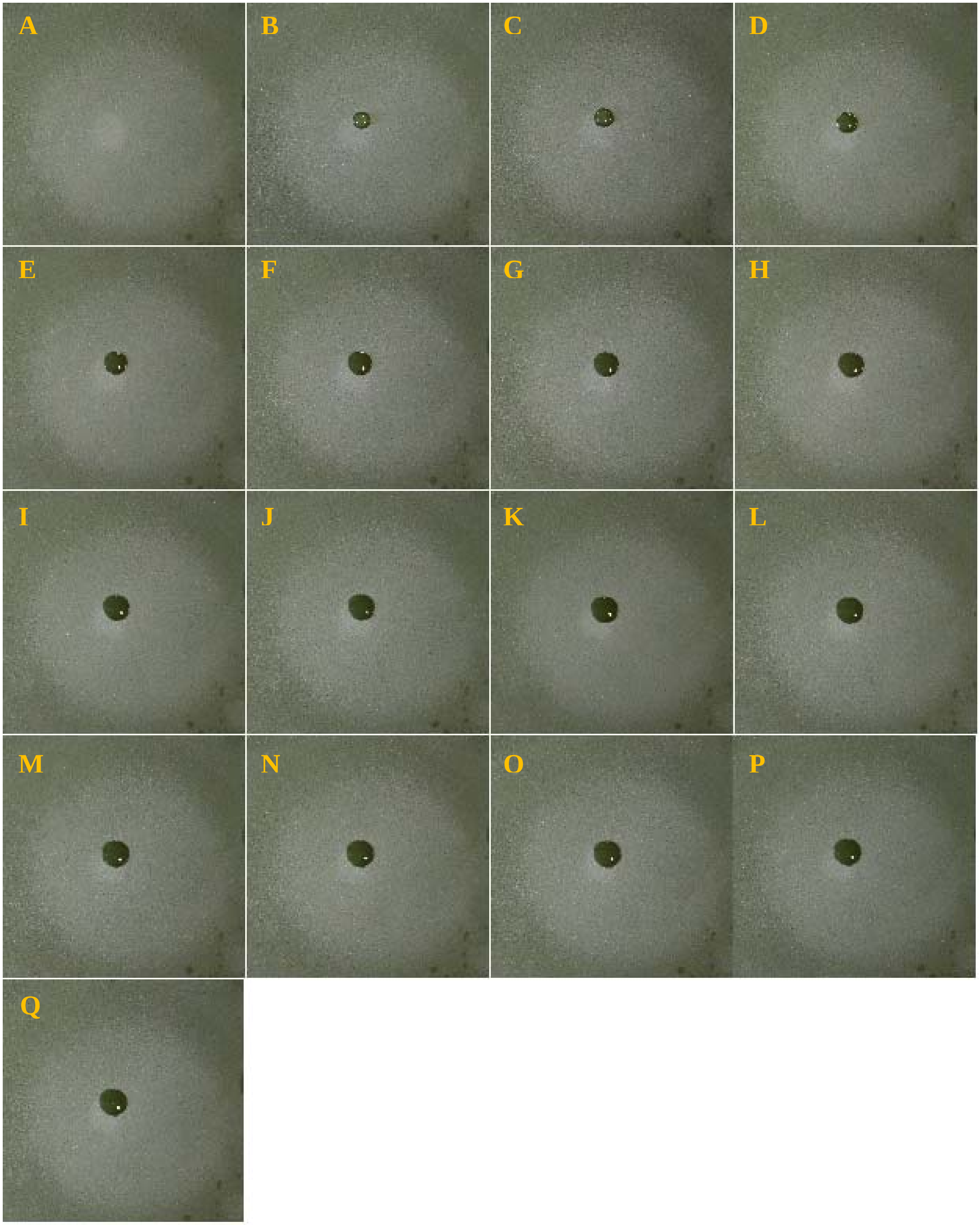


Fig. A10 — DFP on the nonporous polymer with Fomblin Y lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

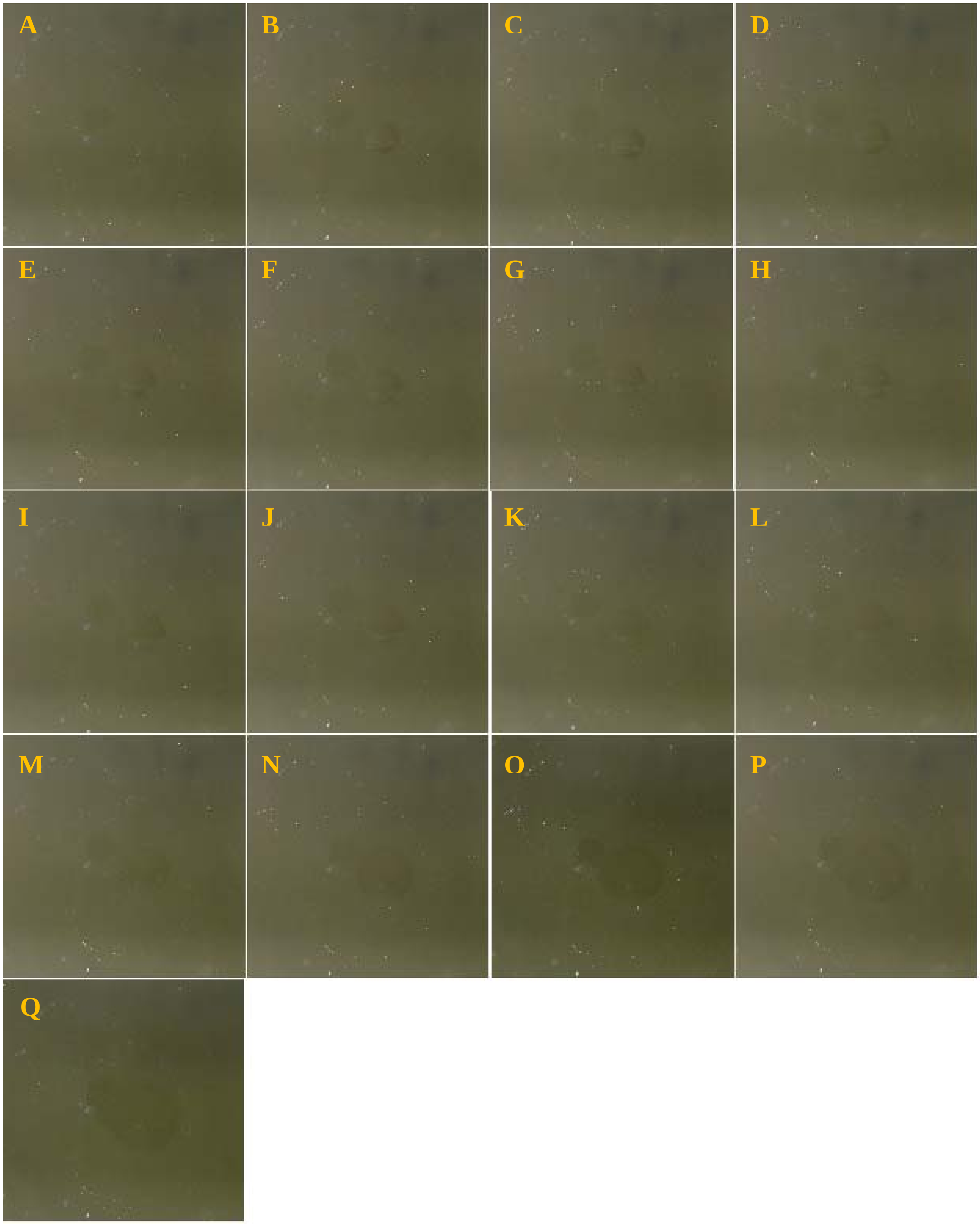


Fig. A11 — MES on the nonporous polymer with Fomblin Y lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

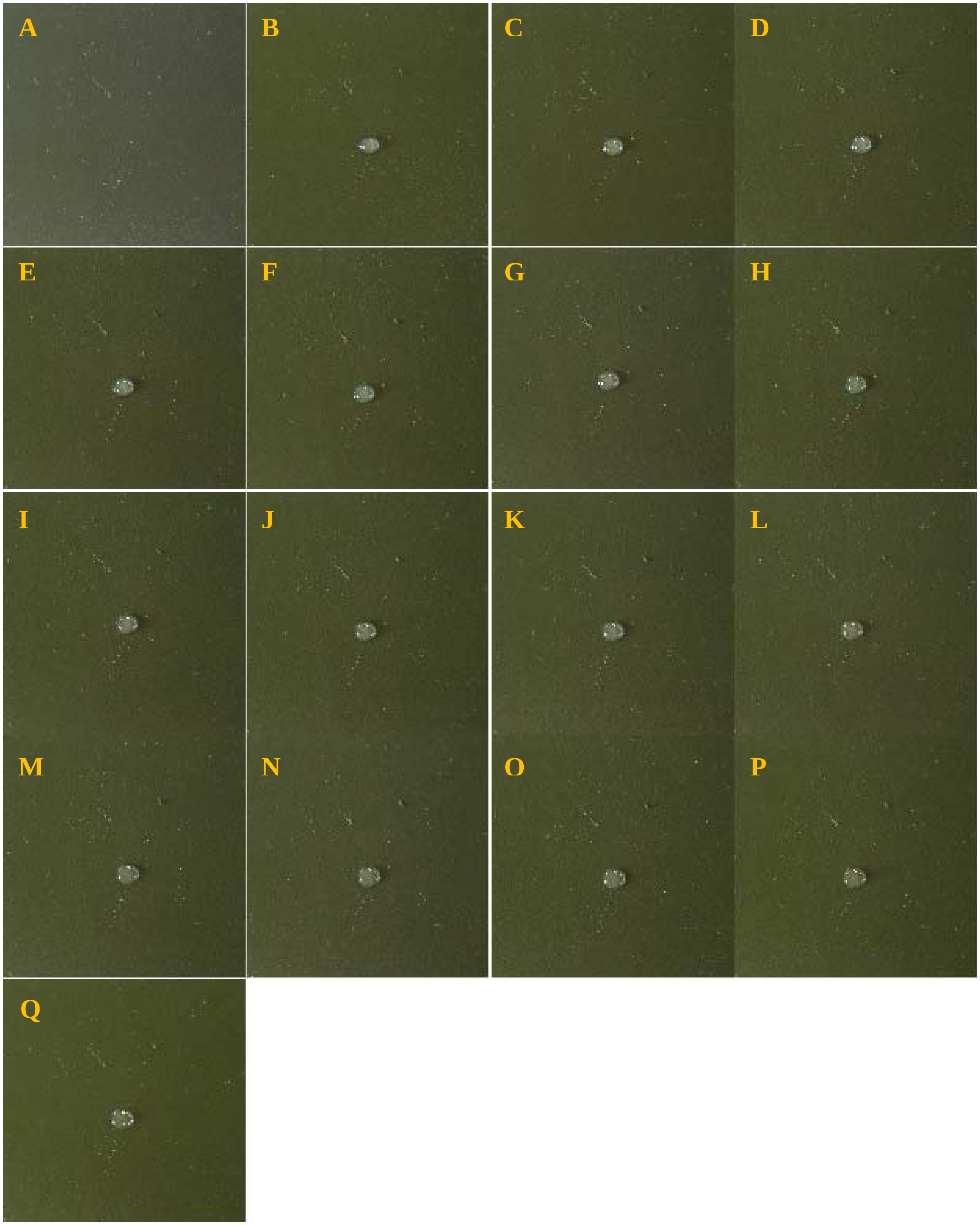


Fig. A12 — DMMP on the nonporous polymer with Fomblin Y lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

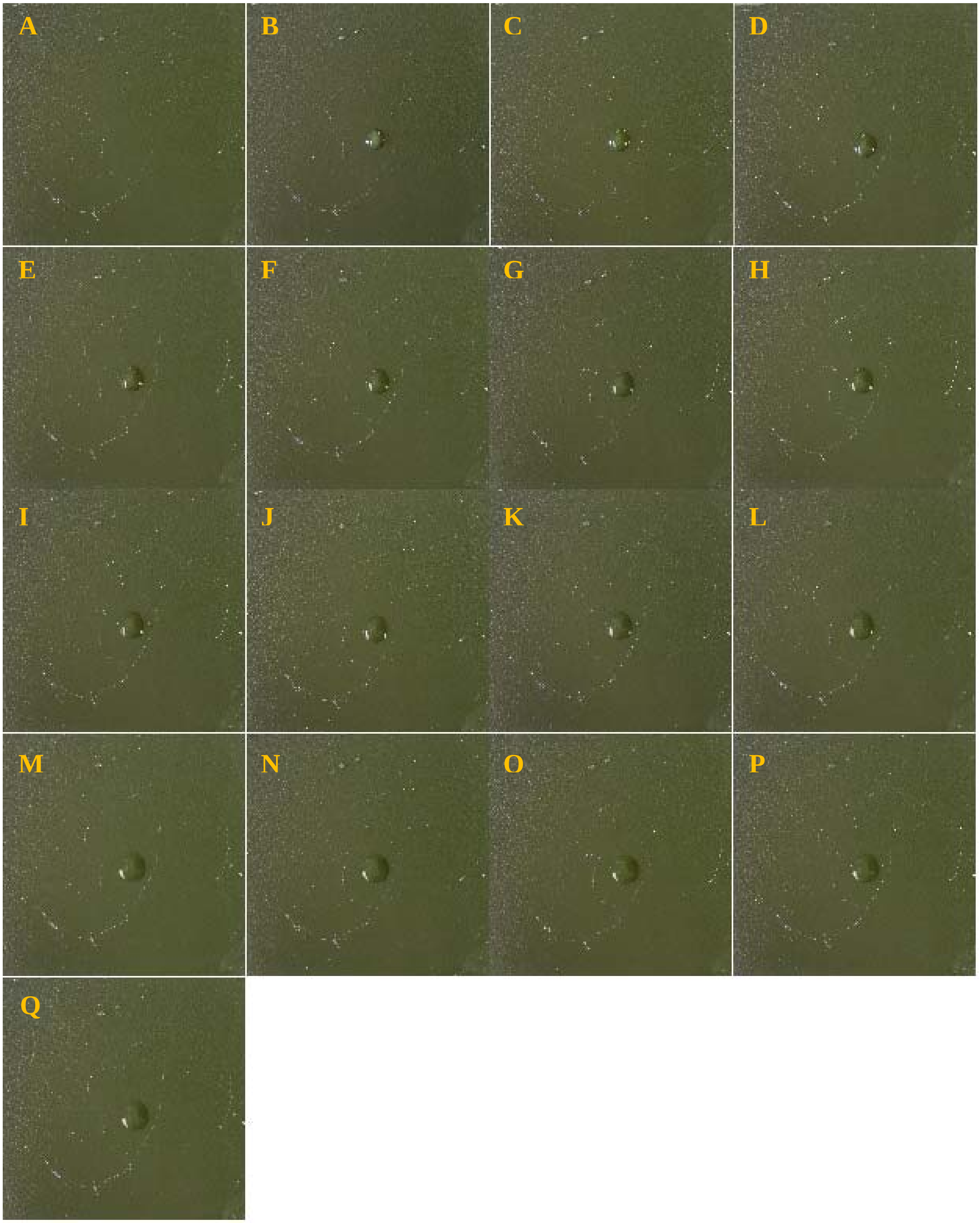


Fig. A13 — DFP on the porous polymer with no lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

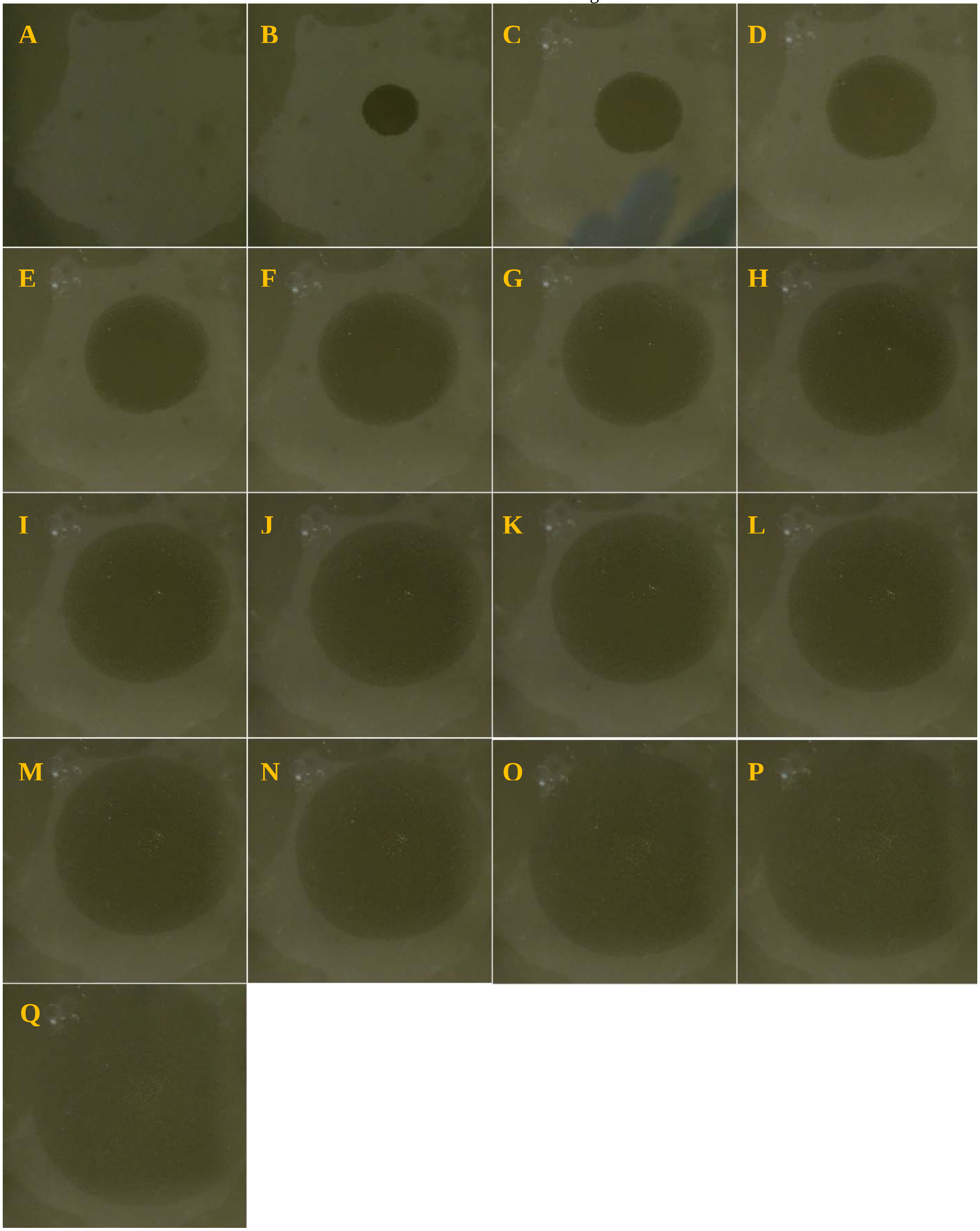


Fig. A14 — MES on the porous polymer with no lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

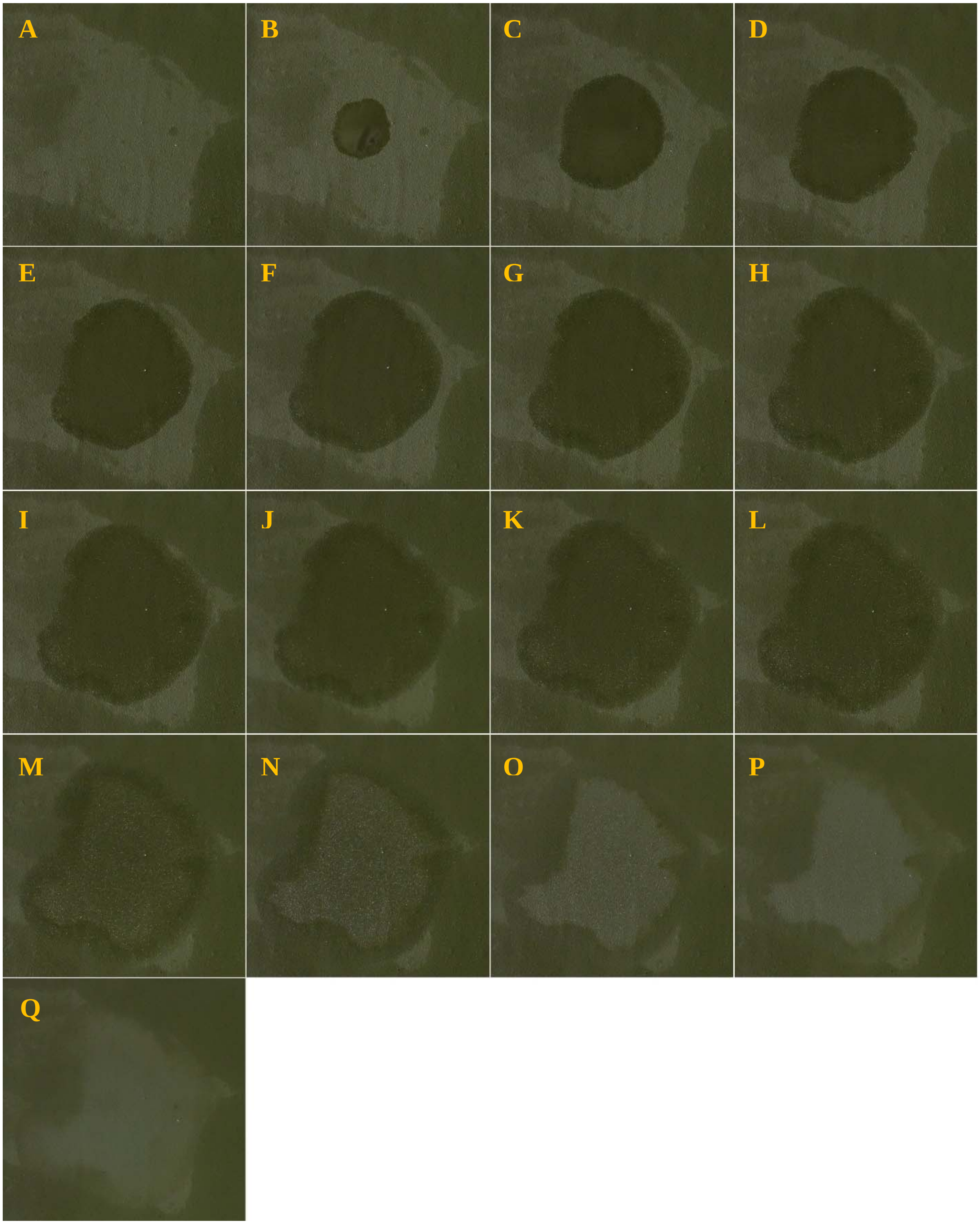


Fig. A15 — DMMP on the porous polymer with no lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target

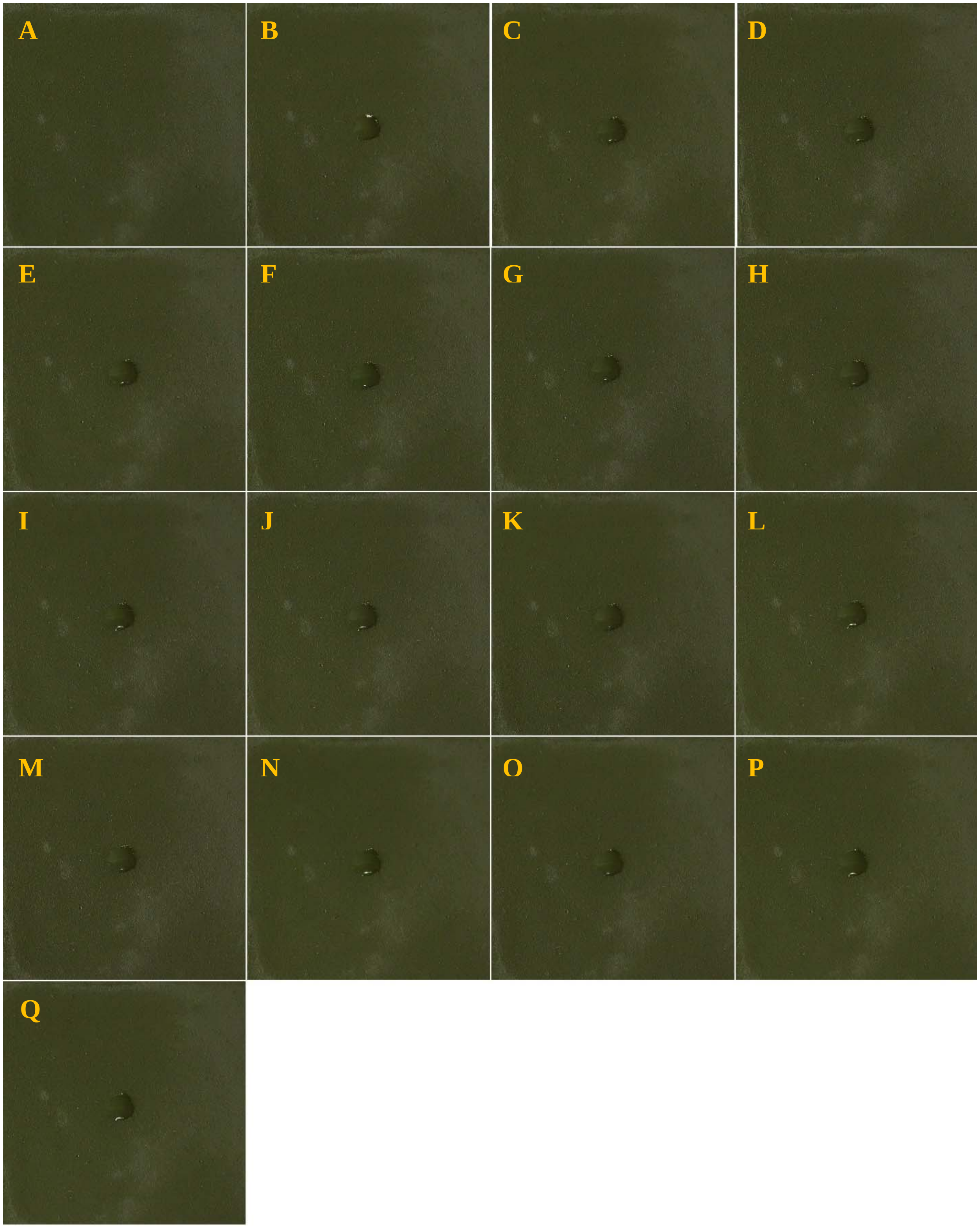


Fig. A16 — DFP on the full SLIPS treatment with Fomblin Y lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

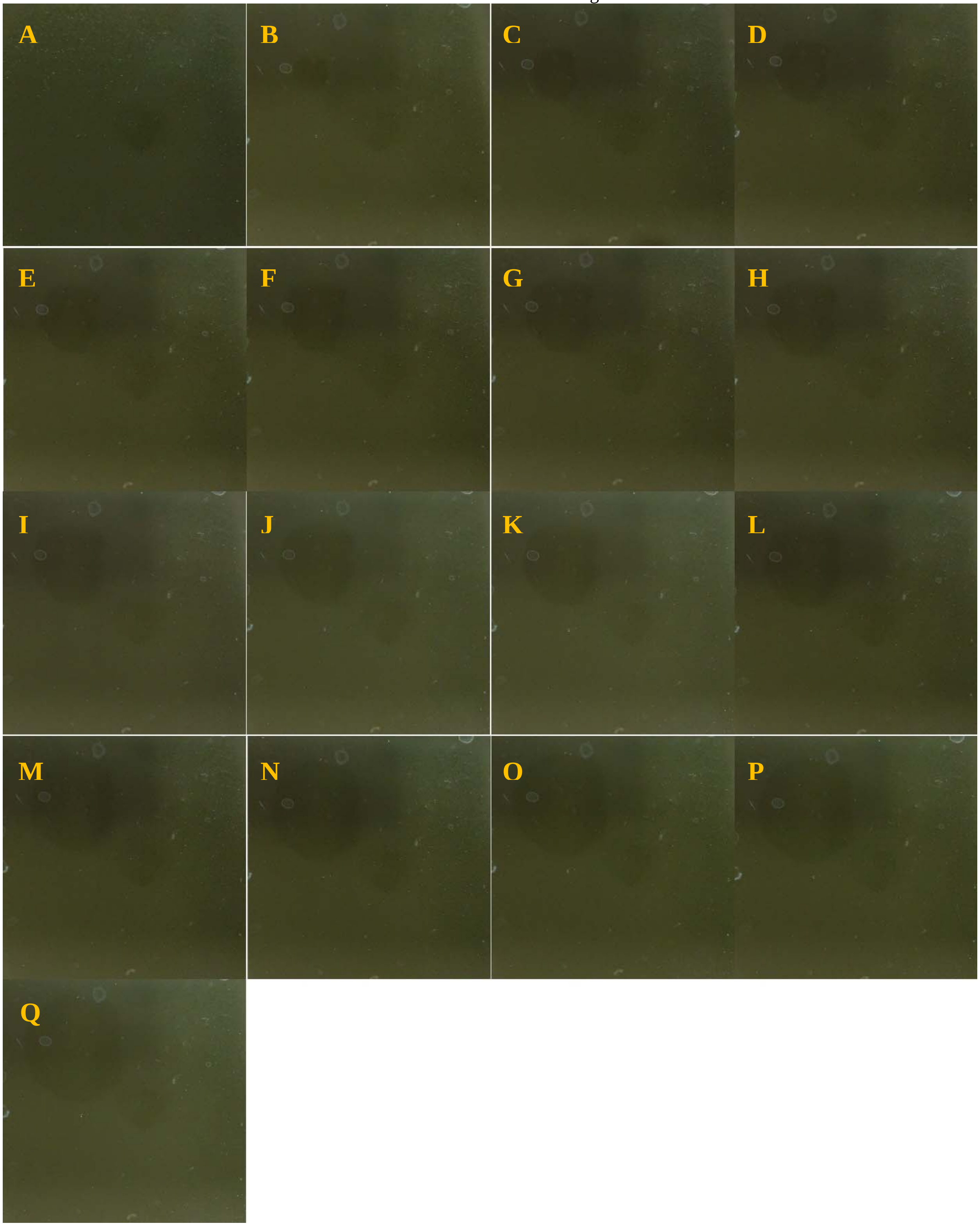


Fig. A17 — MES on the full SLIPS treatment with Fomblin Y lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

Fig. A18 — DMMP on the full SLIPS treatment with Fomblin Y lubricant. 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.

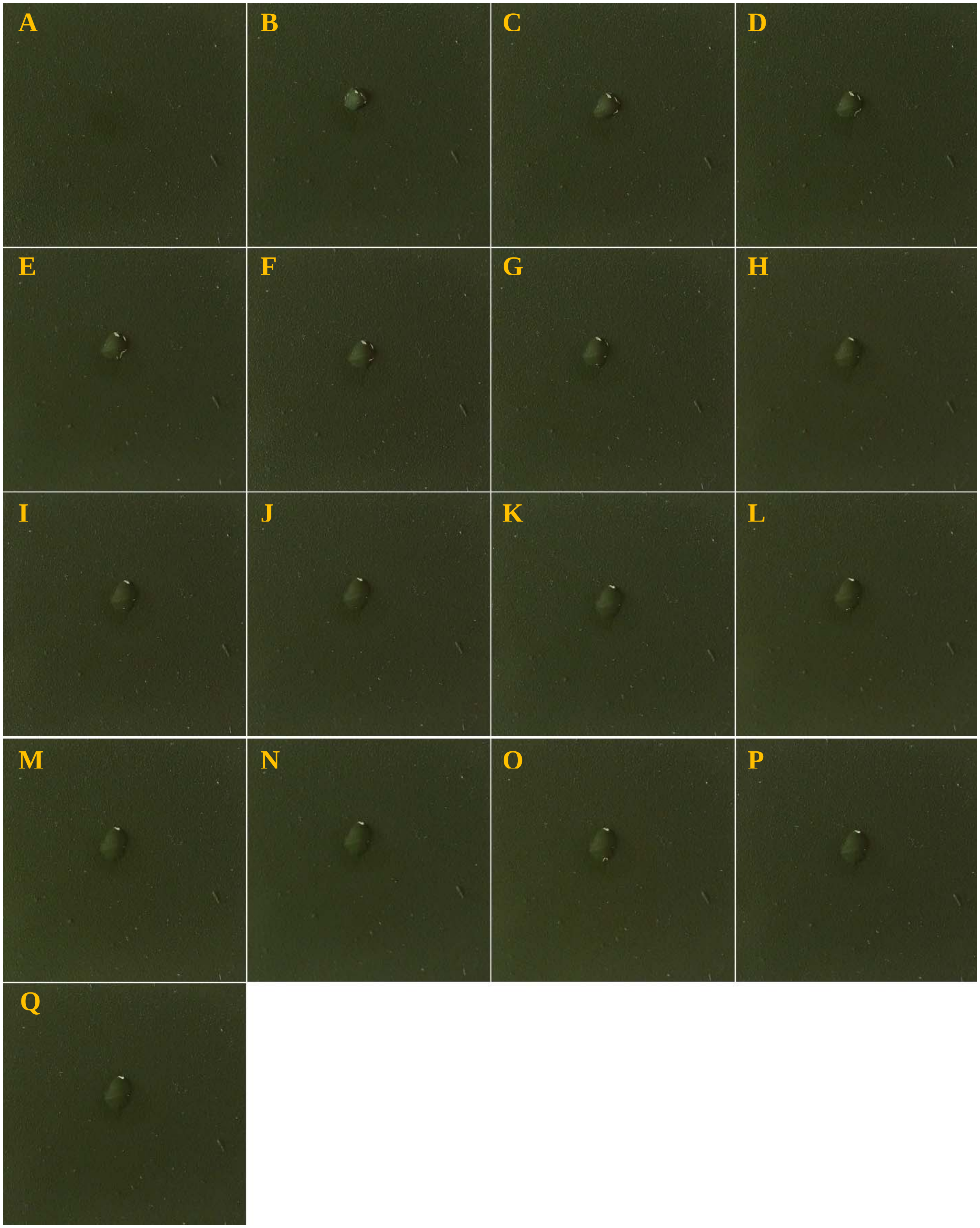


Fig. A19 — DFP on the full SLIPS treatment with Krytox 100 lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

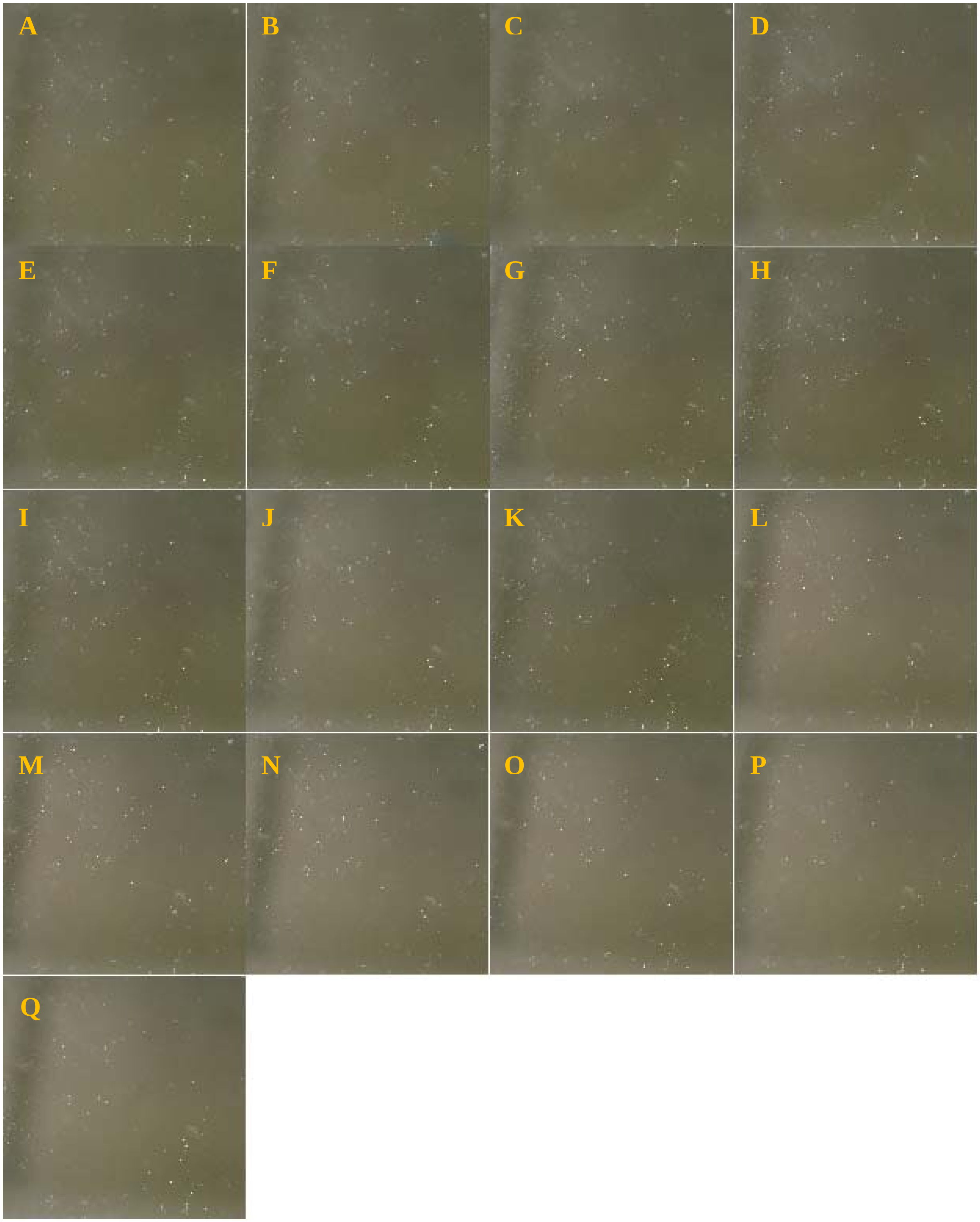


Fig. A20 — MES on the full SLIPS treatment with Krytox 100 lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

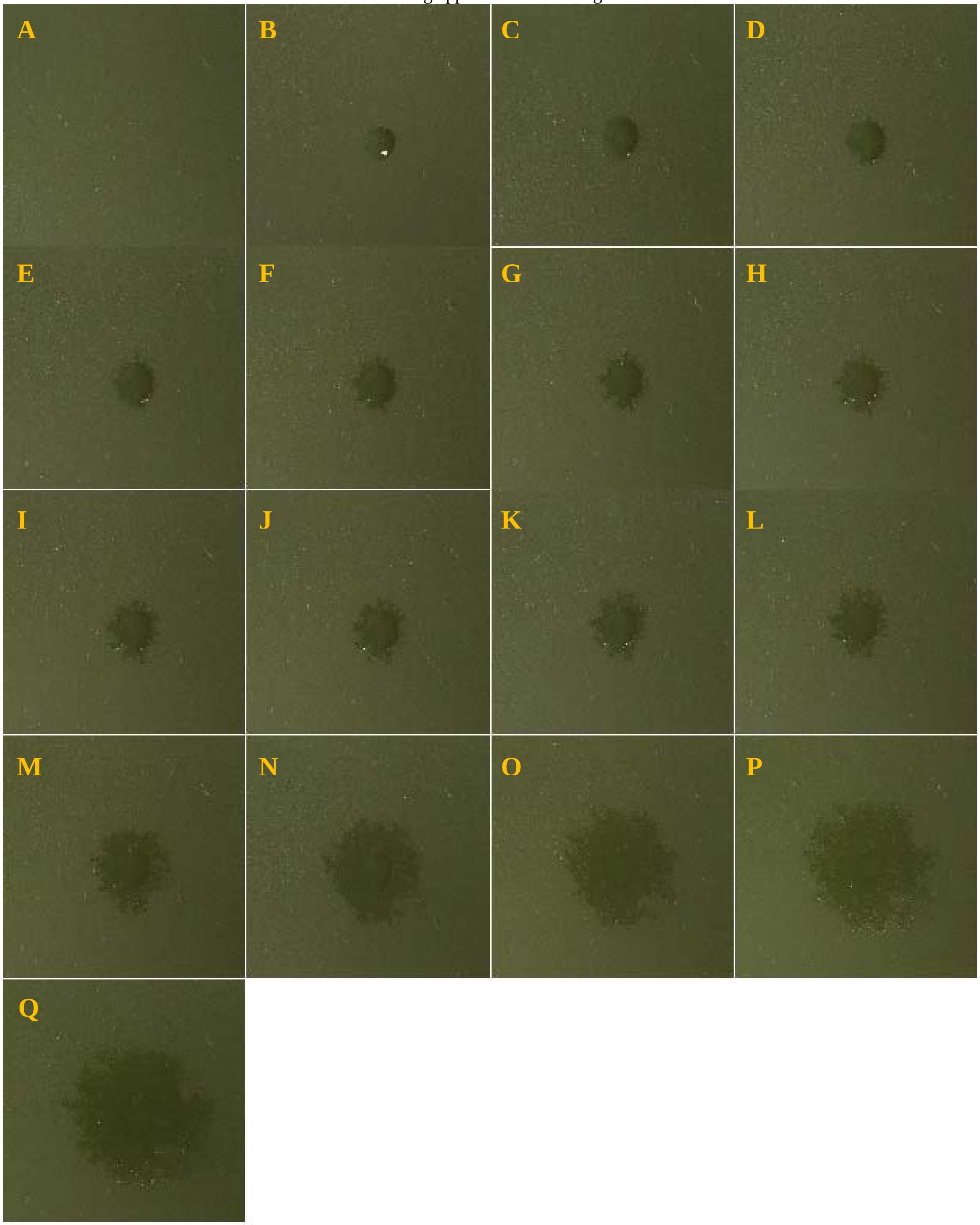


Fig. A21 — DMMP on the full SLIPS treatment with Krytox 100 lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

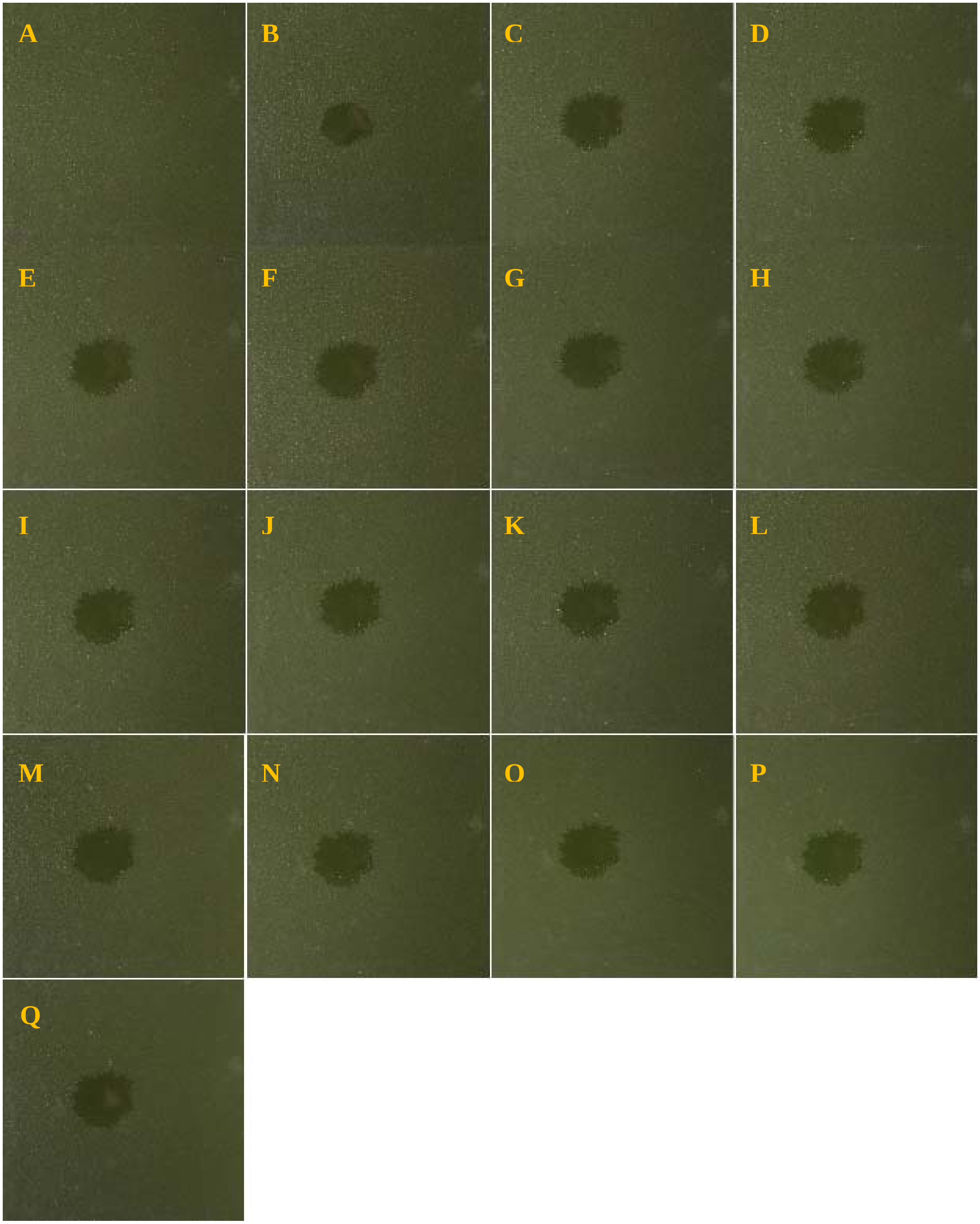


Fig. A22 — DFP on the full SLIPS treatment with Krytox 103 lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

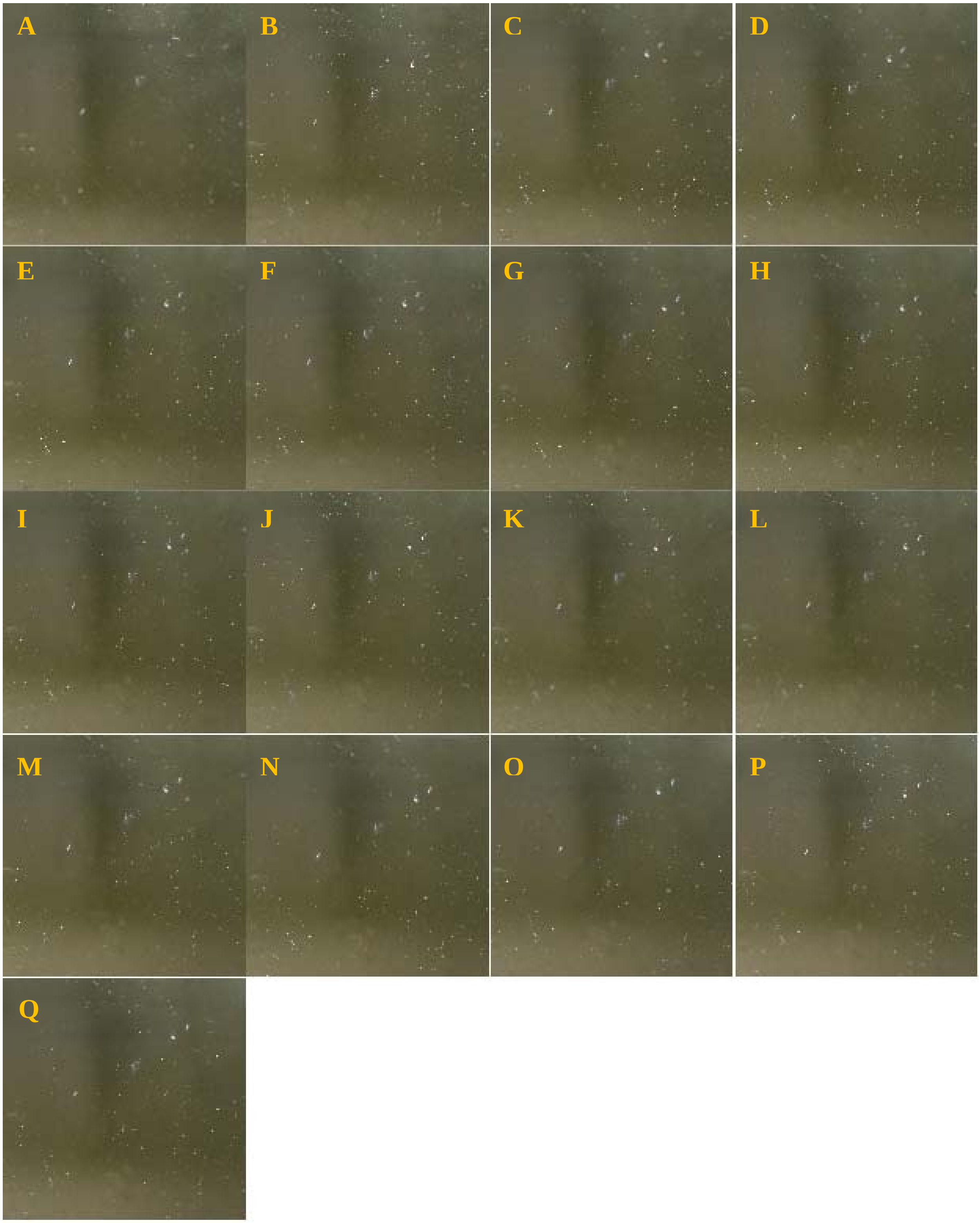


Fig. A23 — MES on the full SLIPS treatment with Krytox 103 lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

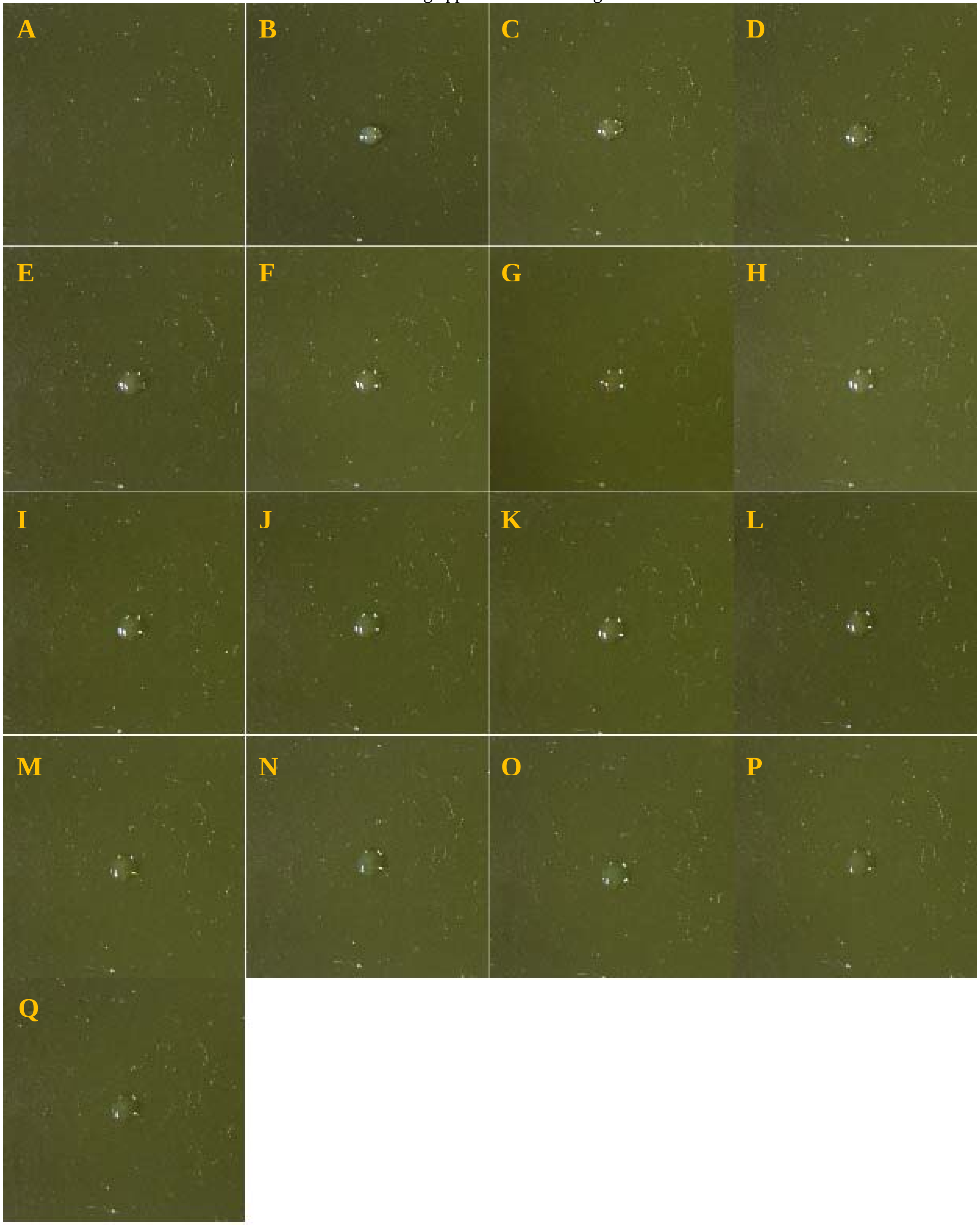
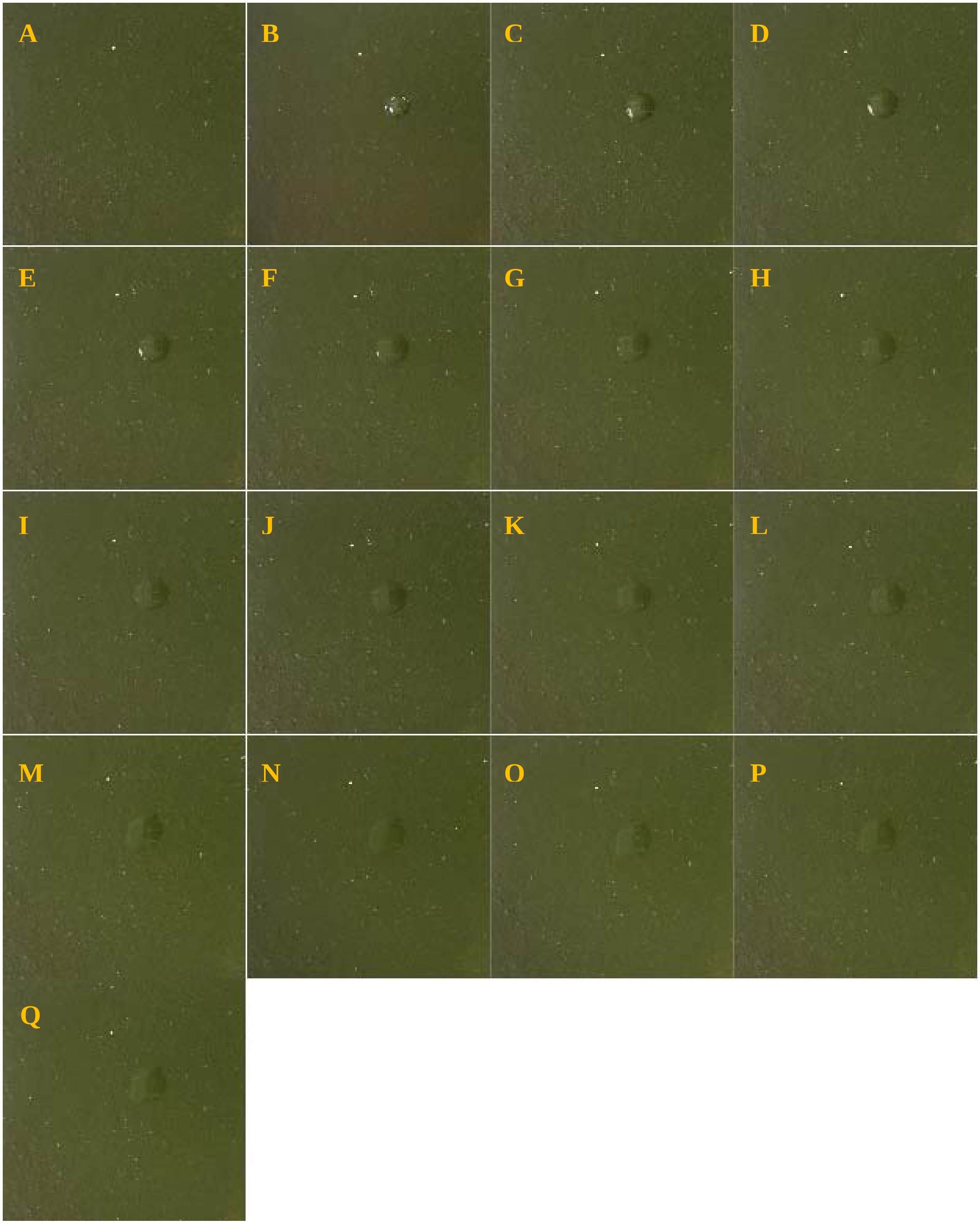


Fig. A24 — DMMP on the full SLIPS treatment with Krytox 103 lubricant. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix B

COUPON IMAGES WITH AGENT

Fig. B1 — ECBC analysis of targets on paint and SLIPS coated coupons. Images of a coupon before application (left), 2 to 5 min following application (center), and at 55 min after contamination (final area; right): (A) painted coupon with HD, (B) SLIPS coated coupon with HD, (C) painted coupon with GD, (D) SLIPS coated coupon with GD.

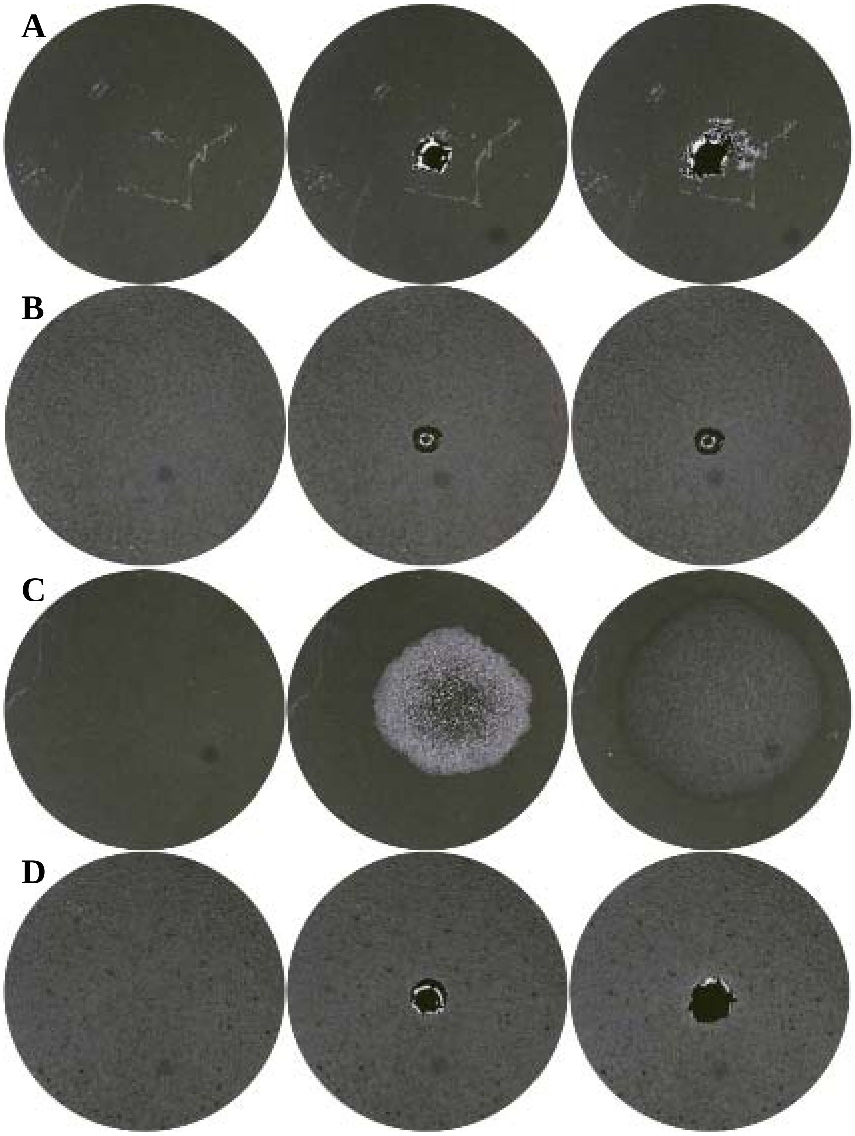


Fig. B2 — ECBC analysis of targets on paint and SLIPS coated coupons. Images of a coupon before application (left), 2 to 5 min following application (center), and at 55 min after contamination (final area; right): (A) painted coupon with VX, (B) SLIPS coated coupon with VX, (C) painted coupon with MES, (D) SLIPS coated coupon with MES.