



NRL/MR/6930--17-9761

# Bioinspired Surface Treatments for Improved Decontamination: Slippery Omniphobic Covalently Attached Liquid (SOCAL)

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December 13, 2017

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 13-12-2017		2. REPORT TYPE NRL Memorandum Report		3. DATES COVERED (From - To) October 7, 2015 – August 30, 2017	
4. TITLE AND SUBTITLE  Bioinspired Surface Treatments for Improved Decontamination: Slippery Omniphobic Covalently Attached Liquid (SOCAL)				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)  Brandy J. White, Brian J. Melde, Anthony P. Malanoski, and Martin H. Moore				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 69-1H46	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory, Code 6930 4555 Overlook Avenue, SW Washington, DC 20375-5320				8. PERFORMING ORGANIZATION REPORT NUMBER  NRL/MR/6930--17-9761	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Defense Threat Reduction Agency DTRA-Joint CBRN Center of Excellence BLDG E-2800 APG-EA, MD 21010				10. SPONSOR / MONITOR'S ACRONYM(S) DTRA-CB10125	
				11. SPONSOR / MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
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 omniphobic covalently attached liquid (SOCAL) and that liquid utilized as the lubricant in a slippery liquid-infused porous surface (SLIPS) based on a porous organosilicate 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.					
15. SUBJECT TERMS Coatings                      Paint Decontamination					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT  SAR	18. NUMBER OF PAGES  35	19a. NAME OF RESPONSIBLE PERSON Brandy J. White
a. REPORT Unclassified Unlimited	b. ABSTRACT Unclassified Unlimited	c. THIS PAGE Unclassified Unlimited			19b. TELEPHONE NUMBER (include area code) (202) 404-6100



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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 omniphobic covalently attached liquid (SOCAL) and that liquid utilized as the lubricant in a slippery liquid-infused porous surface (SLIPS) based on a porous organosilicate layer. Curing variations of the SOCAL coating were initially evaluated on glass supports. The SOCAL was then deposited alone on polyurethane paint coated aluminum coupons, and it was deposited as the lubricating layer on four variations of organosilicate textured surfaces to produce covalent SLIPS coatings. 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.



# **BIOINSPIRED SURFACE TREATMENTS FOR IMPROVED DECONTAMINATION: SLIPPERY OMNIPHOBIC COVALENTLY ATTACHED LIQUID (SOCAL)**

## **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 omniphobic covalently attached liquid (SOCAL).[1]

In attempts to control surface wetting and penetration of liquids into surfaces, the lotus leaf effect is commonly harnessed. This involves the use of a textured surface providing air-liquid and air-solid interfaces. There are a couple of problems that generally cause failures for this approach. First, at high pressure, liquid will intrude into the textured surface resulting in a defeat of the repellent characteristic. In addition, the surface features that produce this effect tend to be fragile. Slippery liquid-infused porous surfaces (SLIPS) offer an alternative to this approach. These coatings comprise a film of lubricating liquid with a textured substrate (micro/nano or both).[2-5] The results are a surface that is effectively smooth on the molecular scale and a liquid-liquid interaction interface. Typically, these SLIPS treatments offer a self-healing mechanism for damage to the surfaces, especially damage with a long, narrow surface profile. The liquid lubricant of the SLIPS treatment 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. A shortfall of these SLIPS materials is related to this mobile liquid that can be depleted and must not be displaceable by contacting liquids. In addition, sliding angles on these treatments are dependent on surface tension.

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 treatments involve complex deposition methods or lead to nondurable coatings. The approach evaluated here offers a very simple synthetic process, an acid-catalyzed graft polycondensation of dimethyldimethoxysilane, suitable for dip- and spin-coating and likely adaptable to a squeegee application. Polydimethylsiloxane (PDMS) tends to produce durable coatings. In addition to evaluation of this coating alone, we have evaluated the SOCAL approach as a substitute for the lubricating liquid in a SLIPS formulation. The silicate-based SLIPS treatments used under this study are based on a surfactant-templated nanoporous organosilicate either without modification or modified with methyl groups to provide a functionalized textured surface.[6, 7] The coatings are deposited and extracted or left as synthesized to provide empty pores or pores filled with the surfactant template, respectively. Finally, the surface is treated with the SOCAL process rather than being infused with the typical oils. For the complete system, aluminum coupons painted with a polyurethane paint system were treated with the porous silicate layer by spin-coating. They were subsequently treated with the SOCAL (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.

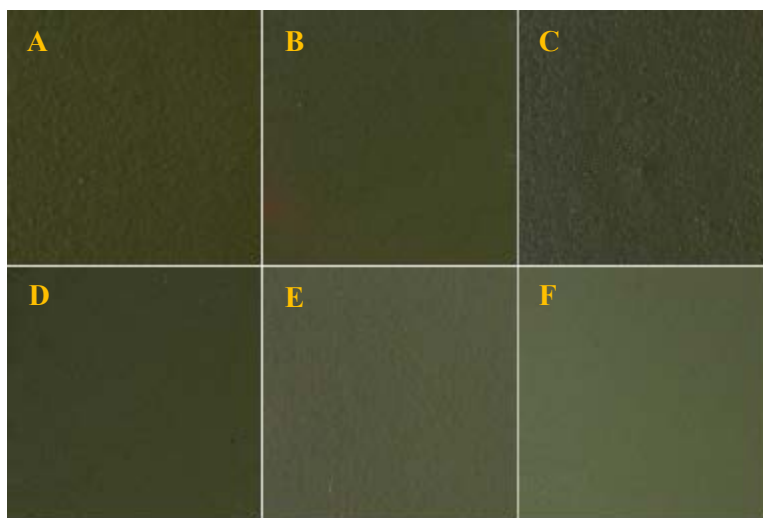


Fig. 1 — Images of a painted coupon (A); the SOCAL only treated coupon (B); the SOCAL lubricated, extracted ARSiO<sub>2</sub> treatment (C); the SOCAL lubricated, as synthesized ARSiO<sub>2</sub> (D); the SOCAL lubricated, extracted TEOS (E); and the SOCAL lubricated, as synthesized TEOS (F) .

## METHODS

### SOCAL surface treatment

The sol used for dip-coating (also suitable for spin-coating) consisted of a mass ratio of 1:10:100 H<sub>2</sub>SO<sub>4</sub>:dimethoxydimethylsilane:2-propanol. For example, 0.15 g H<sub>2</sub>SO<sub>4</sub>, 1.5 g dimethoxydimethylsilane, and 15 g 2-propanol were combined in a closed 30 mL PTFE jar and incubated at room temperature for more than 30 min. This sol could be used for dip-coating standard glass microscope slides. For dip-coating of painted coupons, a mixture of 1 g H<sub>2</sub>SO<sub>4</sub>, 10 g dimethoxydimethylsilane, and 100 g 2-propanol was prepared in a closed 240 mL PTFE jar and incubated for more than 30 min before use.

Glass microscope slides for treatment were cleaned with piranha solution (70% H<sub>2</sub>SO<sub>4</sub>, 30% H<sub>2</sub>O<sub>2</sub>) and dried at 110°C. Microscope slides were dip-coated in the SOCAL sol with up and down speeds of 25 mm/min. Dipped slides were immediately placed in a covered beaker containing a jar of humidor gel crystals to age in a humidified environment at room temperature. The utilized reference recommends aging in 60-70% relative humidity at 21°C.[1] Samples were aged for differing lengths of time, 20 min, 30 min, 1 h, 2 h, and >16 h before rinsing with water, ethanol, and toluene. Samples were dried with a stream of nitrogen.

### SOCAL for lubrication of ARSiO<sub>2</sub> SLIPS

The method for deposition of the methyl-functionalized (ARSiO<sub>2</sub>) textured surface was adapted from previous work.[6, 7] The ARSiO<sub>2</sub> sol was prepared in a 120 mL PTFE jar. A mixture of 0.05 g 2M HCl, 1.69 g H<sub>2</sub>O, 2 g tetraethyl orthosilicate, 1.71 g methyltriethoxysilane, and 35.38 g ethanol was stirred at room temperature. Surfactant, 1.45 g Pluronic F127, was added, and the sol mixture was stirred >2 h at

room temperature. The sol was spin-cast on painted aluminum coupons at 500 RPM for 30 s; coupons were rinsed with ethanol prior to deposition. Coated coupons were heated in an oven 1 °C/min to 100°C and held for 6 h. Samples of the sol material were drop-cast in a dish and cured with the spin-cast coupons. Some of the coupons were retained as synthesized while others were immersed in ethanol and heated in an oven at 65°C for 1.5-2 d to extract surfactant. The drop-cast “bulk” coating was also extracted in ethanol; this process could proceed 2-4 d. After extraction, materials were rinsed with ethanol and dried at 65°C. Nitrogen adsorption analysis of extracted “bulk” coating yielded a BET surface area 247 m<sup>2</sup>/g, single point total pore volume 0.290 cm<sup>3</sup>/g, and a BJH adsorption pore size distribution peak at ca. 51 Å (Figure 2). The isotherm exhibited a type IV shape indicative of a mesoporous material. This porous surface treatment, referred to as MSS, has previously been described for a silicone oil lubricated SLIPS treatment in our report Bioinspired Surface Treatments for Improved Decontamination: Silicate-Based Slippery Liquid-Infused Porous Surfaces (SLIPS).

Following deposition of the textured surface layer, both the as synthesized and the extracted ARSiO<sub>2</sub> coupons were rinsed with 2-propanol and dried with a stream of N<sub>2</sub>. The coupons were then dip-coated in a SOCAL sol with up and down speeds of 25 mm/min. Following dip-coating, coupons were aged in a covered beaker with humidor gel crystals for 20 min. Aged materials were rinsed with H<sub>2</sub>O, ethanol, and toluene, and dried with an N<sub>2</sub> stream. This SOCAL process was also used to deposit the SOCAL treatment directly onto painted coupons with no textured layer.

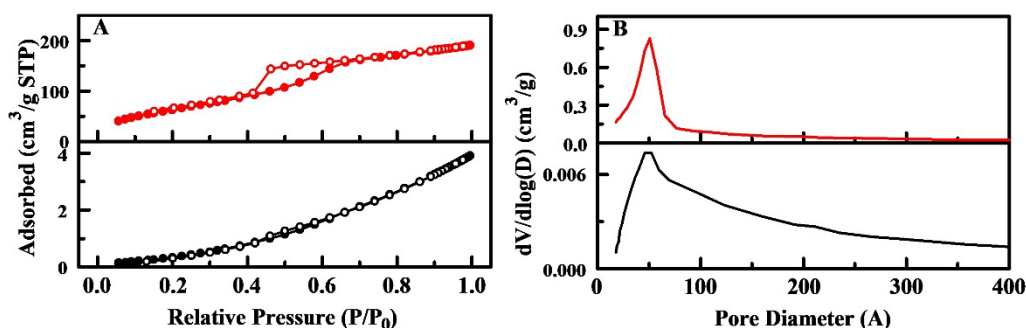


Fig. 2 — Nitrogen adsorption / desorption data (A) and pore size distributions (B) for the ARSiO<sub>2</sub> samples: thin film (black) and bulk (red).

### SOCAL for lubrication of TEOS SLIPS

Textured surfaces incorporating only tetraethyl orthosilicate (TEOS) were also evaluated. The TEOS only sol was prepared in a 120 mL PTFE jar. A mixture of 0.05 g 2M HCl, 1.69 g H<sub>2</sub>O, 4 g tetraethyl orthosilicate (TEOS), and 35.38 g ethanol was stirred at room temperature. The surfactant, 1.45 g Pluronic F127, was added and the sol mixture was stirred >2 h at room temperature. The sol was spin-cast on ethanol-rinsed, painted aluminum coupons at 500 RPM for 30 s. The sol was similarly spin-cast on glass No. 1 ½ cover slides. Coated surfaces were heated in an oven 1°C/min to 100°C and held for 6 h. Sol was also drop-cast in a dish and cured with the spin-cast coupons. The coated glass samples, some of the aluminum supported coatings, and the drop-cast “bulk” coating were extracted in ethanol at 65°C for 2 d, rinsed with ethanol, and dried. Nitrogen adsorption characterization of extracted material on glass slides yielded a mostly type I isotherm due to non-porous glass slide, but included a small type IV-like feature from the TEOS coating (BET surface area 1.47 m<sup>2</sup>/g for coated glass; Figure 3). The “bulk” coating yielded a distinct type IV isotherm with BET surface area 300 m<sup>2</sup>/g, single point total pore volume 0.300 cm<sup>3</sup>/g, and BJH adsorption pore size distribution peak ca. 46 Å (Figure 3).

Following deposition of the textured surface layer, both the as synthesized and the extracted TEOS textured surfaces were rinsed with 2-propanol and dried with a stream of  $N_2$ . The coupons were then dip-coated in a SOCAL sol with up and down speeds of 25 mm/min. Following dip-coating, coupons were aged in a covered beaker with a humidifier gel crystals for 20 min. Aged materials were rinsed with  $H_2O$ , ethanol, and toluene, and dried with an  $N_2$  stream.

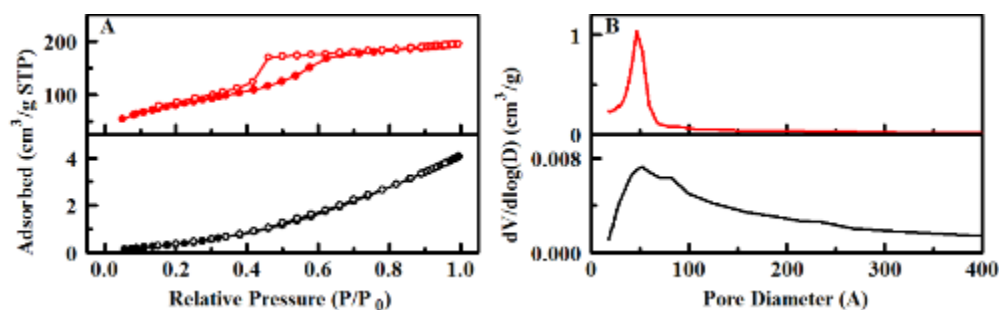


Fig. 3 — Nitrogen adsorption / desorption data (A) and pore size distributions (B) for the TEOS samples: thin film (black) and bulk (red).

## Evaluation of Surfaces

Sessile contact angles for samples evaluated under this effort used three 3  $\mu$ L 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  $\mu$ L droplets. The droplet was applied at  $0^\circ$  after which the supporting platform angle was gradually increased up to  $60^\circ$ . 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  $\mu$ L droplets initiated 2.5 cm above the coupon surface. Changes in base angle of  $10^\circ$  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  $1^\circ$  to identify the minimum required angle. Droplet diameters were determined using tools provided by Adobe Photoshop CS3. Droplets of 5 mL were applied to the surfaces and images were collected at 30 s intervals for 5 min followed by images at 5 min intervals for a total of 30 min. DFP samples were kept covered for the duration of the experiment to minimize evaporation. In some cases, reflections from the glass cover can be seen in the images.

Simulant exposure and evaluation methods were based on the tests developed by Edgewood Chemical Biological Center referred to as Chemical Agent Resistance Method (CARM).[8] Standard target exposures utilized a challenge level of  $10 \text{ g/m}^2$ . The glass coupons were  $0.00188 \text{ m}^2$ ; the  $10 \text{ g/m}^2$  target challenge was applied to the surfaces as four equally sized neat droplets. The painted coupons were  $0.00101 \text{ m}^2$ ; the  $10 \text{ g/m}^2$  target challenge was applied to the surfaces as two equally sized neat droplets. Following application of the target, coupons were aged 1 h prior to use of a gentle stream of air to expel target from the surface. Samples were then rinsed with soapy water (0.59 g/L Alconox in deionized water) The rinsed coupons were soaked in isopropanol for 30 min to extract remaining target; this isopropanol extract was analyzed by the appropriate chromatography method to determine target retention on the surface.

For paraoxon analysis, a Shimadzu High Performance Liquid Chromatography (HPLC) system with dual-plunger parallel flow solvent delivery modules (LC-20AD) and an auto-sampler (SIL-20AC; 40  $\mu$ L 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  $\mu$ m diameter; Phenomenex, Torrance, CA) with an isocratic 45:55 acetonitrile: 1% aqueous acetic acid mobile phase (1.2 mL/min).[9] 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  $\mu$ m 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<sup>2</sup>, 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 SOCAL coating was synthesized on a glass microscope slide substrate. Contact angles for deposition cured for durations between 20 min and overnight were compared to that of the glass substrate alone (Table 1). As shown in Table 1, contact angles for water and ethylene glycol are significantly increased for the SOCAL materials over those observed on glass. The calculated surface energy does not show a dependence on cure time beyond 20 min. Heptane fully wetted all of the evaluated surfaces. The SOCAL surfaces demonstrated shedding of both water and ethylene glycol at incidence angles between 40° and 50°.

The coupons were subjected to simulant exposure, aging, washing, and drying. When the soapy water process was employed on the coated surfaces (Table 2), retention of all targets was low. DMMP and DFP were not retained by any of the SOCAL treatments. Paraoxon retention was lowest for SOCAL samples cured for 20 or 30 mins. MES retention was lowest for samples cured for less than 1 h; samples cured for longer than the 1 h period retained more MES than the glass surface alone. While the retention by the short cure duration samples here was distinctly less than that applied, retention of targets by the glass support material is also very low. The smooth nature of the glass support makes for highly homogenous and consistent coatings. Application of this type of coating on the roughness of a painted surface is evaluated in the next section.

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

Coupon	Liquid	Sessile Angle	Sliding Angle	Shedding Angle	Geometric Surface Energy (mJ/m <sup>2</sup> )
<b>Glass Support</b>					
Glass Only	water	36.8 ± 0.29	>60	>60	59.1 ± 0.2
	ethylene glycol	26.3 ± 0.10	>60	>60	
	n-heptane	--	--	--	
SOCAL cured for 20 min	water	103.8 ± 0.52	>60	45.4 ± 4.2	12.0 ± 0.5
	ethylene glycol	94.5 ± 0.82	>60	39.2 ± 4.9	
	n-heptane	--	--	--	
SOCAL cured for 30 min	water	104.0 ± 1.0	>60	39.0 ± 1.4	15.0 ± 1.5
	ethylene glycol	85.6 ± 1.7	>60	40.0 ± 1.0	
	n-heptane	--	--	--	
SOCAL cured for 1 h	water	100.7 ± 0.89	>60	47.5 ± 0.7	12.1 ± 0.59
	ethylene glycol	93.7 ± 1.1	>60	44.8 ± 0.4	
	n-heptane	--	--	--	
SOCAL cured for 3 h	water	102.4 ± 0.52	>60	48.0 ± 1.0	11.6 ± 0.65
	ethylene glycol	91.6 ± 2.5	>60	41.0 ± 1.0	
	n-heptane	--	--	--	
SOCAL cured for >16 h	water	104.4 ± 0.46	>60	49.5 ± 1.0	13.3 ± 1.5
	ethylene glycol	88.0 ± 2.1	>60	43.5 ± 0.7	
	n-heptane	--	--	--	

Table 2 – Target Retention (g/m<sup>2</sup>) Following 1 h Aging on Glass Supports. ND indicates target levels below the detection threshold for the method employed.

Coupon	Paraoxon	MES	DMMP	DFP
<b>Glass Support</b>				
Glass Only	0.17	0.22	0.00	0.03
SOCAL cured for 20 min	0.07	0.09	ND	ND
SOCAL cured for 30 min	ND	0.08	ND	ND
SOCAL cured for 1 h	0.14	0.03	ND	ND
SOCAL cured for 3 h	0.10	0.51	ND	ND
SOCAL cured for >16 h	0.09	0.70	ND	ND

### Aluminum Surfaces.

The SOCAL treatment was applied to aluminum coupons painted with a water-borne polyurethane system. In addition, the SOCAL was used to lubricate SLIPS variations. The first SLIPS treatment was based on a textured methyl functionalized silicate layer (ARSiO<sub>2</sub>) adapted from a manuscript focused on anti-reflective (AR) and self-cleaning coatings for photovoltaic cells.[6, 7] Both extracted and as synthesized (surfactant not removed) versions of the ARSiO<sub>2</sub> coating were applied to painted aluminum coupons and subsequently treated with the SOCAL. In this approach the SOCAL is a substitute for the lubricating oil typically used in a SLIPS surface. A variation on this ARSiO<sub>2</sub> coating used only tetraethyl orthosilicate (TEOS) with no methyl groups. Similarly, both extracted and as synthesized versions of this TEOS coating were applied to painted aluminum coupons and subsequently treated with the SOCAL. As

shown in Table 3 (also Figure 4), the SOCAL treatment produces higher water and ethylene glycol wetting angles than those observed for the paint alone or for the Fomblin Y oiled paint. The coating does not produce sliding or shedding behavior for water or ethylene glycol below 60°.

Application of the SOCAL lubricated extracted ARSiO<sub>2</sub> surface to a painted coupon led to surface energies comparable to those previously observed for the silicone oil lubricated ARSiO<sub>2</sub> on glass (24.3 to 48.8 mJ/m<sup>2</sup> depending on the oil).[7] Both water and ethylene glycol wetting angles were lower for the SOCAL lubricated ARSiO<sub>2</sub> surfaces (extracted and as synthesized) than for the SOCAL alone surface. SOCAL lubricated TEOS surfaces yielded similar results with the SOCAL ARSiO<sub>2</sub> surface giving the lowest surface energy of the materials considered. As shown in Table 3, a Fomblin Y lubricated SLIPS surface using a similar silicate layer produces significantly lower surface energy associated with higher wetting angles as well as shedding angles for the liquids considered.

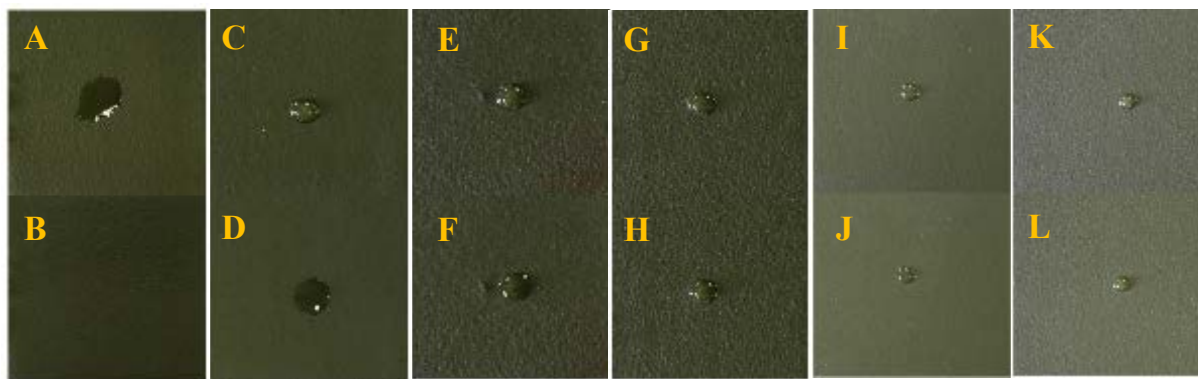


Fig. 4 — Images of a painted coupon and painted coupons treated with either the SOCAL or SOCAL-SLIPS formulations. Standing droplets of MES are shown: painted coupon with MES immediately following application (A) and at 30 min (B); SOCAL on paint with MES immediately following application (C) and at 30 min (D); SOCAL lubricated, extracted ARSiO<sub>2</sub> SLIPS with MES immediately following application (E) and at 30 min (F); SOCAL lubricated, as synthesized ARSiO<sub>2</sub> SLIPS with MES immediately following application (G) and at 30 min (H); SOCAL lubricated, extracted TEOS SLIPS with MES immediately following application (I) and at 30 min (J); SOCAL lubricated, as synthesized TEOS SLIPS with MES immediately following application (K) and at 30 min (L).

The tendency of droplets to spread across the surfaces was also evaluated (Figure 4; 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 (Figure 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 during the course of the 30 min incubation. On the SOCAL only surface, DMMP does not spread during the 30 min period. After the 10 min image, MES begins to slowly spread across this surface. DFP spreads slightly more slowly for the SOCAL surface than on the paint only surface, reaching coupon edges at 10 min.

There is no spread of MES or DMMP on the SOCAL lubricated ARSiO<sub>2</sub> materials; this is similar to the behavior observed for the Fomblin Y lubricated silicate SLIPS material evaluated previously.[7] There is similarly no spread of MES or DMMP on either of the SOCAL lubricated TEOS materials; however, the droplet diameters are smaller on these materials than the droplets on the SOCAL, SOCAL-ARSiO<sub>2</sub>, or Fomblin Y lubricated SLIPS materials. DFP, on the other hand spreads significantly on both the ARSiO<sub>2</sub> and the TEOS SLIPS materials lubricated with SOCAL. This is in contrast to the Fomblin Y lubricated ARSiO<sub>2</sub> SLIPS variants for which no DFP spreading was observed.

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

Coupon	Liquid	Sessile Angle	Sliding Angle	Shedding Angle	Geometric Surface Energy (mJ/m <sup>2</sup> )
<b>Aluminum Support</b>					
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	
SOCAL	water	83.6 ± 1.7	>60	>60	26.2 ± 2.8
	ethylene glycol	82.2 ± 0.83	>60	>60	
	n-heptane	--	--	--	
SOCAL on ARSiO <sub>2</sub> extracted surface	water	81.8 ± 0.70	>60	>60	24.4 ± 0.84
	ethylene glycol	73.9 ± 0.76	>60	>60	
	n-heptane	--	--	--	
SOCAL on ARSiO <sub>2</sub> as synthesized surface	water	73.0 ± 1.9	>60	>60	42.1 ± 4.9
	ethylene glycol	77.4 ± 1.3	>60	>60	
	n-heptane	--	--	--	
SOCAL on TEOS extracted surface	water	80.2 ± 1.5	>60	>60	26.3 ± 0.99
	ethylene glycol	80.5 ± 1.3	>60	>60	
	n-heptane	--	--	--	
SOCAL on TEOS as synthesized surface	water	80.5 ± 0.61	>60	>60	26.2 ± 2.8
	ethylene glycol	75.1 ± 1.0	>60	>60	
	n-heptane	--	--	--	
Extracted MFSS – Fomblin Y	water	111.0 ± 0.9	>60	32.0 ± 6.4	12.0 ± 0.8
	ethylene glycol	93.7 ± 0.8	>60	33.0 ± 5.8	
	n-heptane	26.4 ± 1.6	>60	>60	

The coupons were subjected to several cycles of simulant exposure (10 g/m<sup>2</sup>), aging, washing, and drying over a period of several weeks. No significant changes in the appearance or wetting characteristics were noted during this period. When the soapy water process was employed (Figure 6; Table 4), retention of all targets was less for the Fomblin Y lubricated SLIPS treatments than for the paint only surfaces. The SOCAL only surface showed retention slightly higher than a surface oiled with only the fluorocarbon oil (Fomblin Y). Retention of targets here was similar to that observed for silicone oil lubricated SLIPS treatments (NRL/MR/6930—17-9734). The more hydrophobic SOCAL lubricated ARSiO<sub>2</sub> SLIPS formulations showed lower retention of paraoxon and MES with very little DMMP or DFP retained by any of the formulations evaluated under this study.

For comparison purposes, paint only coupons that were not rinsed prior to isopropanol extraction retained the following: paraoxon – 9.84 g/m<sup>2</sup>, MES – 9.54 g/m<sup>2</sup>, DMMP – 9.90 g/m<sup>2</sup>, DFP - 7.39 g/m<sup>2</sup>. Though the nominal target application was 10 g/m<sup>2</sup>, recovery from surfaces was always less than this value. Losses due to evaporation would be expected, especially for DFP. Additional losses likely occur during the rinse steps due to agent interaction with the untreated region of the coupon; the back of these coupons is unpainted aluminum.

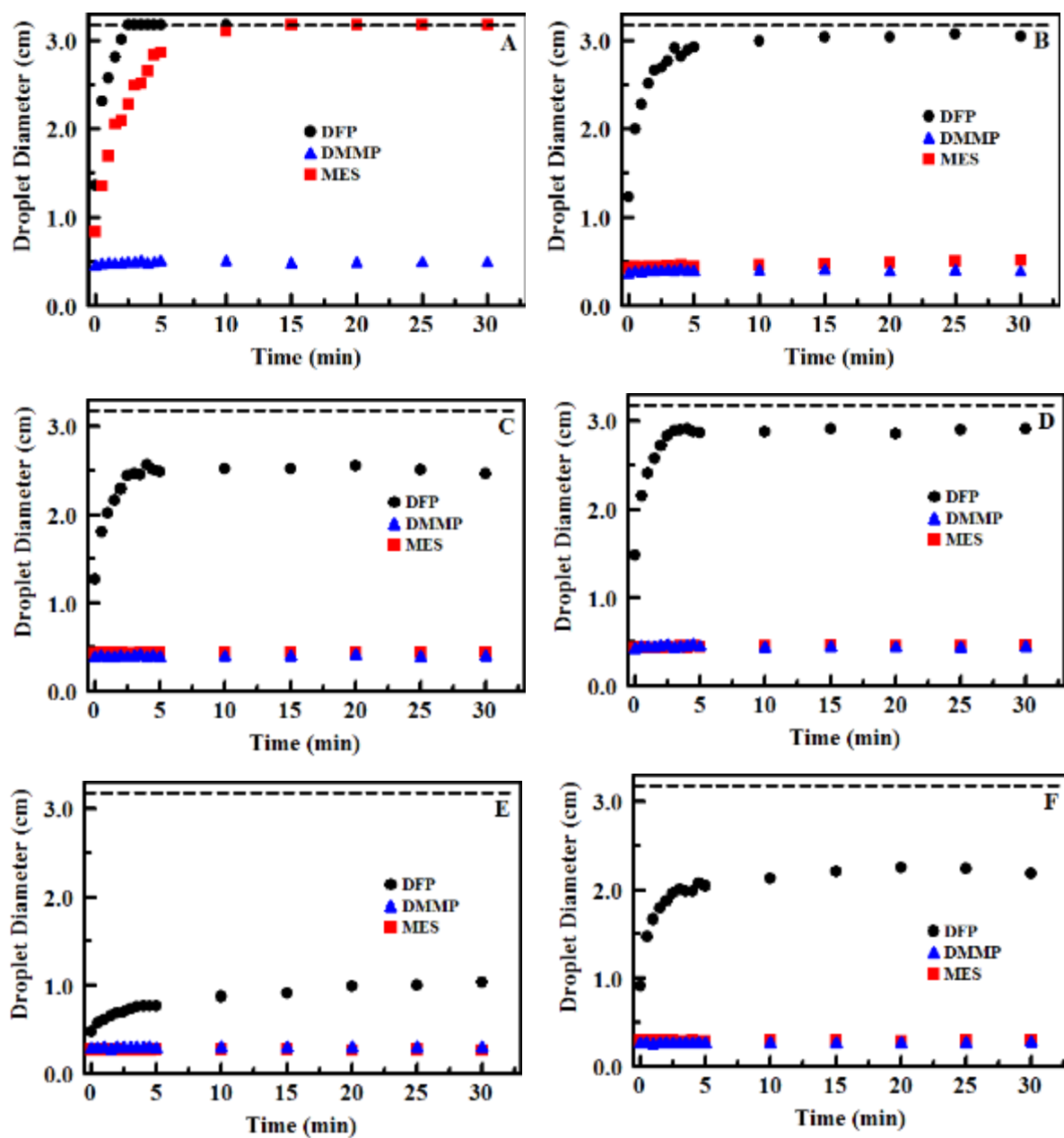


Fig. 5 — Progression of simulant droplet diameters during incubation on the surfaces for DFP (black), DMMP (blue), and MES (red): painted coupon (A); SOCAL (B); SOCAL lubricated, as synthesized ARSiO<sub>2</sub> SLIPS (C); SOCAL lubricated, extracted ARSiO<sub>2</sub> SLIPS (D); SOCAL lubricated, as synthesized TEOS SLIPS (E); SOCAL lubricated, extracted TEOS SLIPS (F).



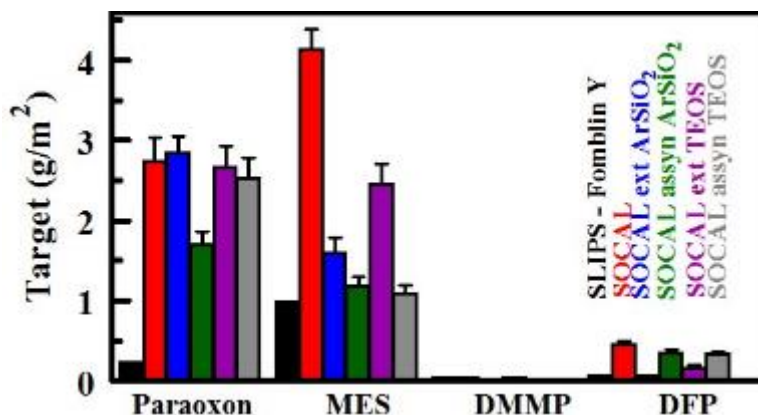


Fig. 6 — Target retention by coupons following treatment with an air stream and rinsing with soapy water: fluoropolymer lubricated SLIPS coating (black); SOCAL (red); SOCAL lubricated, as synthesized ARSiO<sub>2</sub> SLIPS (blue); SOCAL lubricated, extracted ARSiO<sub>2</sub> SLIPS (green); SOCAL lubricated, as synthesized TEOS SLIPS (purple); SOCAL lubricated, extracted TEOS SLIPS (gray).

Table 4 – Target Retention (g/m<sup>2</sup>) Following 1 h Aging on Aluminum Supports

Coupon	Paraoxon	MES	DMMP	DFP
<b>Aluminum Support</b>				
Paint Only	5.48	6.20	4.28	0.52
Fomblin Y Oiled Paint	1.24	2.85	0.59	0.34
SOCAL	2.74	4.14	0.03	0.45
SOCAL on ARSiO <sub>2</sub> extracted surface	2.85	1.59	ND	0.06
SOCAL on ARSiO <sub>2</sub> as synthesized surface	1.70	1.18	0.03	0.35
SOCAL on TEOS extracted surface	2.67	2.46	0.01	0.16
SOCAL on TEOS as synthesized surface	2.53	1.09	0.02	0.34
As synthesized MFSS – Fomblin Y	0.23	0.98	0.04	0.06

ND = not detected

## CONCLUSIONS

These samples provide promising results with target retention similar to SLIPS treatments prepared using silicone oils. Though this does not represent the best performance observed under this effort, it does provide a pathway for moving from the current disadvantages of SLIPS coatings toward coatings that could provide a solution for prevention of agent retention. Application of the coating produces a slightly wet look on the painted surfaces (Figure 4 and Appendix). Spectrophotometric analysis is necessary to determine the overall impact on color and reflectivity. The long term stability of the coatings should be more thoroughly evaluated.

## ACKNOWLEDGEMENTS

The comments of Dr. Brent Mantooth (ECBC) on methods and agent analysis are appreciated. The authors would also like to thank Dr. Joanna Aizenberg (Harvard University) for her comments on SLIPS treatments and potential methods for addressing lubricant depletion. This research was sponsored by the Defense Threat Reduction Agency (DTRA, CB10125).

## REFERENCES

1. Wang, L.; McCarthy, T. J., Covalently Attached Liquids: Instant Omniphobic Surfaces with Unprecedented Repellency. *Angewandte Chemie International Edition* **2016**, *55*, 244-8.
2. 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.
3. Samaha, M. A.; Gad-el-Hak, M., Polymeric Slippery Coatings: Nature and Applications. *Polymers* **2014**, *6*, (5), 1266-1311.
4. 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.
5. 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.
6. Faustinin, M.; Nicole, L.; Boissiere, C.; Innocenzi, P.; Sanches, C.; Grosso, D., Hydrophobic, Antireflective, Self-Cleaning, and Antifogging Sol-Gel Coatings: An Example of Multifunctional Nanostructured Materials for Photovoltaic Cells. *Chem Mater* **2010**, *22*, 4406-13.
7. White, B.; Melde, B.; Malanoski, A.; Moore, M. *Bioinspired Surface Treatments for Improved Decontamination: Silicate-Based Slippery Liquid-Infused Porous Surfaces (SLIPS)*; Washington, DC, 2017.
8. Lalain, T.; Mantooth, B.; Shue, M.; Pusey, S.; Wylie, D. *Chemical Contaminant and Decontaminant Test Methodology Source Document*; US ARMY REDEC, Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2012.
9. Gebreegzi, Y. T.; Foster, G. D.; Khan, S. U., Simultaneous Determination of Carbaryl, Malathion, Fenitrothion, and Diazinon Residues in Sesame Seeds (*Seasmum indicum* L) *J. Agric. Food Chem.* **2000**, *48*, 5165-5168.

**Appendix**  
**COUPON IMAGES**

Fig. A1 — DFP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 10 (L), 15 (M), 20 (N), 25 (O), and 30 (P) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

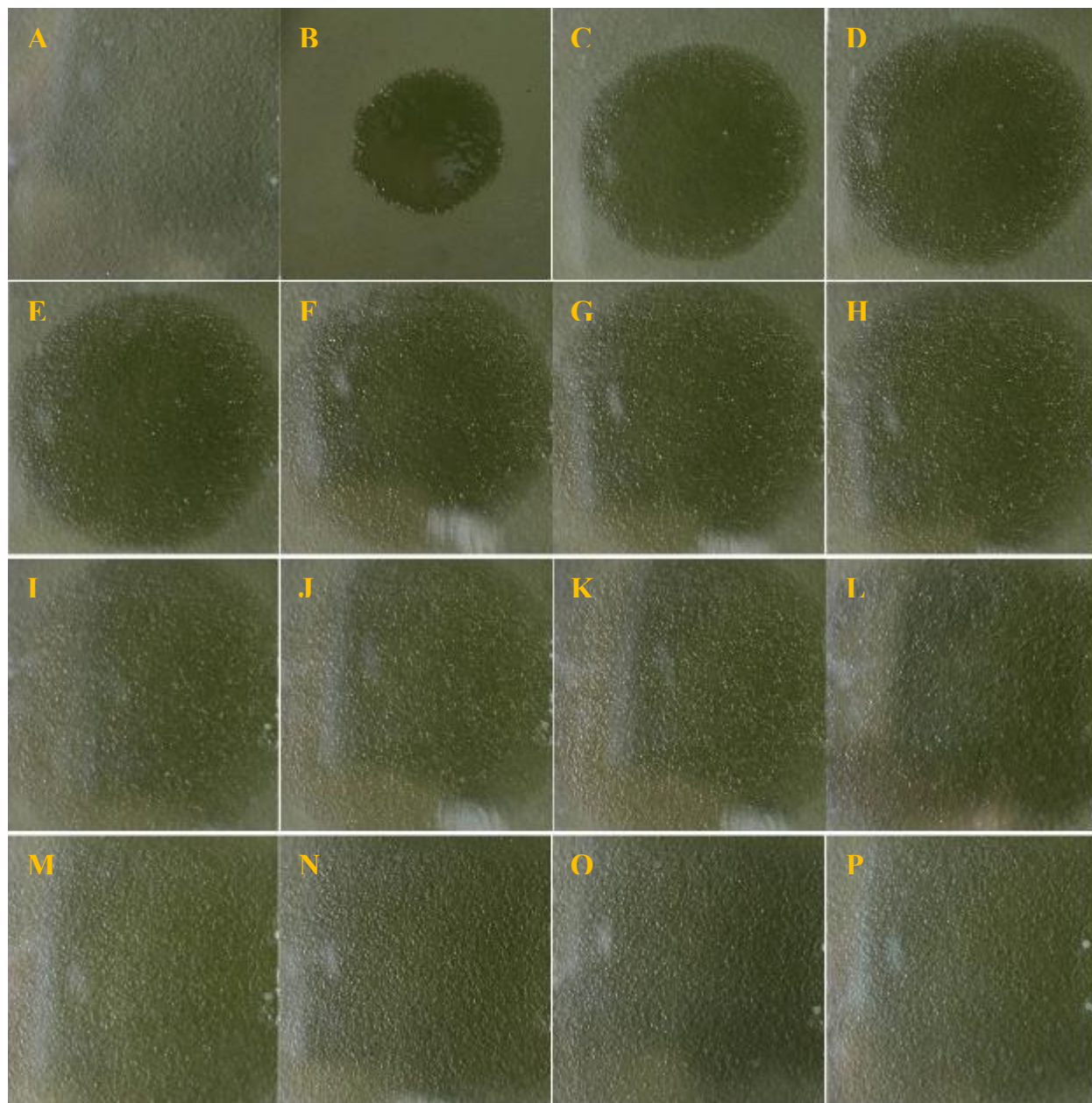


Fig. A2 — MES on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

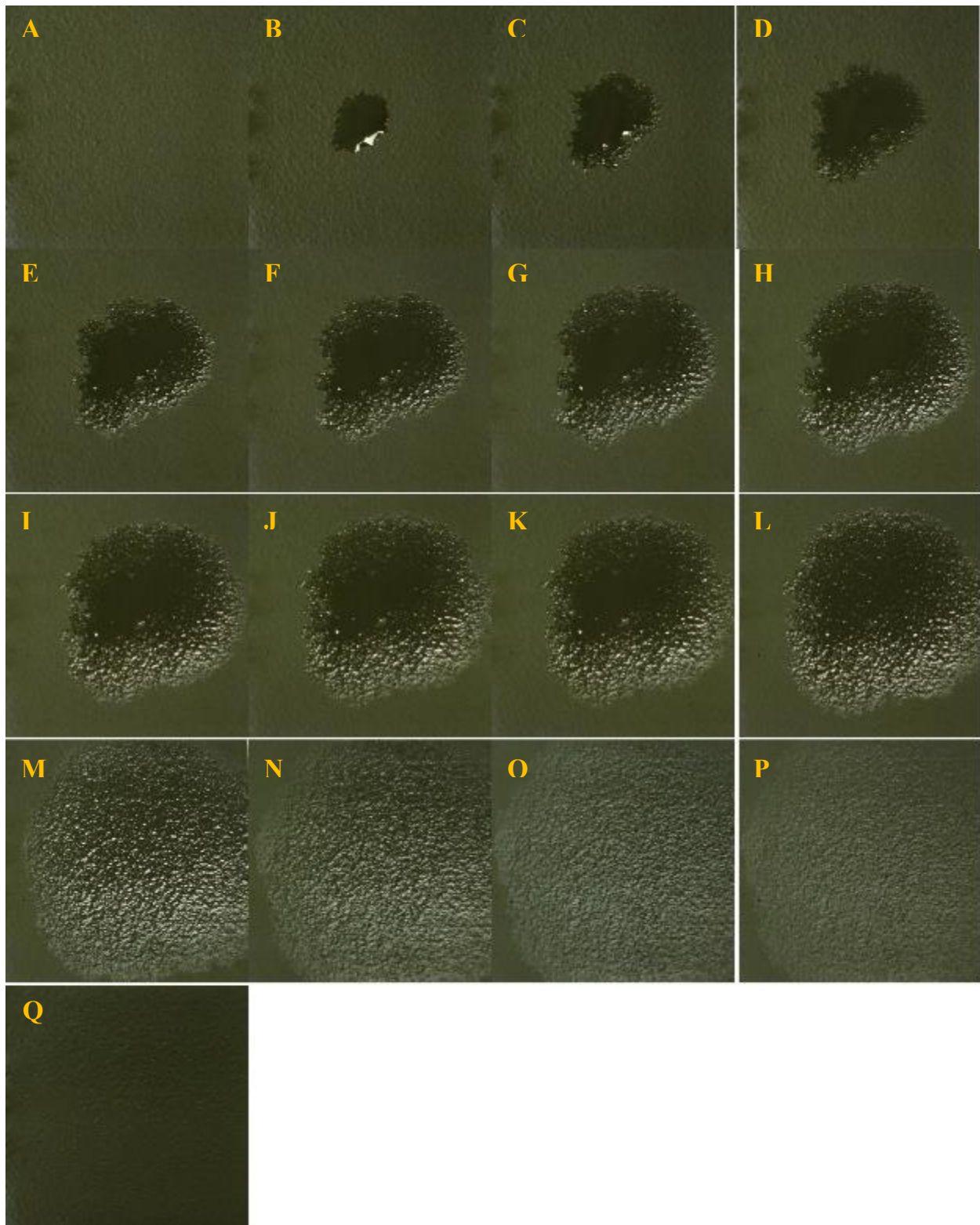




Fig. A3 — DMMP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

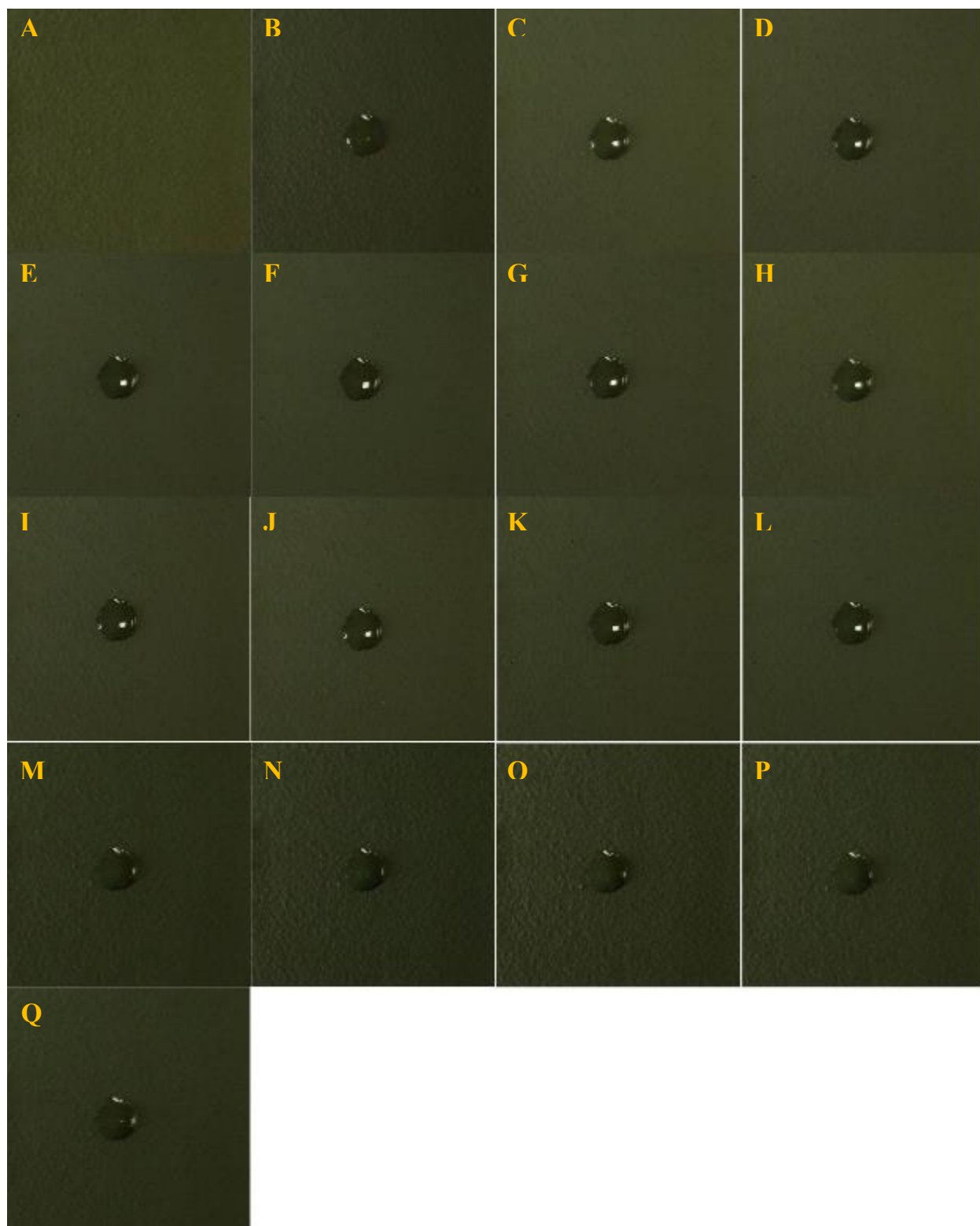


Fig. A4 — DFP on the SOCAL only coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass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

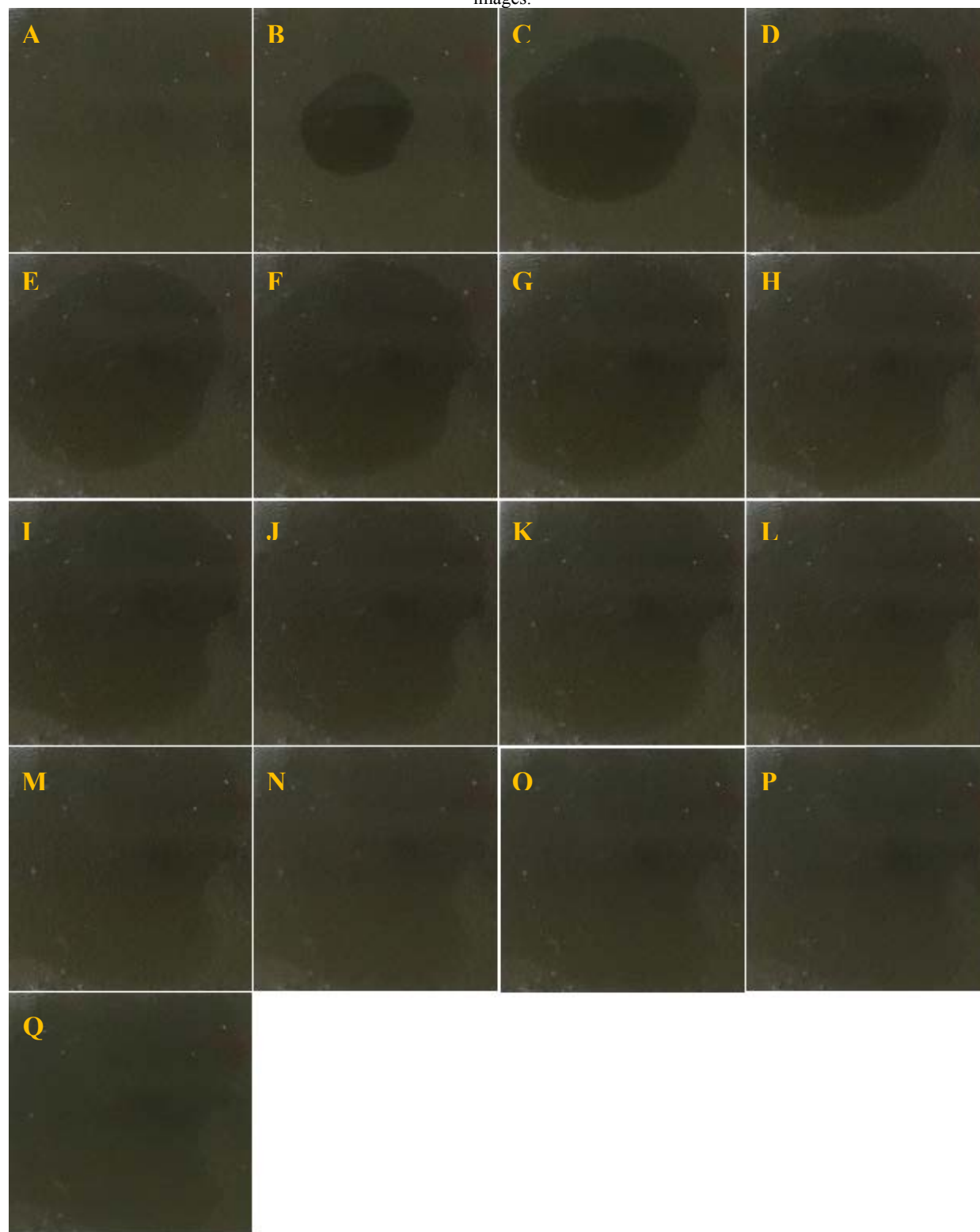


Fig. A5 — MES on the SOCAL only coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

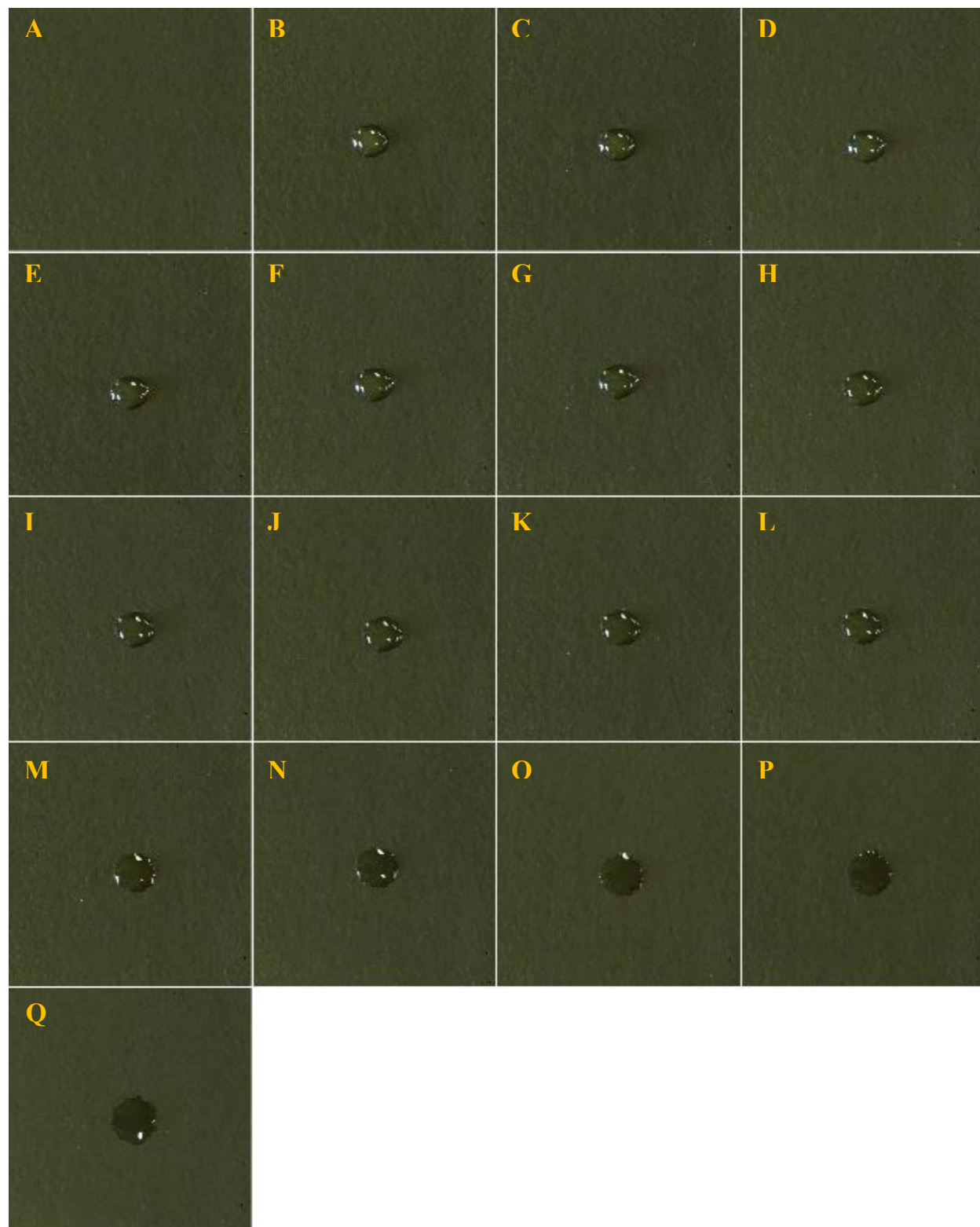




Fig. A6 — DMMP on the SOCAL only coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

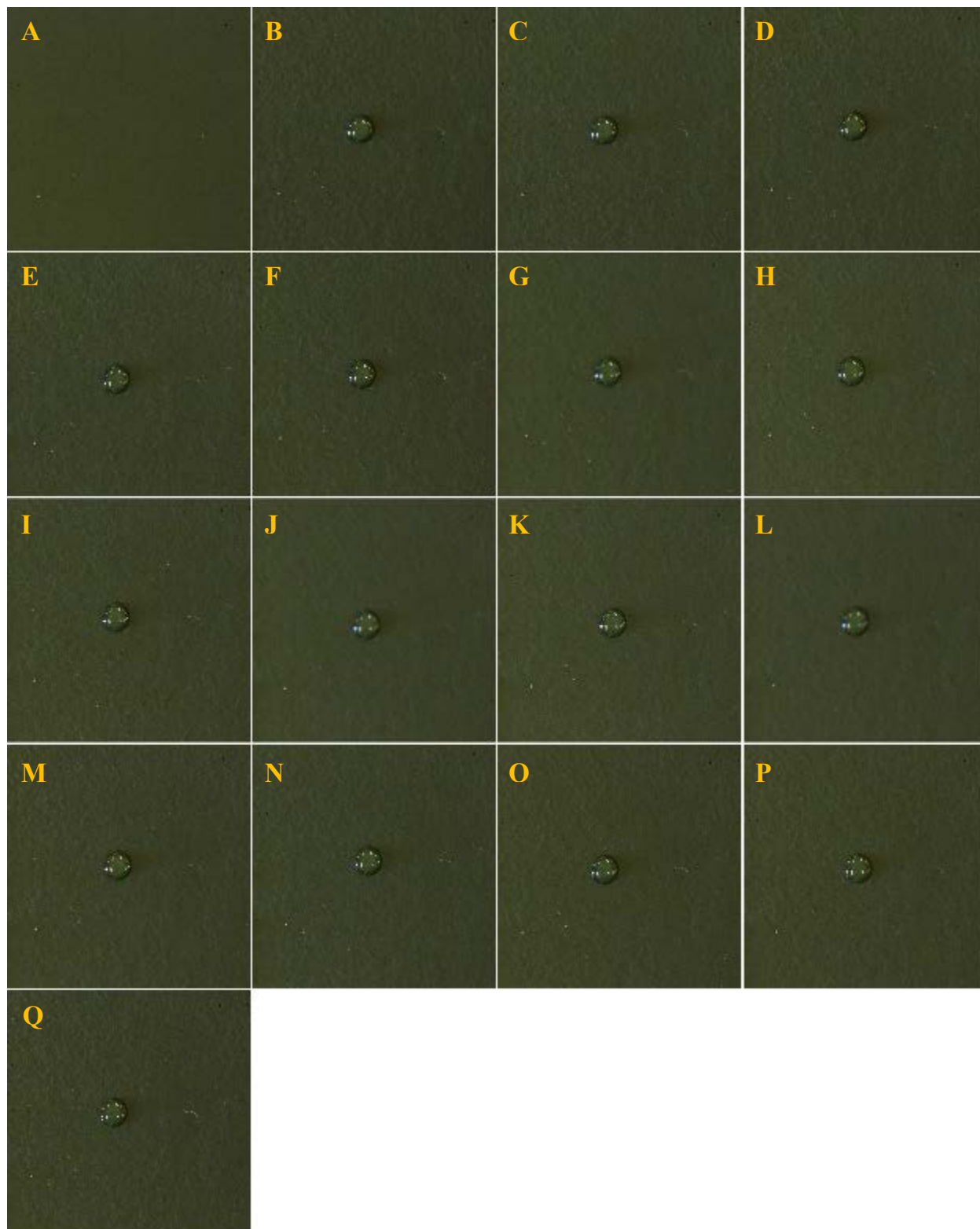


Fig. A7 — DFP on the SOCAL modified ARSiO<sub>2</sub> extracted surface. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

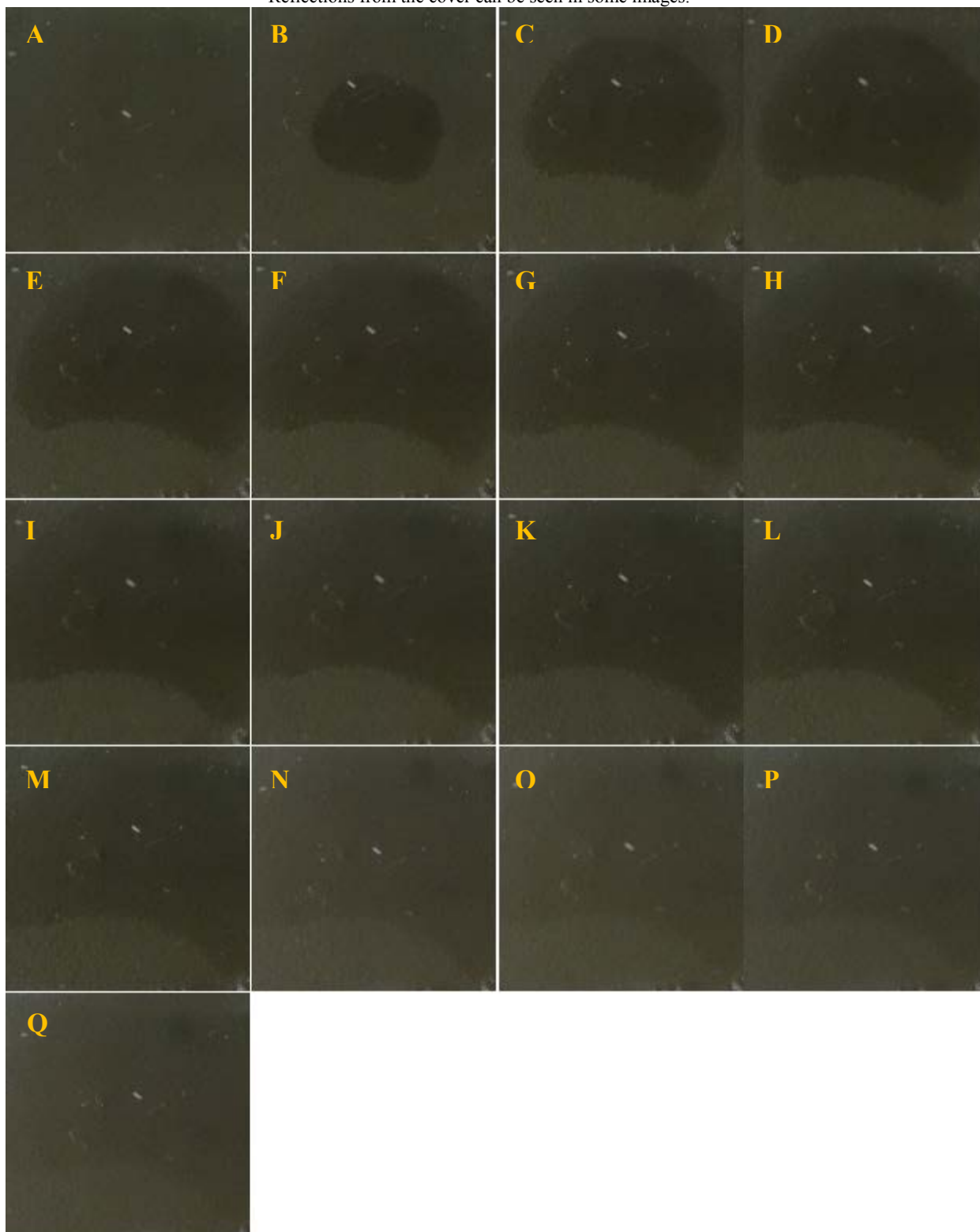


Fig. A8 — MES on the SOCAL modified ARSiO<sub>2</sub> extracted surface. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

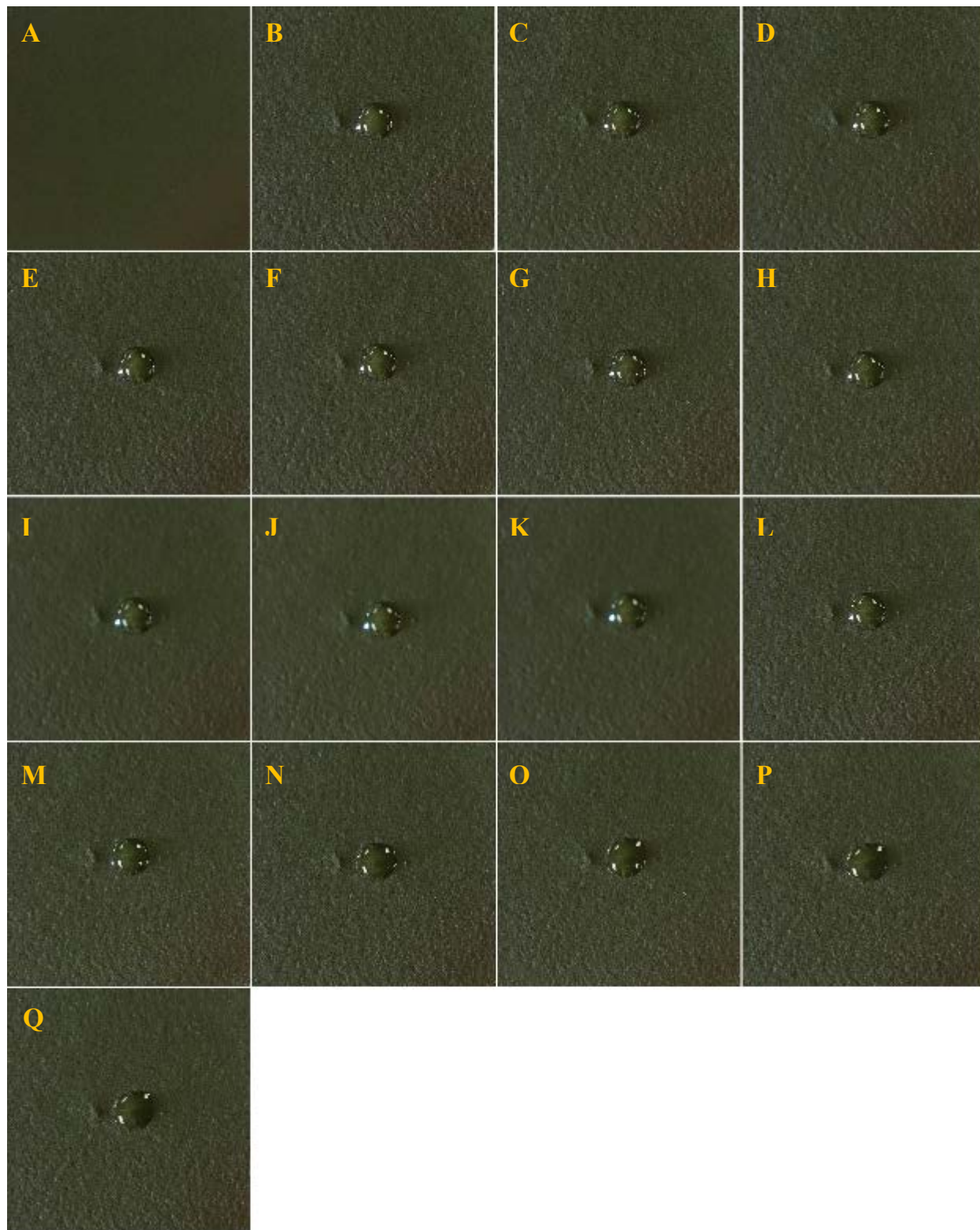


Fig. A9 — DMMP on the SOCAL modified ARSiO<sub>2</sub> extracted surface. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

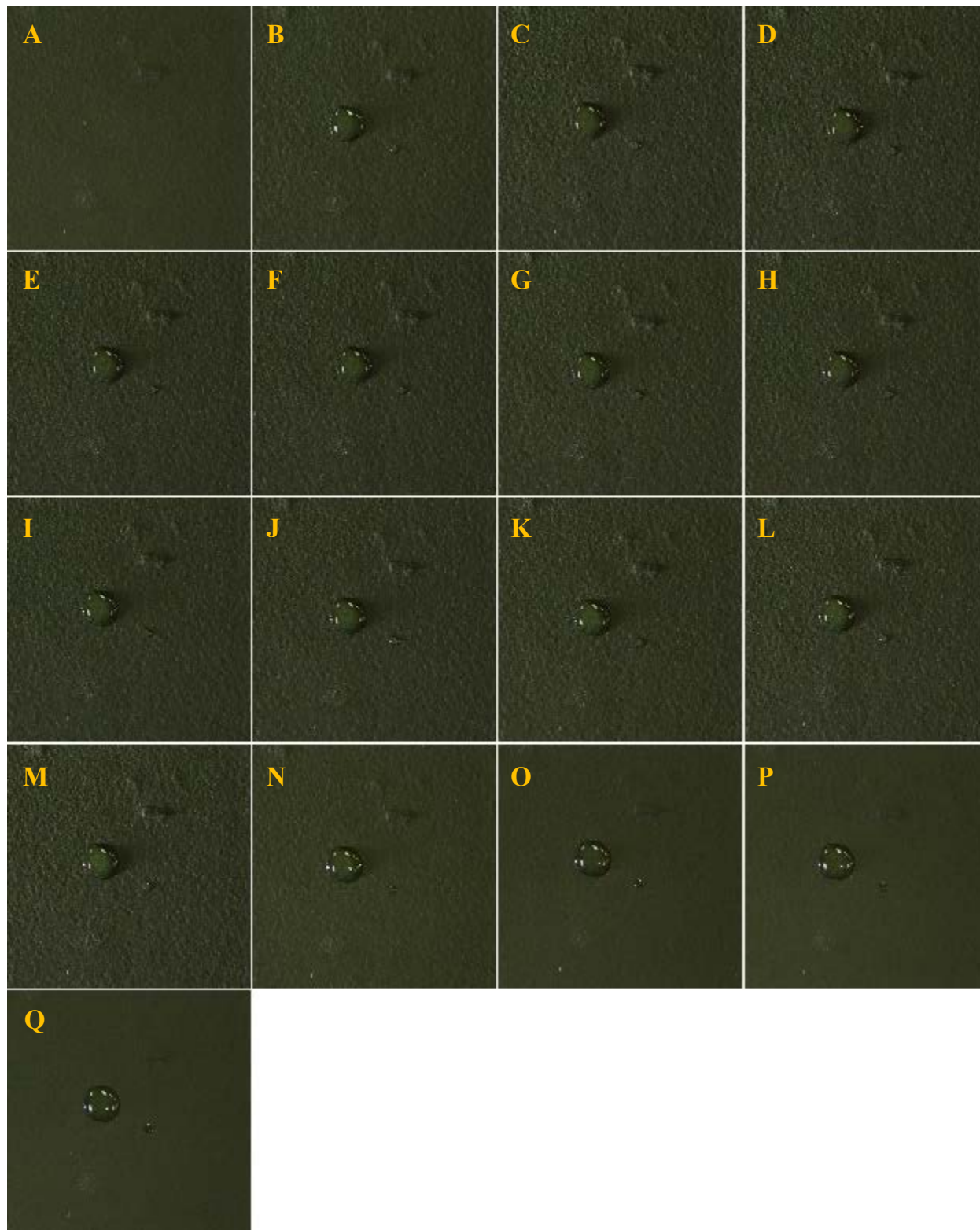




Fig. A10 — DFP on the SOCAL modified ARSiO<sub>2</sub> as synthesized surface. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These 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 SOCAL modified ARSiO<sub>2</sub> as synthesized surface. 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 SOCAL modified ARSiO<sub>2</sub> extracted surface. 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 SOCAL modified TEOS extracted surface. 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.

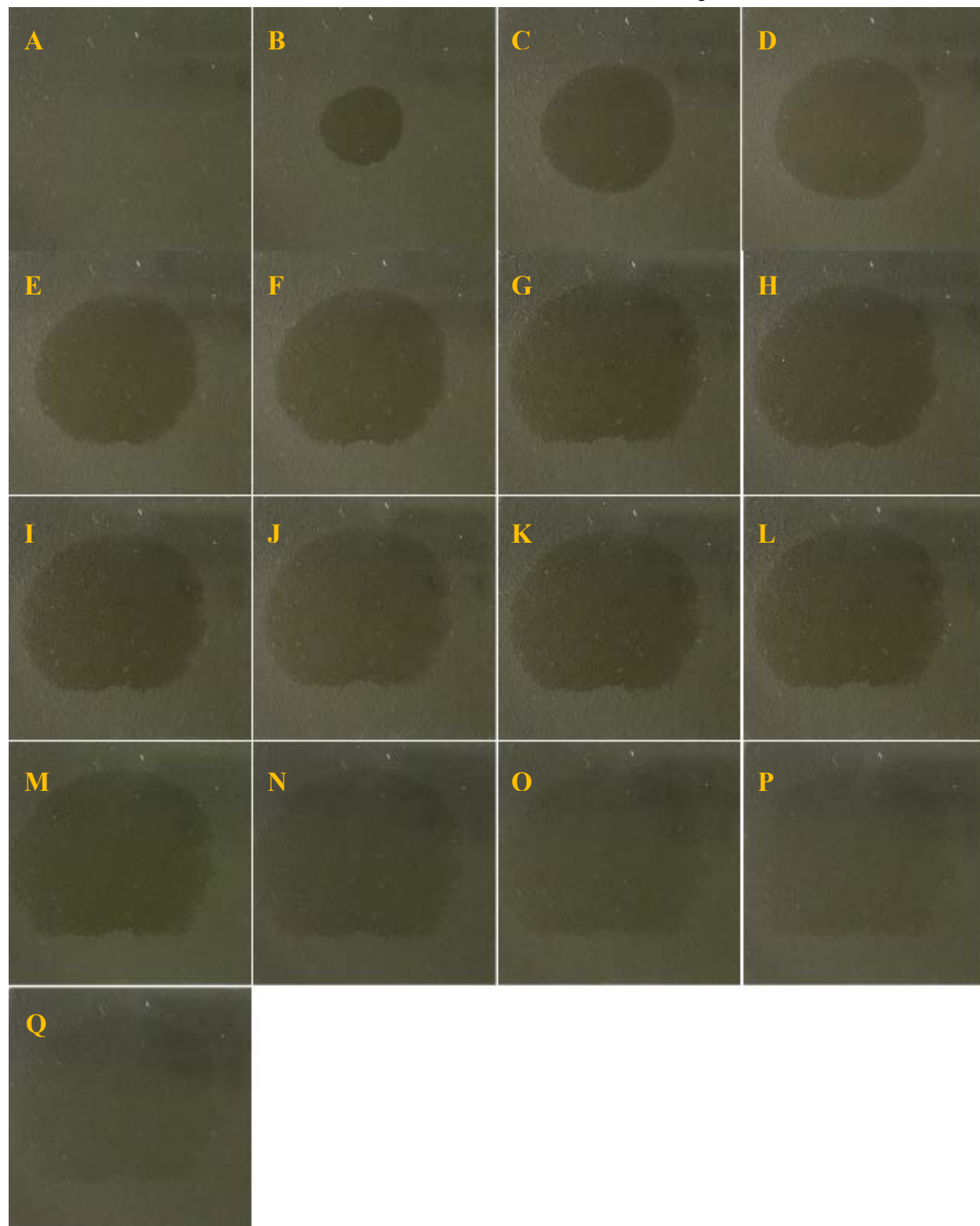




Fig. A14 — MES on the SOCAL modified TEOS extracted surface. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

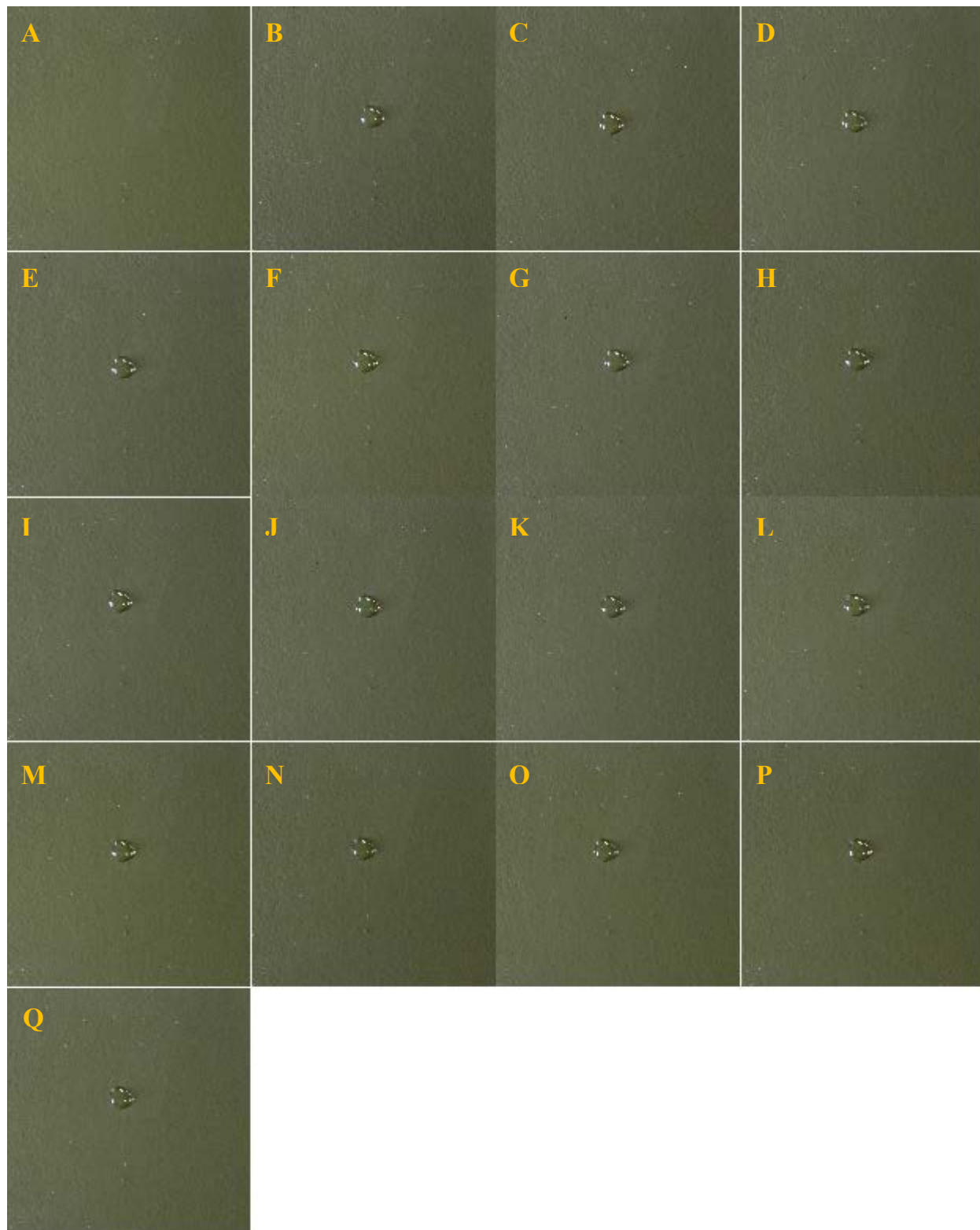


Fig. A15 — DMMP on the SOCAL modified TEOS extracted surface. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

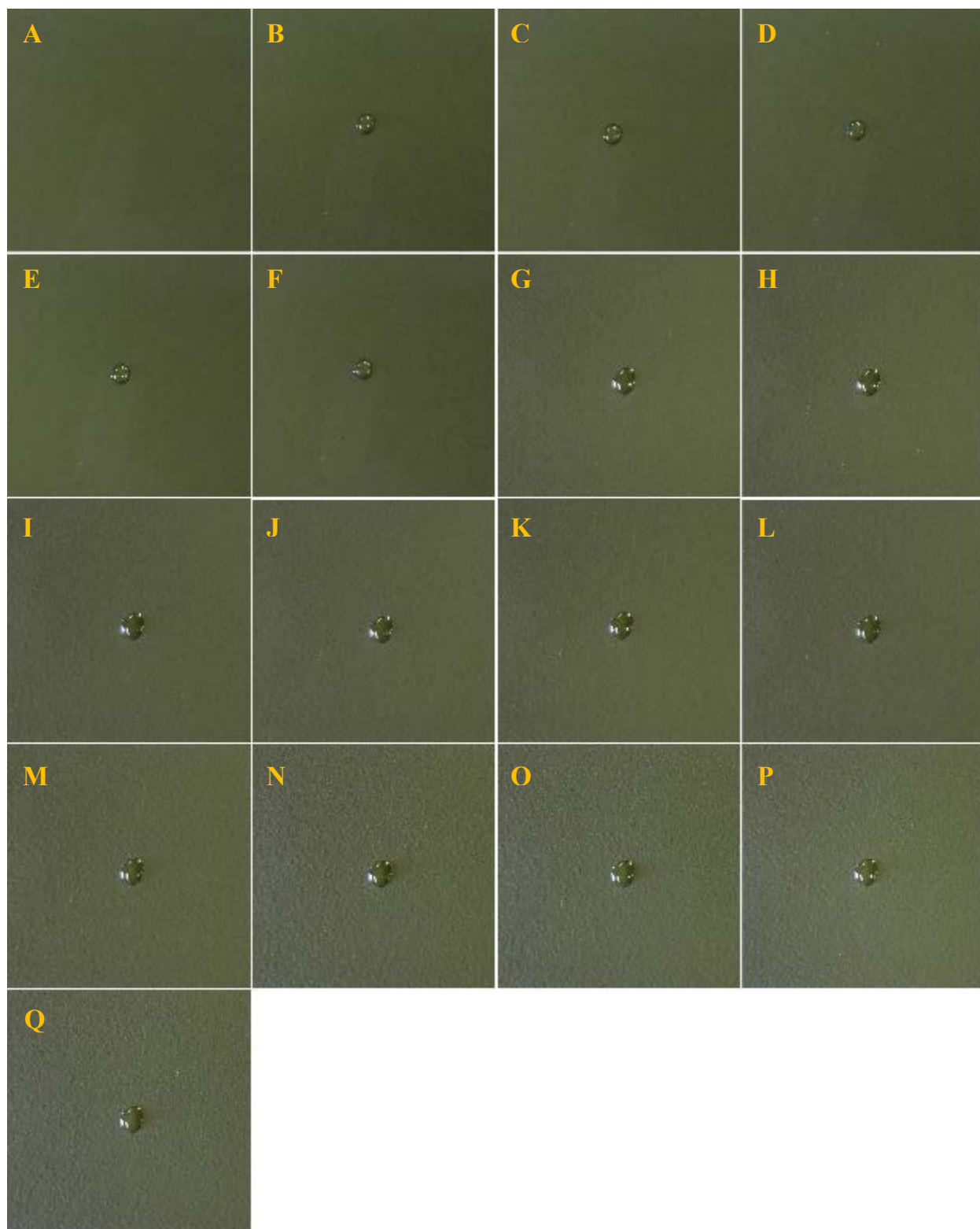


Fig. A16 — DFP on the SOCAL modified TEOS as synthesized surface. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were 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 SOCAL modified TEOS as synthesized surface. 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.

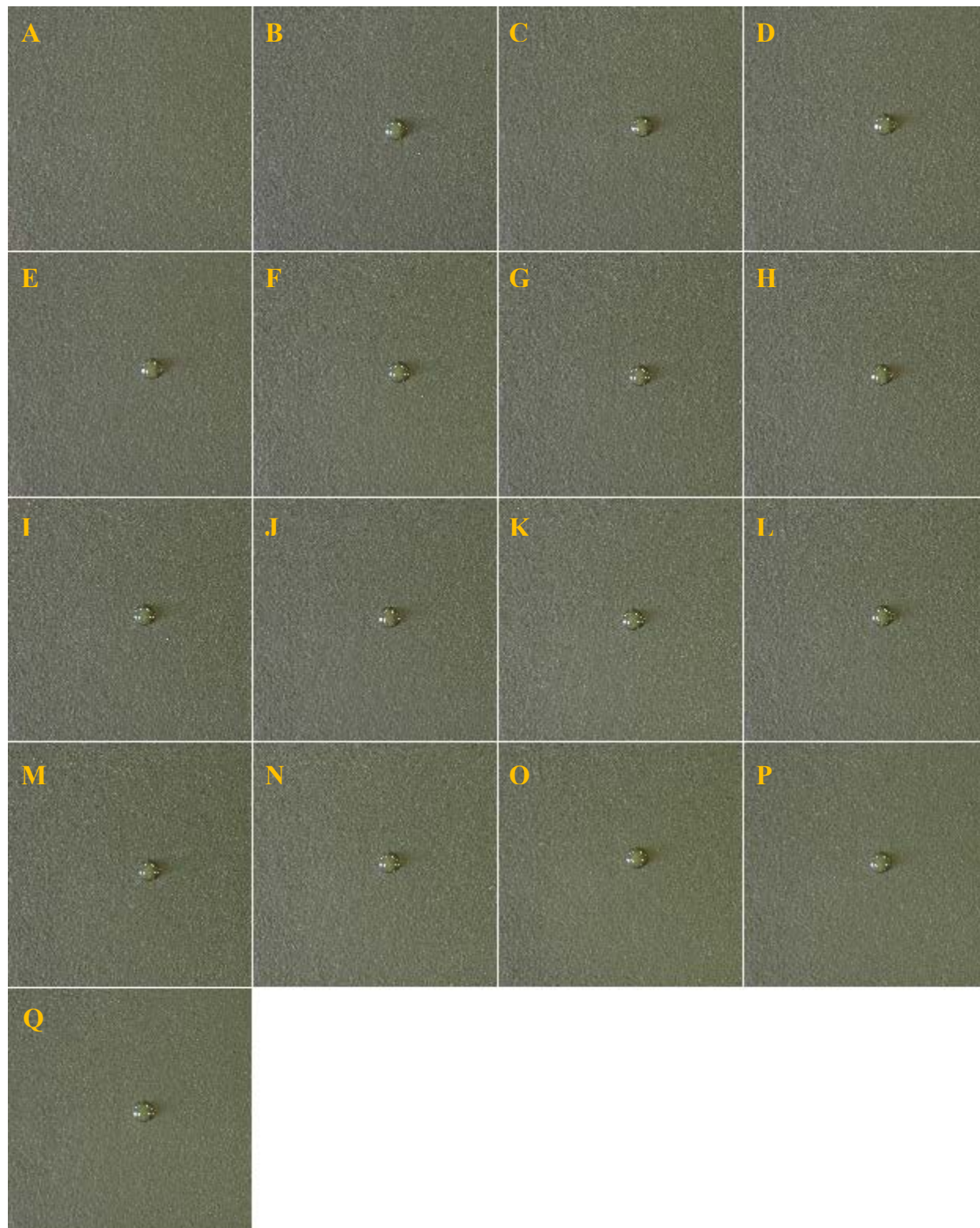




Fig. A18 — DMMP on the SOCAL modified TEOS as synthesized surface. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

