Naval Research Laboratory
Washington, DC 20375-5320

NRL/MR/6930--19-9847

Bioinspired Surface Treatments for Improved Decontamination: Variations on Slippery Omniphobic Covalently Attached Liquid (SOCAL) Coatings

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March 11, 2019

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
11-03-2019

2. REPORT TYPE
Memorandum Report

3. DATES COVERED *(From - To)*
2/10/2018 - 06/19/2018

4. TITLE AND SUBTITLE
Bioinspired Surface Treatments for Improved Decontamination: Variations on Slippery Omniphobic Covalently Attached Liquid (SOCAL) Coatings

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Brandy J. White, Anthony P. Malanoski, Brian J. Melde and Martin H. Moore

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
69-1C75

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Center for Bio/Molecular Science & Engineering
Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375-5344

8. PERFORMING ORGANIZATION REPORT NUMBER
NRL/MR/6930--19-9847

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Defense Threat Reduction Agency
DTRA-Joint CBRN Center of Excellence
BLDG E-2800
APG-EA, 21010

10. SPONSOR / MONITOR'S ACRONYM(S)
DTRA - CB10125

11. SPONSOR / MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

DISTRIBUTION STATEMENT A: 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 variations on a slippery omniphobic covalently attached liquid (SOCAL) utilized as the lubricant in a slippery liquid-infused porous surface (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.

15. SUBJECT TERMS
Coatings, Decontamination, Paint

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
Unclassified Unlimited	Unclassified Unlimited	Unclassified Unlimited	Unclassified Unlimited	66	Brandy J. White
					19b. TELEPHONE NUMBER *(include area code)* (202) 404-6100

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

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CONTENTS

FIGURES

TABLES

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). A prior report (NRL MR 6930-17-9761) detailed 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 evaluated including the coating alone on polyurethane paint and as the lubricating layer on textured surfaces to produce a covalent SLIPS coating. This follow-on study considers additional variations on SOCAL deposition as well as its use as a co-lubricant for the 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.

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BIOINSPIRED SURFACE TREATMENTS FOR IMPROVED DECONTAMINATION: VARIATIONS ON SLIPPERY OMNIPHOBIC COVALENTLY ATTACHED LIQUID (SOCAL) COATINGS

INTRODUCTION

The DoD Chemical and Biological Defense Program (CBDP) seeks to provide protection of forces in a contaminated environment including contamination avoidance, individual protection, collective protection, and decontamination. In January 2015, the Center for Bio/Molecular Science and Engineering at the US 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 prior report (NRL MR 6930-17-9761) detailed results for evaluation of a slippery omniphobic covalently attached liquid (SOCAL). [1] The current document summarizes additional results for varied deposition approaches and the use of SOCAL as a lubricant or co-lubricant for slippery liquid-infused porous surface (SLIPS) treatments.

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 so that they repel liquids of interest. A shortfall of these SLIPS materials is related to the 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-like 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 dimethyldimethyoxysilane, 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. [6-8] Following deposition of the coatings, the surfactant may be removed (extracted) or left in place (as synthesized) to provide empty or filled pores. Finally, the surface is treated

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Manuscript approved February 5, 2019.

with the SOCAL process. Beyond this SOCAL treatment, additional oil has been added to some of the surfaces considered here. 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. The coupons were subjected to standard evaluations including measurement of sessile, sliding, and shedding contact angles and quantification of retention for the simulant compounds.

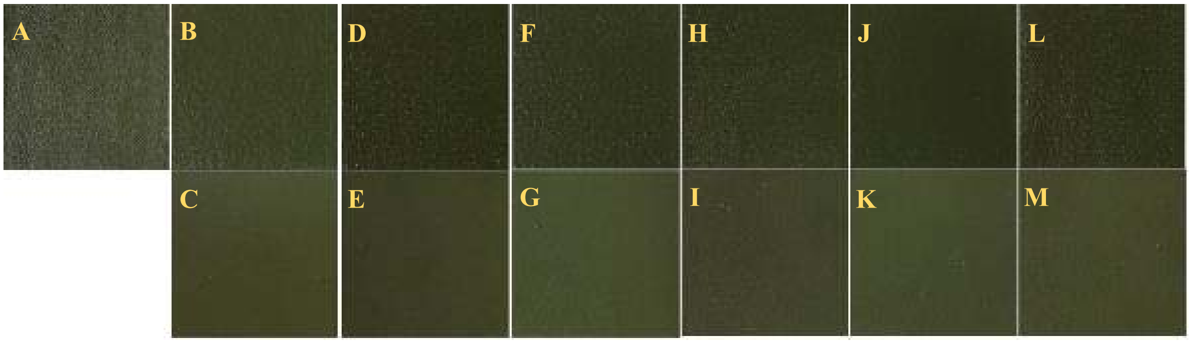

Fig. 1 — Images of a painted coupon (A); and painted coupons treated with SOCAL- ARSiO$_2$ variations: extracted, 25 mm/min, lubricated (B) and unlubricated (C); as synthesized, 25 mm/min, lubricated (D) and unlubricated (E); extracted, 100 mm/min, lubricated (F) and unlubricated (G); as synthesized, 100 mm/min, lubricated (H) and unlubricated (I);extracted, 270 mm/min, lubricated (J) and unlubricated (K); 270 mm/min, lubricated (L) and unlubricated (M).

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_2SO_4:dimethoxydimethylsilane:2-propanol. For example, 0.15 g H_2SO_4, 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_2SO_4, 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.

SOCAL for lubrication of ARSiO$_2$ SLIPS

The method for deposition of the methyl-functionalized (ARSiO$_2$) textured surface was adapted from previous work. [6, 7] The ARSiO$_2$ sol was prepared in a 120 mL PTFE jar. A mixture of 0.05 g 2M HCl, 1.69 g H_2O, 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^2/g, single point total pore volume 0.290 cm^3/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 in other reports. [7, 8]

Following deposition of the textured surface layer, both the as synthesized and the extracted $ARSiO_2$ coupons 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, 100, 270 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_2O, ethanol, and toluene, and dried with an N_2 stream. This SOCAL process was also used to deposit the SOCAL treatment directly onto painted coupons with no textured layer.

Evaluation of Surfaces

Sessile contact angles for samples evaluated under this effort used three 3 µL droplets per surface with each droplet measured independently three times for each of three targets, water, ethylene glycol, and n-heptane. Geometric surface energy was calculated based on the water and ethylene glycol interactions using software designed for the DROPimage goniometer package. Sliding angles were determined using 5 µL droplets. The droplet was applied at 0° after which the supporting platform angle was gradually increased up to 60°. Sliding angles for each of the liquids were identified as the angle for which movement of the droplet was identified. Shedding angles for each liquid were determined using 12 µL droplets initiated 2.5 cm above the coupon surface. Changes in base angle of 10° were utilized to identify the range of droplet shedding angle based on a complete lack of droplet retention by the surface (not sliding). The angle was then reduced in steps of 1° to identify the minimum required angle. Droplet diameters were determined using tools provided by Adobe Photoshop CS3. Droplets of 5 µL were applied to the surfaces and images were collected at 30 s intervals for 5 min followed by images at 5 min intervals for a total of 30 min. DFP samples were kept covered for the duration of the experiment to minimize evaporation. In some cases, reflections from the glass cover can be seen in the images.

Simulant exposure and evaluation methods were based on the tests developed by Edgewood Chemical Biological Center referred to as Chemical Agent Resistance Method (CARM). [9] 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 0.00101 m^2; the 10 g/m^2 target challenge was applied to the surfaces as two equally sized neat droplets. Following application of the target, coupons were aged 1 h prior to use of a gentle stream of air to expel target from the surface. Samples were then rinsed with soapy water (0.59 g/L Alconox in deionized water). The rinsed coupons were soaked in isopropanol for 30 min to extract remaining target; this isopropanol extract was analyzed by the appropriate chromatography method to determine target retention on the surface.

For analysis of the targets, 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

The SOCAL lubricated $ARSiO_2$ SLIPS treatment was applied to aluminum coupons painted with a water-borne polyurethane system. This SLIPS treatment was based on a textured methyl functionalized silicate layer ($ARSiO_2$) 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 $ARSiO_2$ coating were applied to painted aluminum coupons and subsequently treated with the

SOCAL using deposition via dip coating at 25, 100, and 270 mm/min. In this approach, the SOCAL is a substitute for the lubricating oil typically used in a SLIPS surface. As shown in Figure 2 (also Table 1), the SOCAL-ARSiO$_2$ treatment produces higher water and ethylene glycol wetting angles than those observed for the paint alone (or for Fomblin Y oiled paint). In the original SOCAL study, surface energy was lower on the extracted SLIPS surface with SOCAL lubricant. [8] The as synthesized surface did not produce this effect. All SOCAL-SLIPS surfaces under the current study produced lower surface energy than the original coatings. The 270 mm/min deposition produced the lowest surface energy with the as synthesized SLIPS surface offering the lowest energy of the evaluated treatments. Other SLIPS variations under this study produced highly similar results. The addition of polydimethylsiloxane (PDMS) oil to the surfaces as a secondary lubricant had only a marginal impact on the surface energy (Table 2, Figure 2). In fact, the wetting angles observed for ethylene glycol were slightly reduced following lubrication. The coatings do not produce sliding or shedding behavior for water or ethylene glycol below 60° and are wetted by heptane.

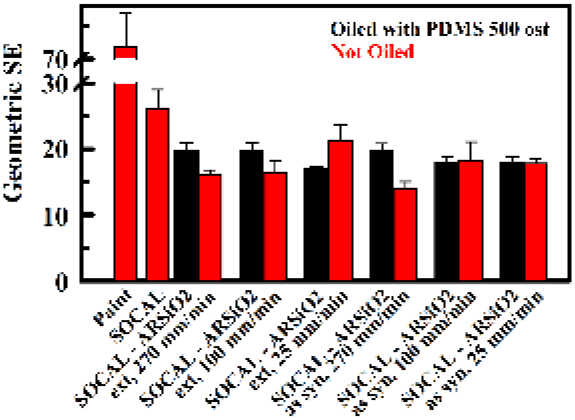

Fig. 2 — Calculated geometric surface energies for the SOCAL-ARSiO$_2$ variants with (black) and without (red) additional lubricating oil.

The tendency of droplets to spread across the surfaces was also evaluated (Figure 3; Appendices). For these studies, droplets of the simulants (5 µL) were utilized. The spread of the droplets was quantified by measuring the diameter of the droplets in the images over time (Figure 4). For the paint only samples, MES and DFP spread quickly, reaching the edges of the coupon. DMMP does not spread during the course of the 30 min incubation. There is no spread of any of the targets, DFP, MES, or DMMP, on the SOCAL lubricated ARSiO$_2$ materials regardless of the presence of additional lubrication; this is an improvement over previously observed behaviors. [7, 8]

Table 1 – Sessile, Sliding, and Shedding Contact Angles on SOCAL-ARSiO$_2$ Surfaces

Coupon	**Liquid**	**Sessile Angle**	**Sliding Angle**	**Shedding Angle**	**Geometric Surface Energy (mJ/m^2)**
Aluminum Support					
Paint Only	water	47.5 ± 1.1	>60	>60	71.9 ± 5.1
	ethylene glycol	55.7 ± 2.1	>60	>60	
	n-heptane	--	--	--	
Fomblin Y Oiled Paint	water	73.1 ± 2.1	>60	46.7 ± 3.3	32.2 ± 1.6
	ethylene glycol	52.5 ± 0.61	>60	49.8 ± 4.9	
	n-heptane	40.1 ± 2.9	>60	36.6 ± 3.3	
SOCAL	water	83.6 ± 1.7	>60	>60	26.2 ± 2.8
	ethylene glycol	82.2 ± 0.83	>60	>60	
	n-heptane	--	--	--	
Original SOCAL on ARSiO$_2$ extracted surface	water	81.8 ± 0.70	>60	>60	24.4 ±0.84
	ethylene glycol	73.9 ± 0.76	>60	>60	
	n-heptane	--	--	--	
Original SOCAL on ARSiO$_2$ 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 ARSiO$_2$ extracted surface; 270 mm/min deposition	water	95.2 ± 0.7	>60	>60	16.0 ± 0.8
	ethylene glycol	90.6 ± 1.0	>60	>60	
	n-heptane	--	--	--	
SOCAL on ARSiO$_2$ extracted surface; 100 mm/min deposition	water	95.1 ± 1.8	>60	>60	16.4 ± 1.9
	ethylene glycol	90.1 ± 0.7	>60	>60	
	n-heptane	--	--	--	
SOCAL on ARSiO$_2$ extracted surface; 25 mm/min deposition	water	91.8 ± 1.6	>60	>60	21.3 ± 2.5
	ethylene glycol	89.8 ± 1.0	>60	>60	
	n-heptane	--	--	--	
SOCAL on ARSiO$_2$ as synthesized surface; 270 mm/min deposition	water	97.8 ± 1.3	>60	>60	14.0 ± 1.0
	ethylene glycol	92.5 ± 0.5	>60	>60	
	n-heptane	--	--	--	
SOCAL on ARSiO$_2$ as synthesized surface; 100 mm/min deposition	water	94.1 ± 2.1	>60	>60	18.2 ± 2.9
	ethylene glycol	93.0 ± 0.6	>60	>60	
	n-heptane	--	--	--	
SOCAL on ARSiO$_2$ as synthesized surface; 25 mm/min deposition	water	94.9 ± 0.4	>60	>60	17.8 ± 0.7
	ethylene glycol	93.9 ± 0.6	>60	>60	
	n-heptane	--	--	--	

Table 2 – Sessile, Sliding, and Shedding Contact Angles on Oiled SOCAL-ARSiO$_2$ Surfaces

Coupon	Liquid	Sessile Angle	Sliding Angle	Shedding Angle	Geometric Surface Energy (mJ/m^2)
Aluminum Support					
SOCAL on ARSiO$_2$ extracted surface; 270 mm/min deposition	water	97.8 ± 1.1	>60	>60	19.8 ± 1.2
	ethylene glycol	77.0 ± 1.0	>60	>60	
	n-heptane	--	--	--	
SOCAL on ARSiO$_2$ extracted surface; 100 mm/min deposition	water	98.2 ± 1.0	>60	>60	19.9 ± 1.1
	ethylene glycol	76.9 ± 0.9	>60	>60	
	n-heptane	--	--	--	
SOCAL on ARSiO$_2$ extracted surface; 25 mm/min deposition	water	99.5 ± 0.3	>60	>60	17.1 ± 0.2
	ethylene glycol	80.8 ± 0.3	>60	>60	
	n-heptane	--	--	--	
SOCAL on ARSiO$_2$ as synthesized surface; 270 mm/min deposition	water	94.0 ± 1.5	>60	>60	19.6 ± 1.2
	ethylene glycol	77.1 ± 0.8	>60	>60	
	n-heptane	--	--	--	
SOCAL on ARSiO$_2$ as synthesized surface; 100 mm/min deposition	water	94.3 ± 1.2	>60	>60	17.8 ± 0.9
	ethylene glycol	79.5 ± 0.9	>60	>60	
	n-heptane	--	--	--	
SOCAL on ARSiO$_2$ as synthesized surface; 25 mm/min deposition	water	95.2 ± 1.5	>60	>60	18.0 ± 0.8
	ethylene glycol	77.4 ± 1.0	>60	>60	
	n-heptane	--	--	--	

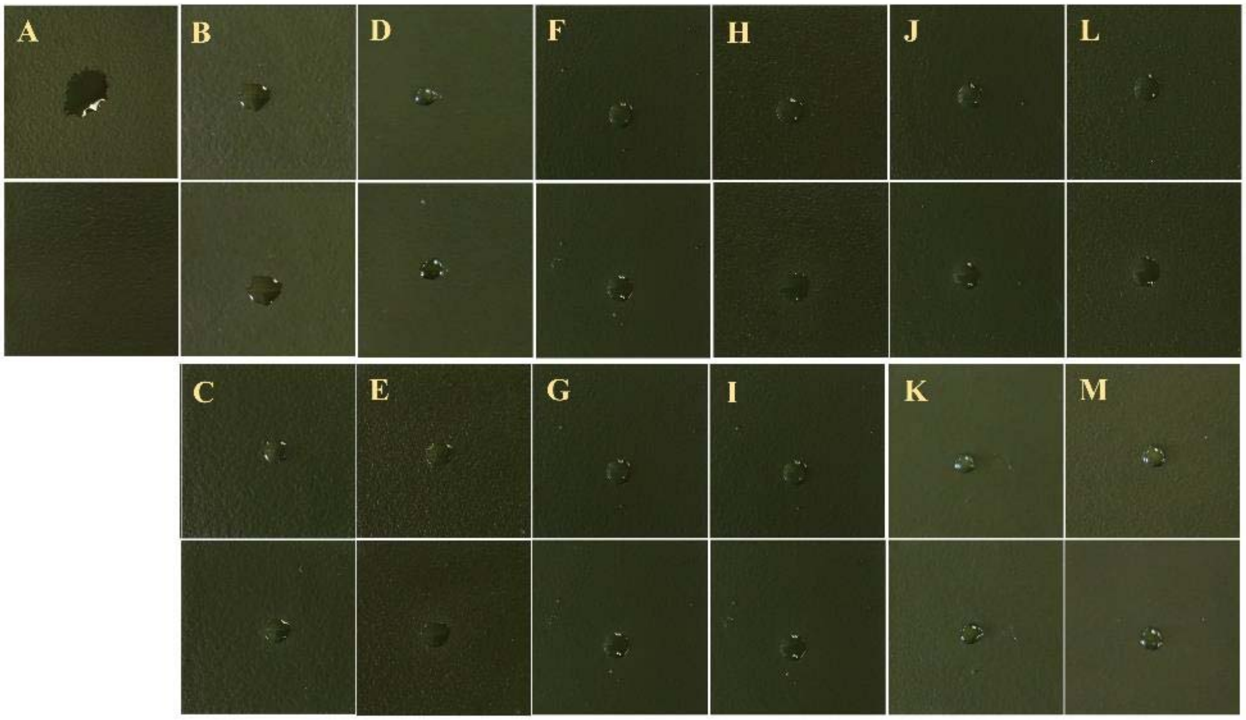

Fig. 3 — Images of a painted coupon and painted coupons treated with SOCAL- ARSiO$_2$ variations with standing droplets of MES immediately following application (top) and at 30 min (bottom) are shown: painted only (A); extracted, 25 mm/min, lubricated (B) and unlubricated (C); as synthesized, 25 mm/min, lubricated (D) and unlubricated (E); extracted, 100 mm/min, lubricated (F) and unlubricated (G); as synthesized, 100 mm/min, lubricated (H) and unlubricated (I);extracted, 270 mm/min, lubricated (J) and unlubricated (K); 270 mm/min, lubricated (L) and unlubricated (M).

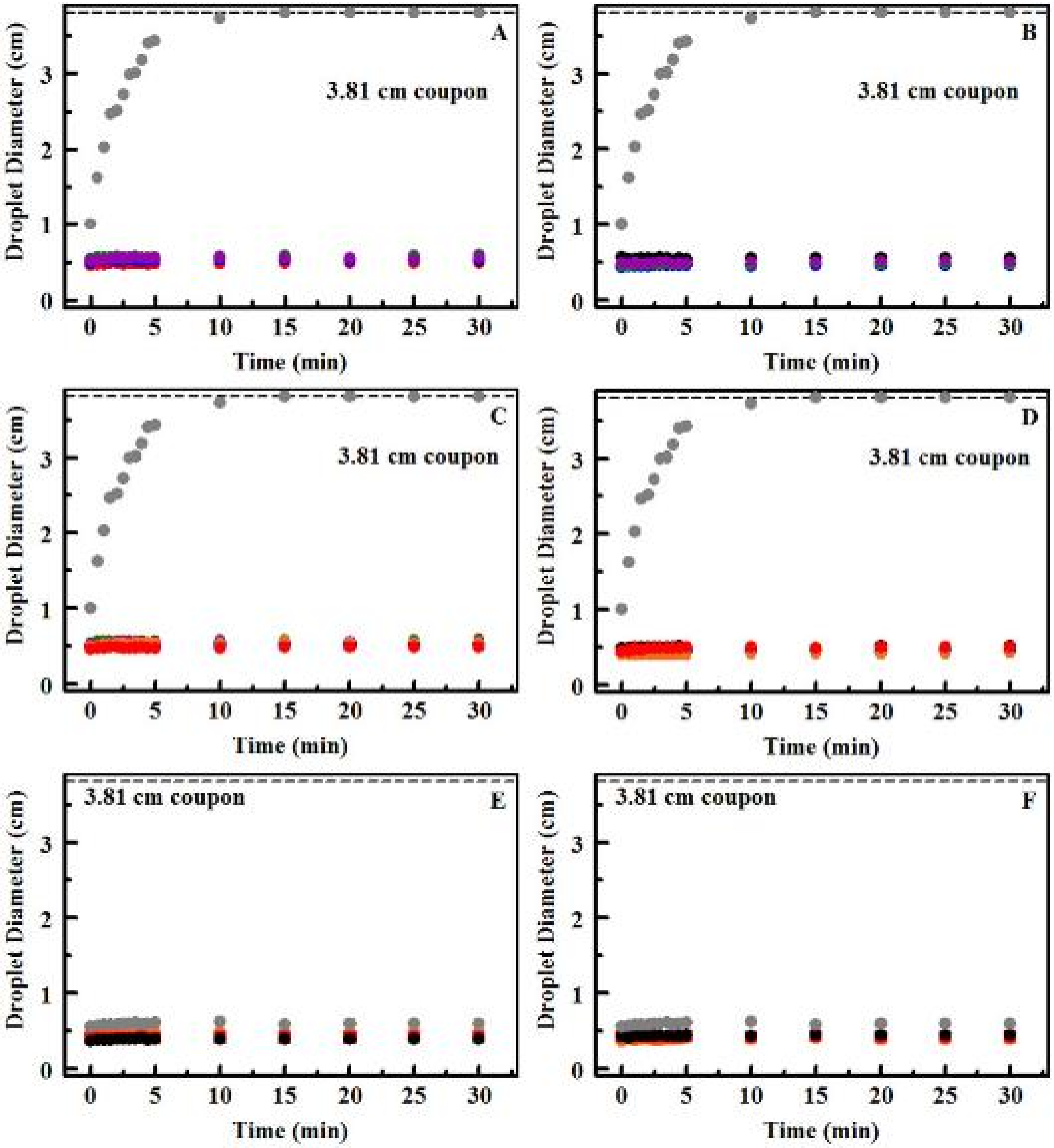

Fig. 4 — Progression of simulant droplet diameters during incubation on the PDMS oiled SOCAL-ARSiO2 surfaces (left) and on the unlubricated SOCAL-ARSiO2 surfaces (right) for DFP (A, B), MES (C, D), and DMMP (E, F): extracted, 25 mm/min (black); extracted, 100 mm/min (red); extracted, 270 mm/min (blue); as synthesized, 25 mm/min (green); as synthesized, 100 mm/min deposition (orange); as synthesized, 270 mm/min (purple); and paint only (gray).

When the soapy water decontamination process was employed (Figure 5; Table 3), retention of all targets was less for SOCAL-ARSiO2 coated coupons than that observed for the paint only coupons. In previous work, the SOCAL only surface showed retention slightly higher than a surface oiled with only the fluorocarbon oil (Fomblin Y). Retention of targets by the original SOCAL-ARSiO2 was less than that noted for the SOCAL only surface with the as synthesized surface outperforming the extracted surface. Here, slightly less retention was noted for the as synthesized variants. Overall, 100 mm/min deposition showed better performance than either 270 mm/min or 25 mm/min. Lubrication of the SOCAL-ARSiO2 samples using PDMS oil improved performance of coatings deposited at higher speeds with less or even negative impact noted at lower deposition speeds. Lubrication with Fomblin Y positively impacted performance of all surfaces.

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

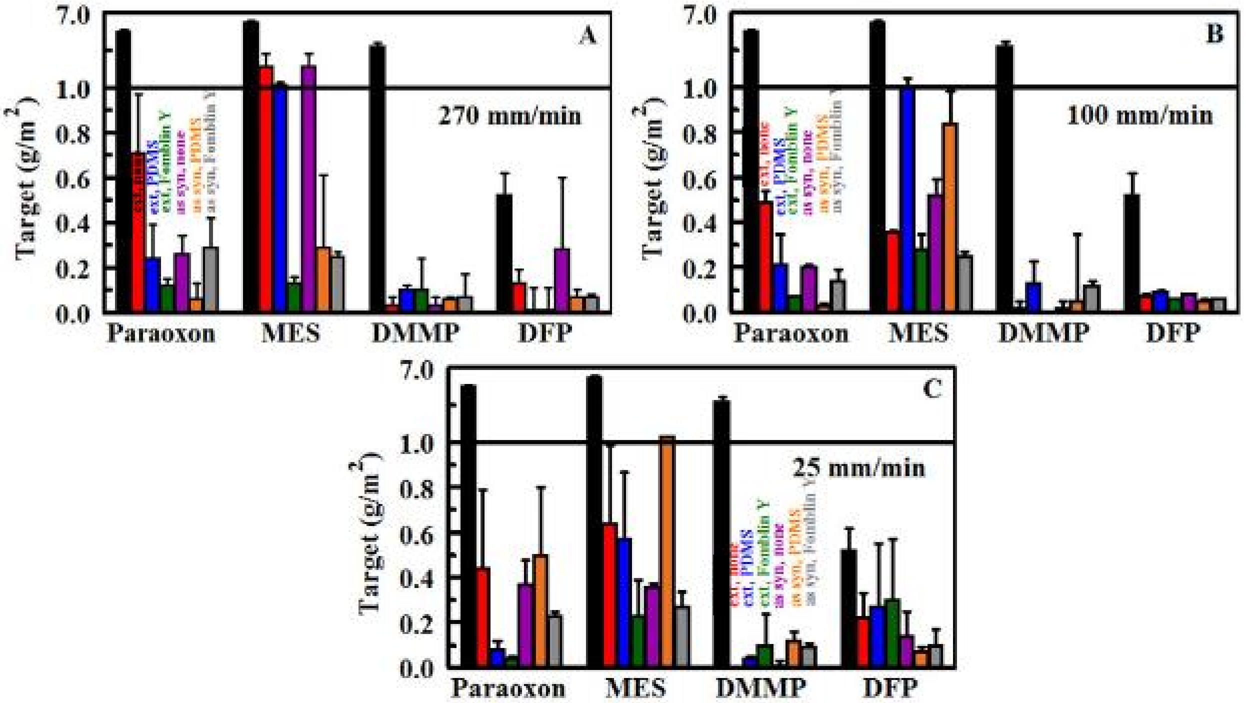

Fig. 5 — Target retention by coupons following treatment with an air stream and rinsing with soapy water: (A) 270 mm/min variations; (B) 100 mm/min variations; (C) 25 mm/min variations: paint only (black); extracted, no lubrication (red); extracted, PDMS (blue); extracted, Fomblin Y (green); as synthesized, no lubrication (purple); as synthesized, PDMS (orange); as synthesized, Fomblin Y (gray).

Table 3 – Target Retention (g/m^2) Following 1 h Aging on SOCAL-ARSiO$_2$

SOCAL Deposition (mm/min)	**Coupon**	**Additional Lubrication**	**Paraoxon**	**MES**	**DMMP**	**DFP**
Aluminum Support						
	Paint Only		5.48	6.20	4.28	0.52
		PDMS	1.22	6.35	0.80	0.53
		Fomblin Y	1.24	2.85	0.59	0.34
270	$ARSiO_2$, extracted	None	0.71	2.17	0.03	0.13
		PDMS	0.24	1.21	0.10	0.01
		Fomblin Y	0.12	0.13	0.10	0.01
	$ARSiO_2$, as synthesized	None	0.26	2.69	0.03	0.28
		PDMS	0.06	0.29	0.06	0.07
		Fomblin Y	0.29	0.25	0.07	0.07
100	$ARSiO_2$, extracted	None	0.49	0.36	0.02	0.07
		PDMS	0.21	1.21	0.13	0.09
		Fomblin Y	0.07	0.28	ND	0.06
	$ARSiO_2$, as synthesized	None	0.20	0.52	0.02	0.08
		PDMS	0.03	0.84	0.05	0.05
		Fomblin Y	0.14	0.25	0.12	0.06
25	$ARSiO_2$, extracted	None	0.44	0.64	ND	0.22
		PDMS	0.08	0.57	0.04	0.27
		Fomblin Y	0.04	0.23	0.10	0.30
	$ARSiO_2$, as synthesized	None	0.37	0.36	0.01	0.14
		PDMS	0.05	1.42	0.12	0.07
		Fomblin Y	0.23	0.27	0.09	0.10
	SOCAL only [8]	None	2.74	4.14	0.03	0.45
	SOCAL on $ARSiO_2$ extracted [8]	None	2.85	1.59	ND	0.06
	SOCAL on $ARSiO_2$ as synthesized [8]	None	1.70	1.18	0.03	0.35

CONCLUSIONS

These samples provide promising results with significantly reduced target retention as compared to paint only surfaces. Though this does not represent the best performance observed under the overall 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 3 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 authors would 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).

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Appendix A

PAINT ONLY 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.

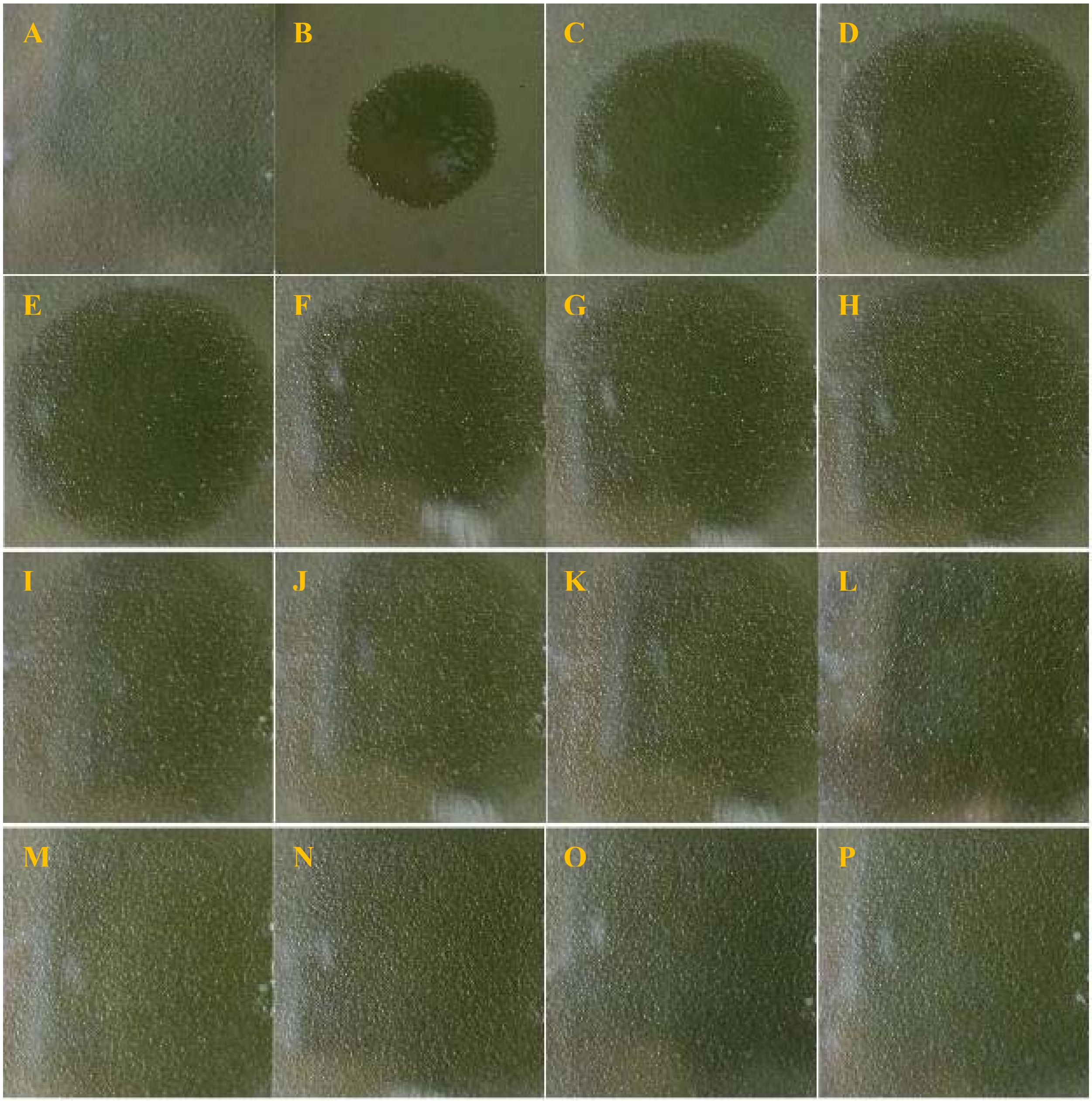


Fig. A2 — MES on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

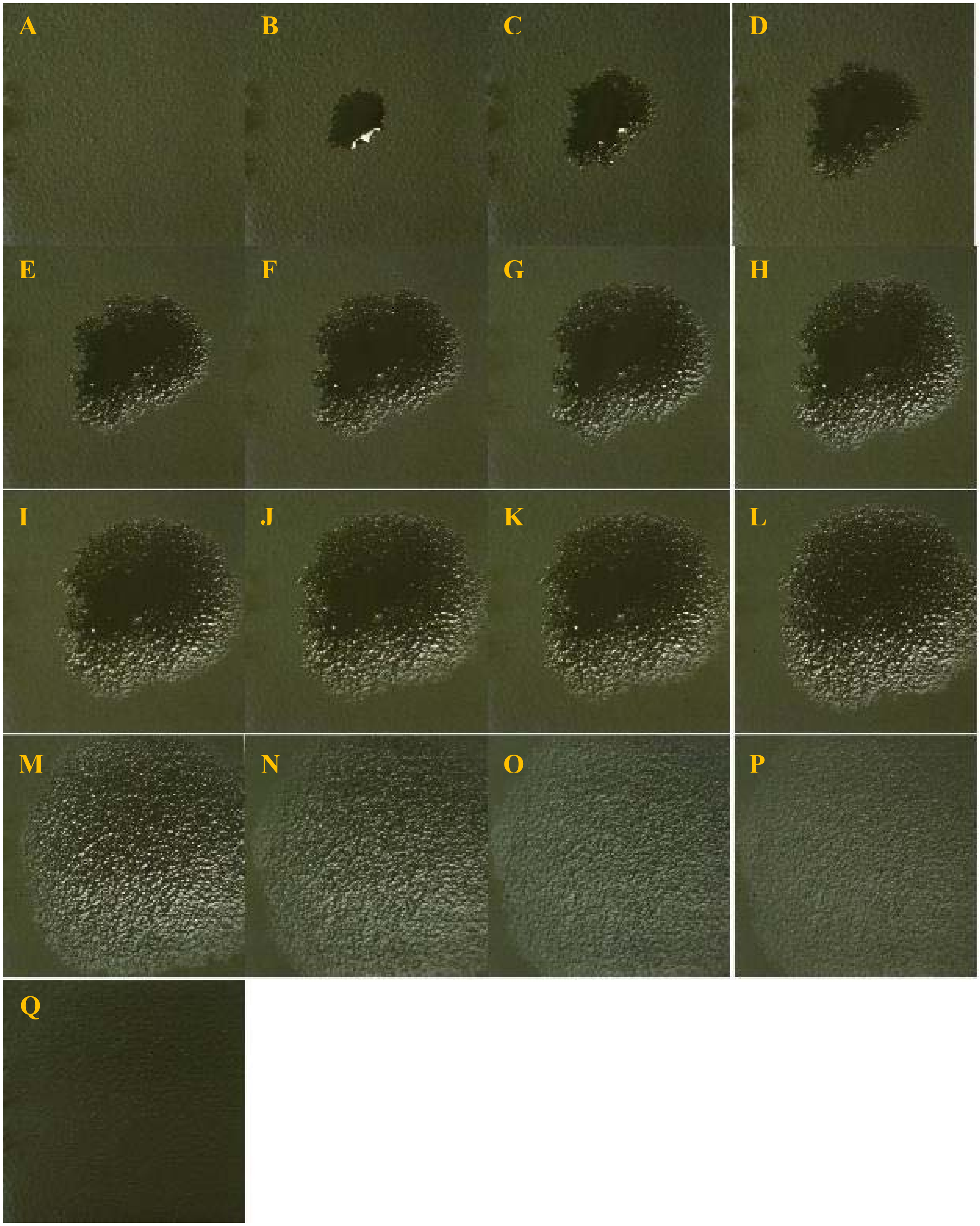
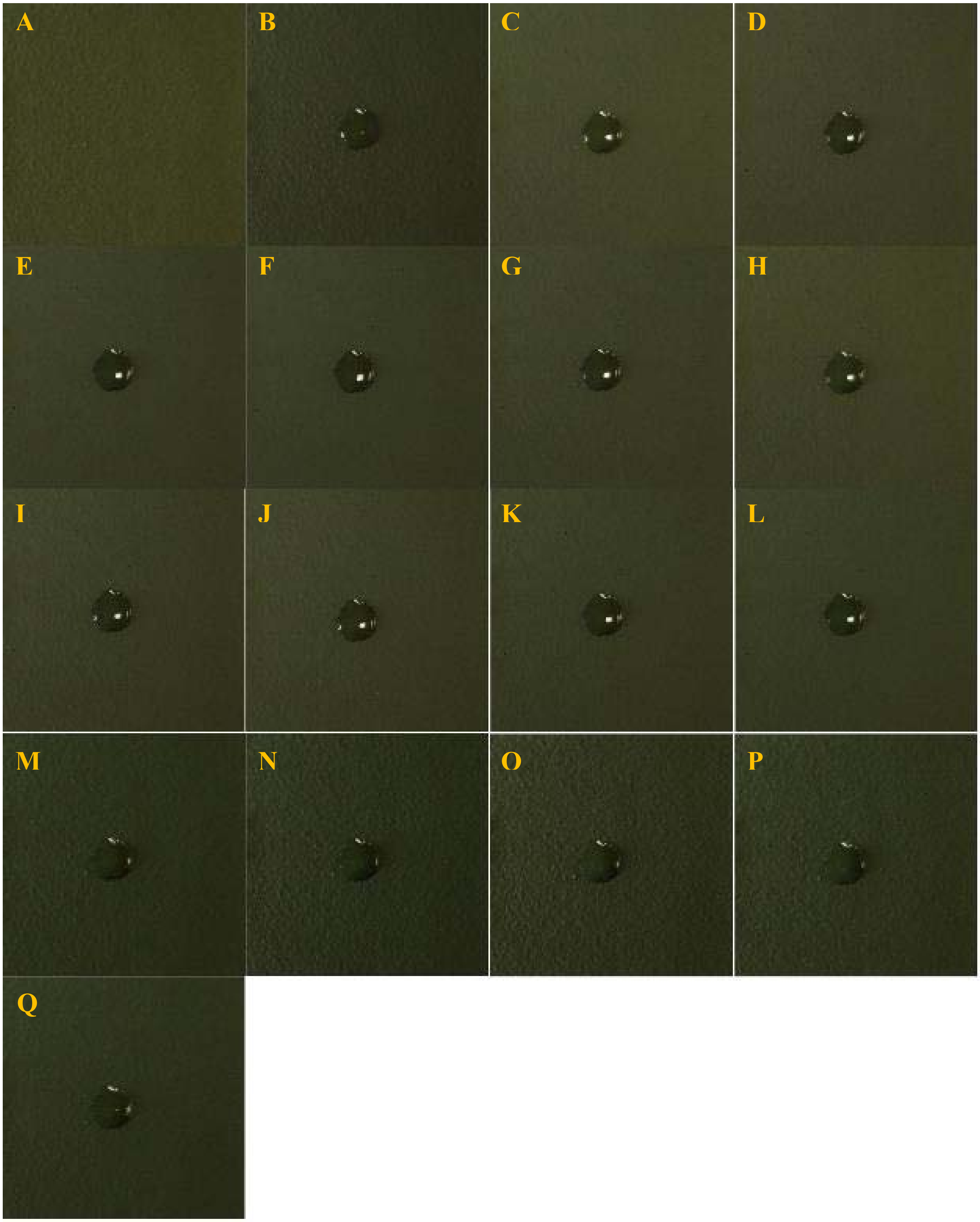


Fig. A3 — DMMP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix B

EXTRACTED, 25 MM/MIN COUPON IMAGES

Fig. B1 — DFP on SOCAL-ARSiO, extracted, 25 mm/min, no lubrication. 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.

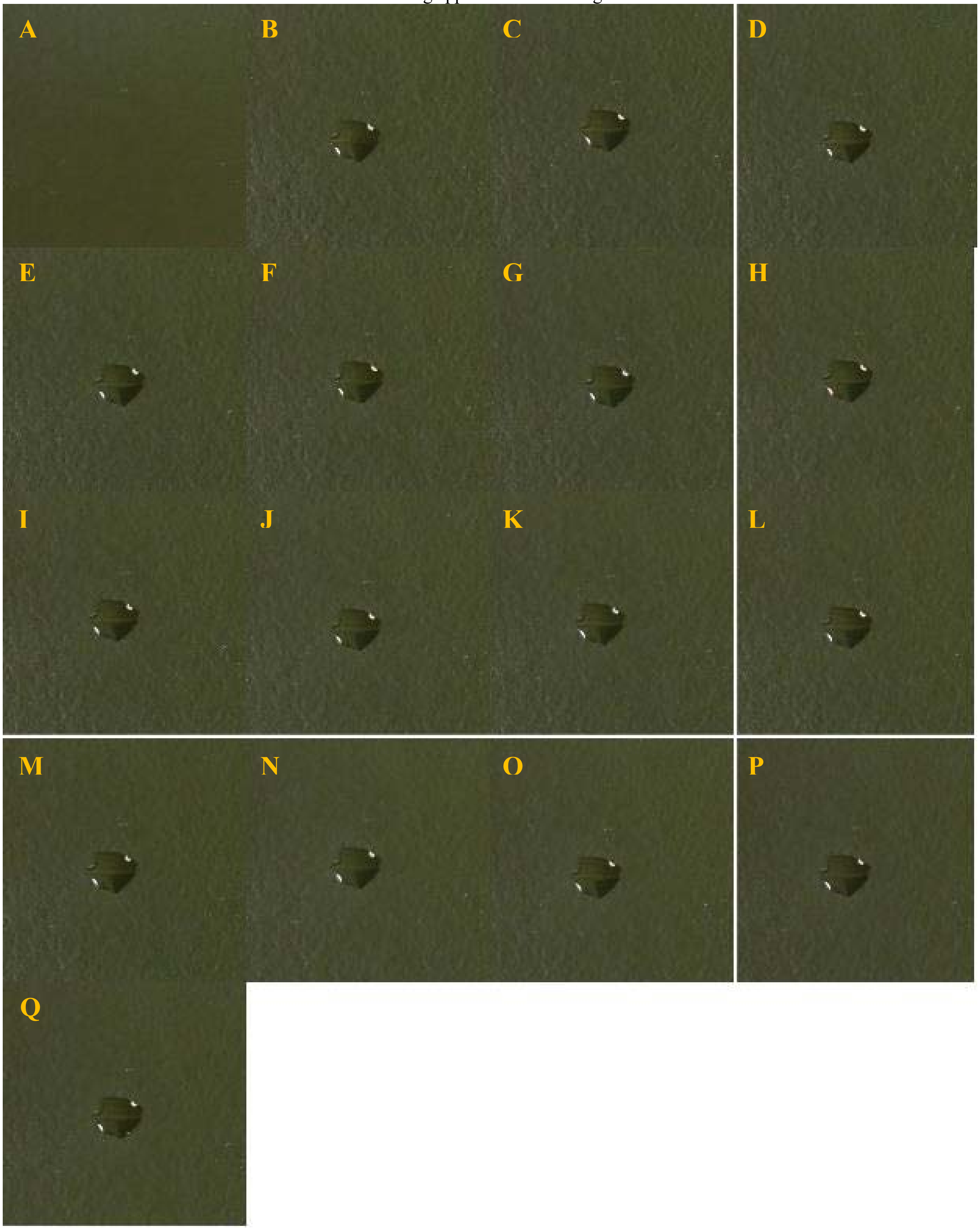


Fig. B2 — MES on SOCAL-ARSiO, extracted, 25 mm/min, no lubrication. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

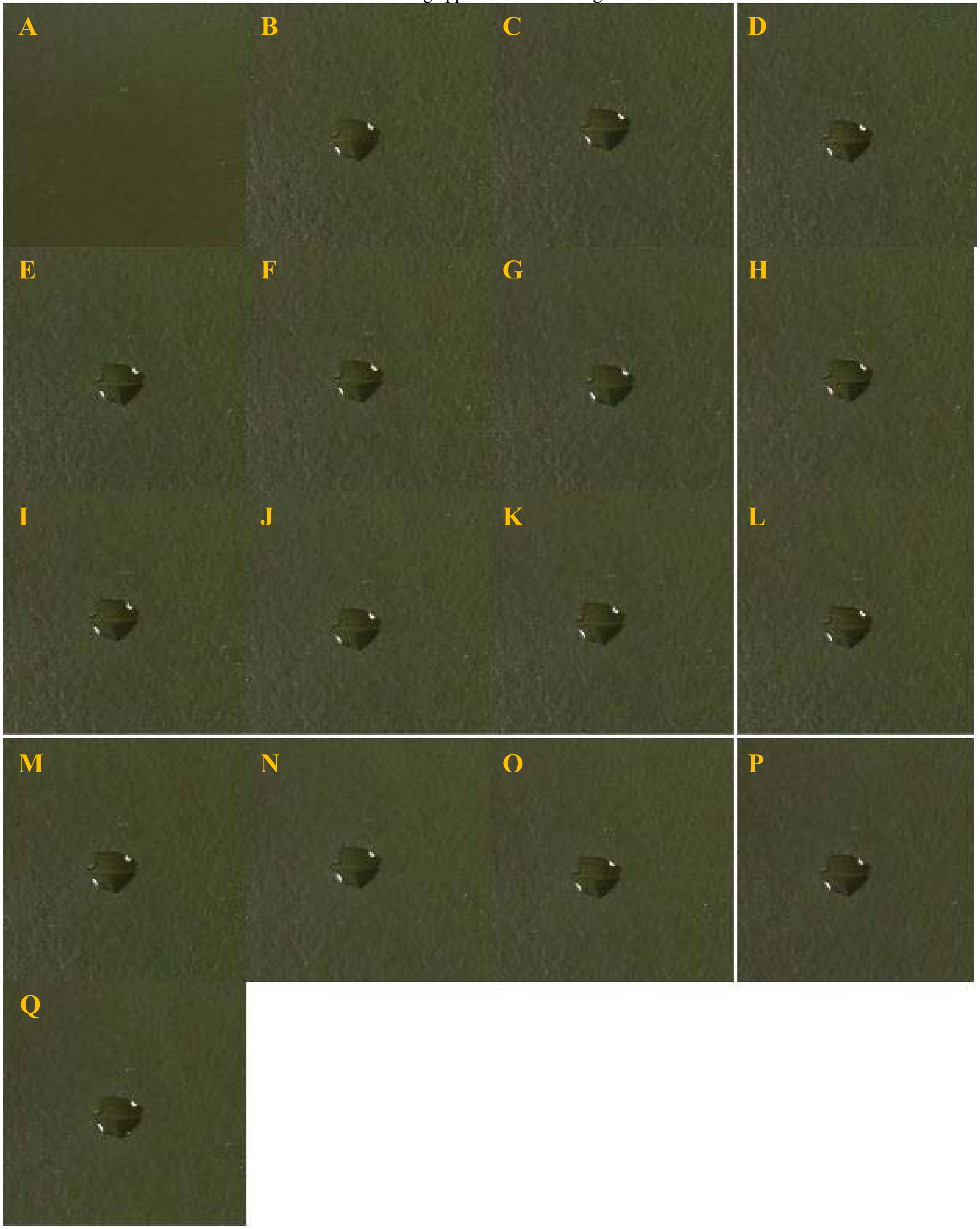
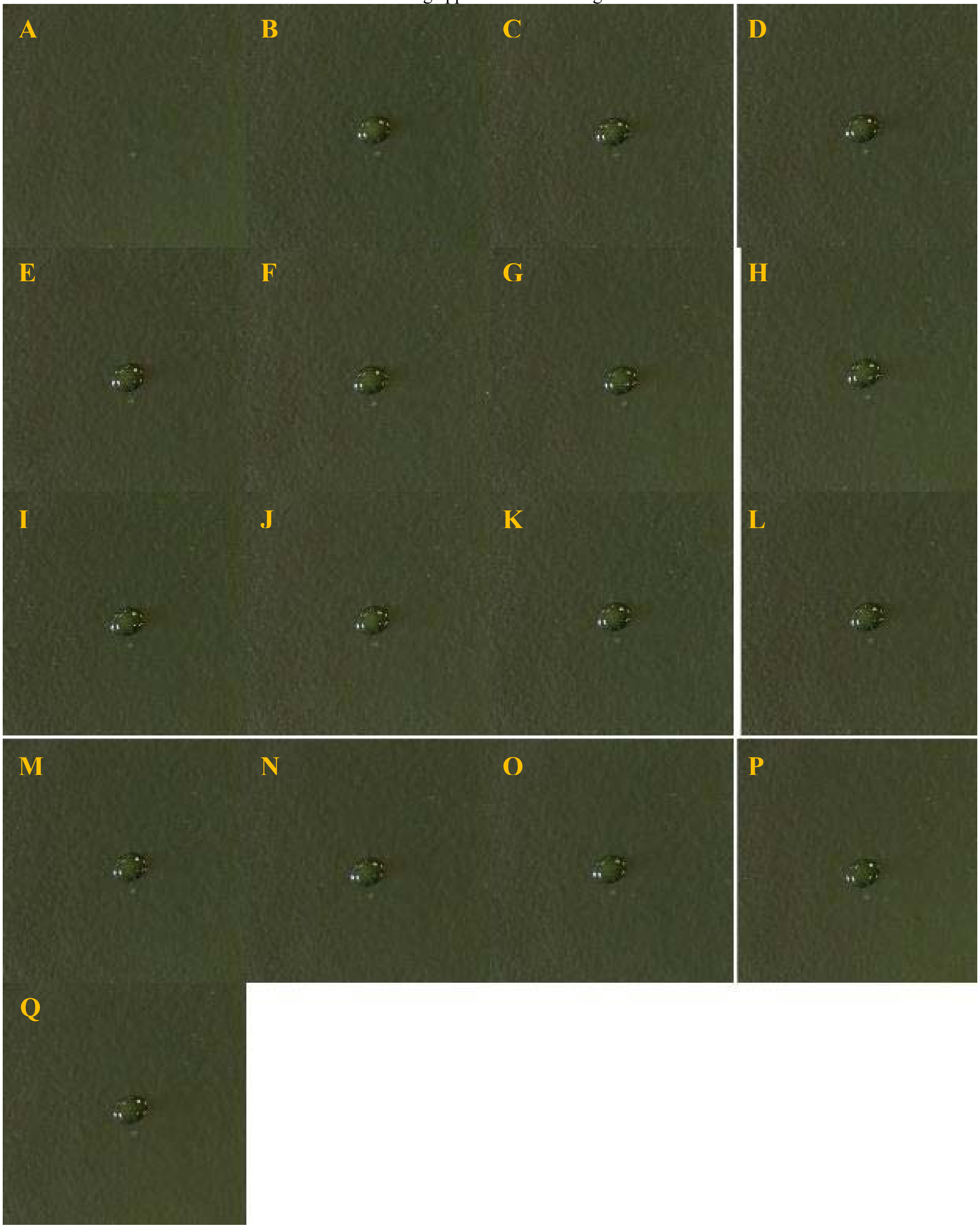


Fig. B3 — DMMP on SOCAL-ARSiO, extracted, 25 mm/min, no lubrication. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix C

EXTRACTED, 100 MM/MIN COUPON IMAGES

Fig. C1 — DFP on SOCAL-ARSiO, extracted, 100 mm/min, no lubrication. 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.

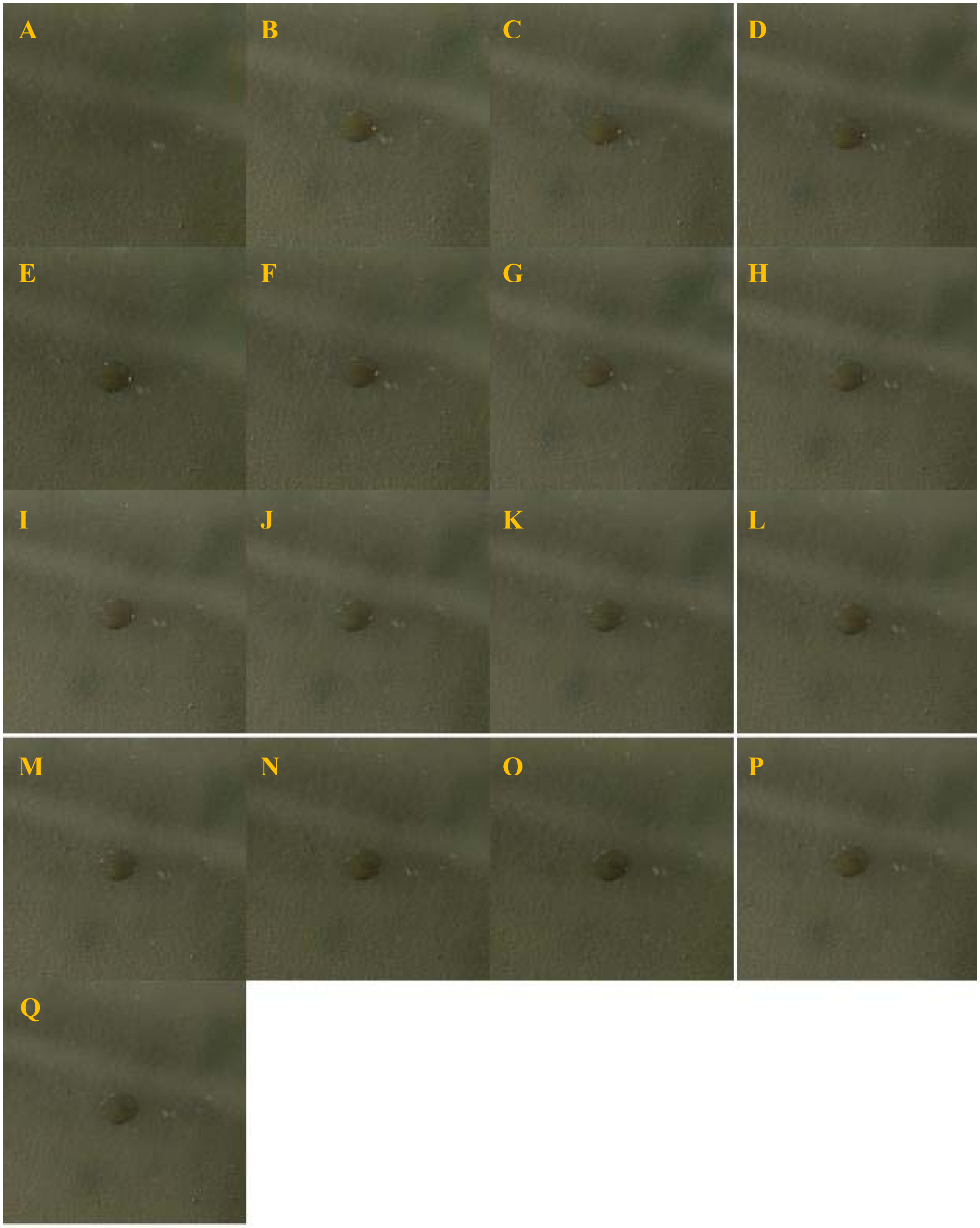


Fig. C2 — MES on SOCAL-ARSiO, extracted, 100 mm/min, no lubrication. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

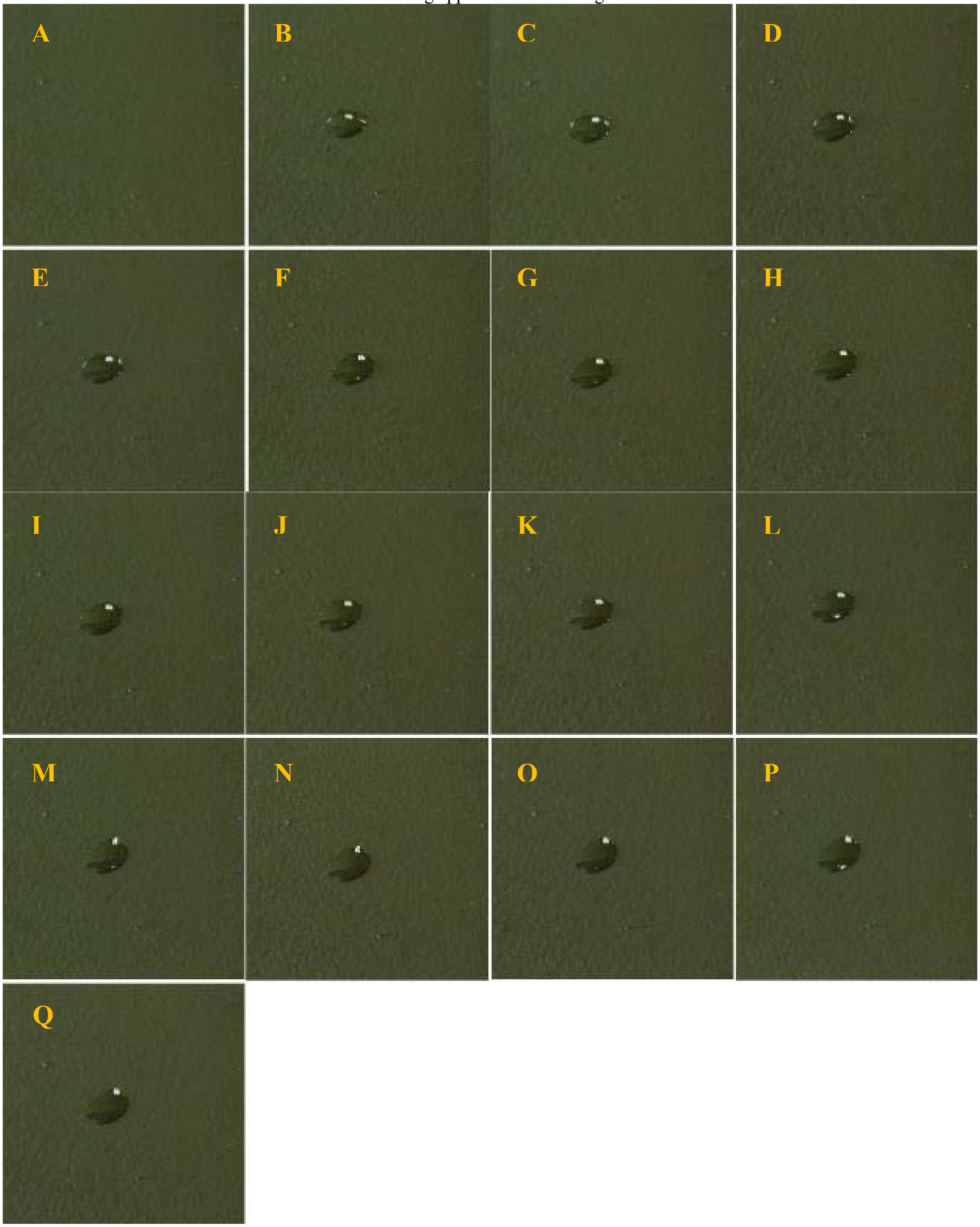
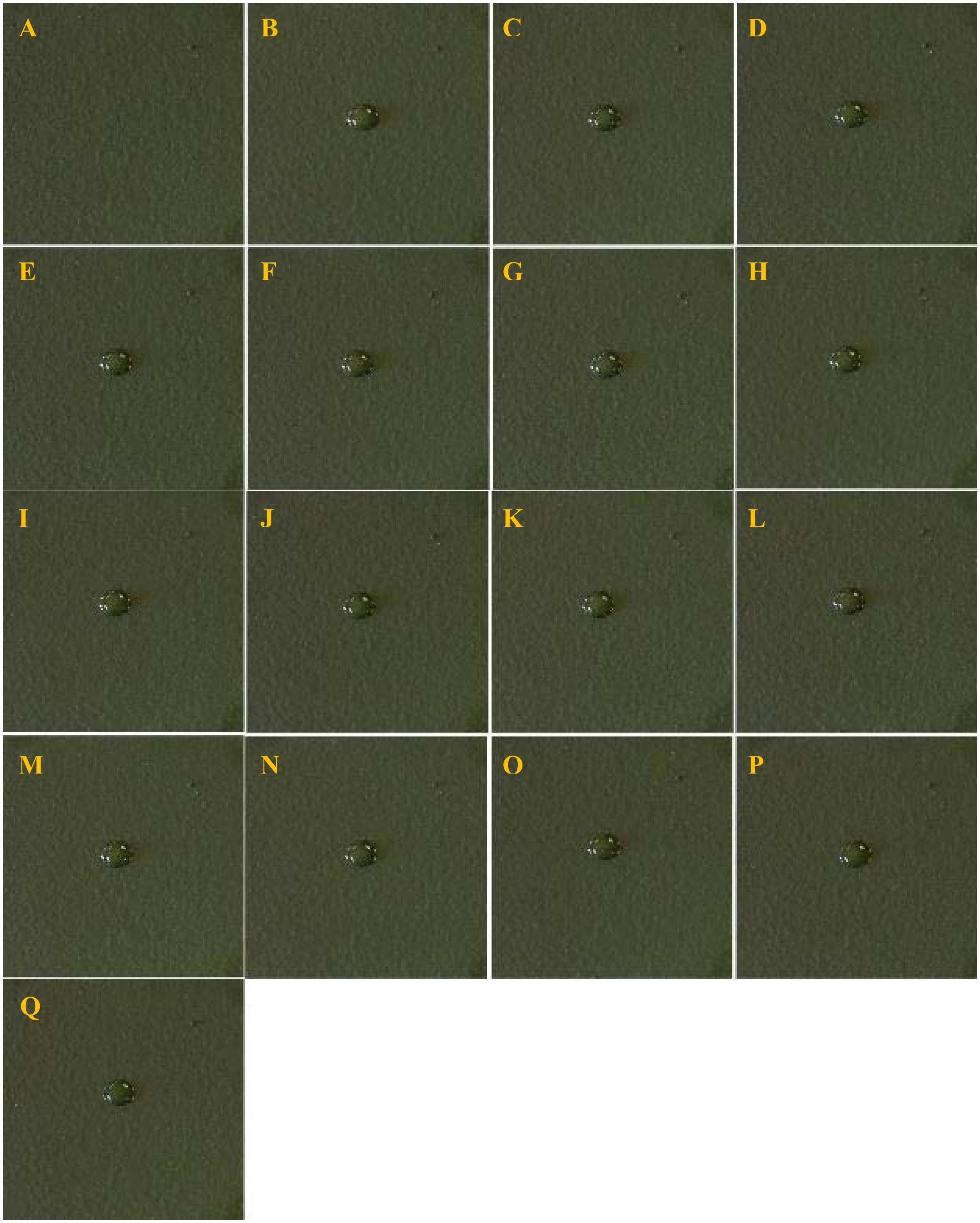


Fig. C3 — DMMP on SOCAL-ARSiO, extracted, 100 mm/min, no lubrication. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix D

EXTRACTED, 270 MM/MIN COUPON IMAGES

Fig. D1 — DFP on SOCAL-ARSiO, extracted, 270 mm/min, no lubrication. 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.

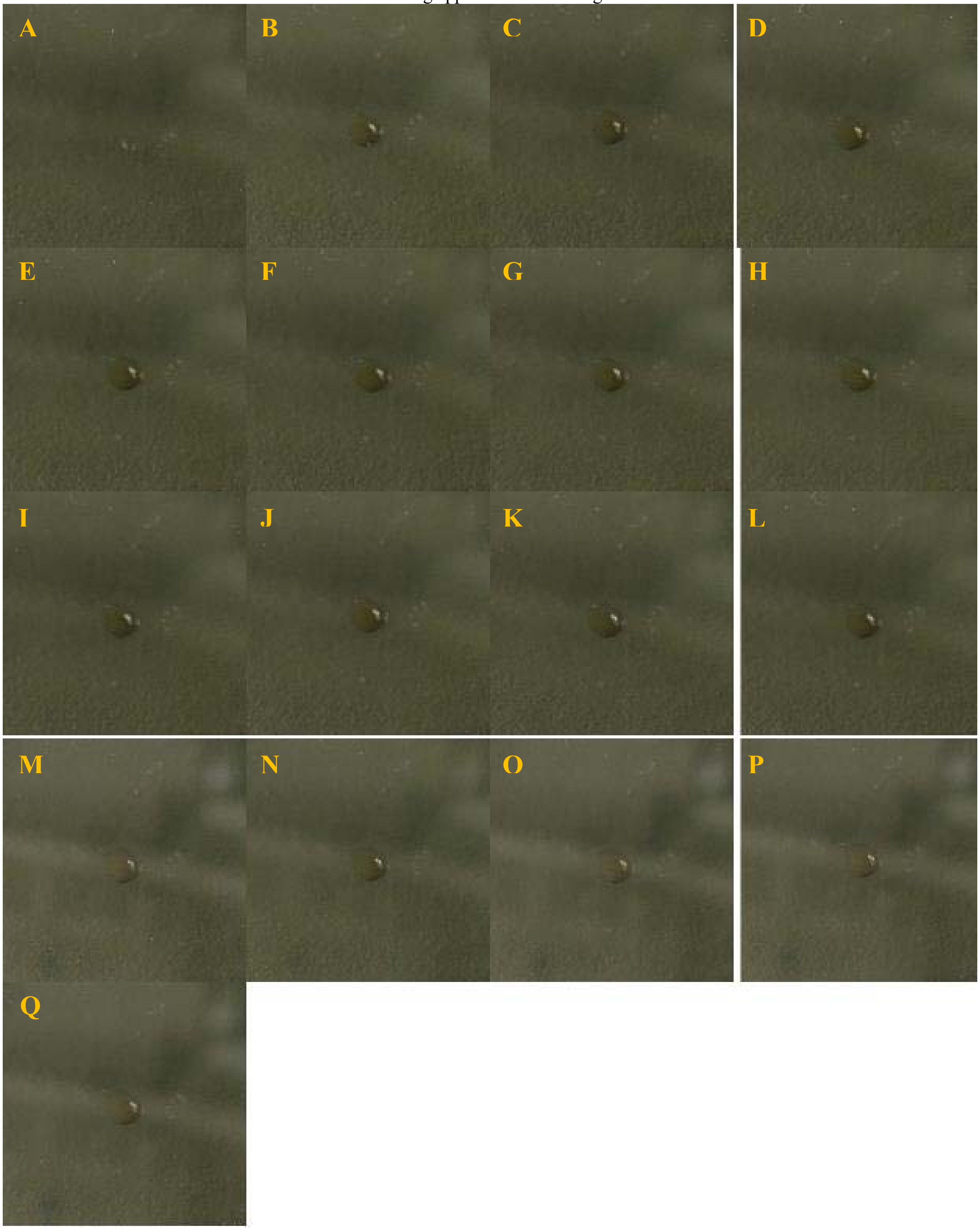


Fig. D2 — MES on SOCAL-ARSiO, extracted, 270 mm/min, no lubrication. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

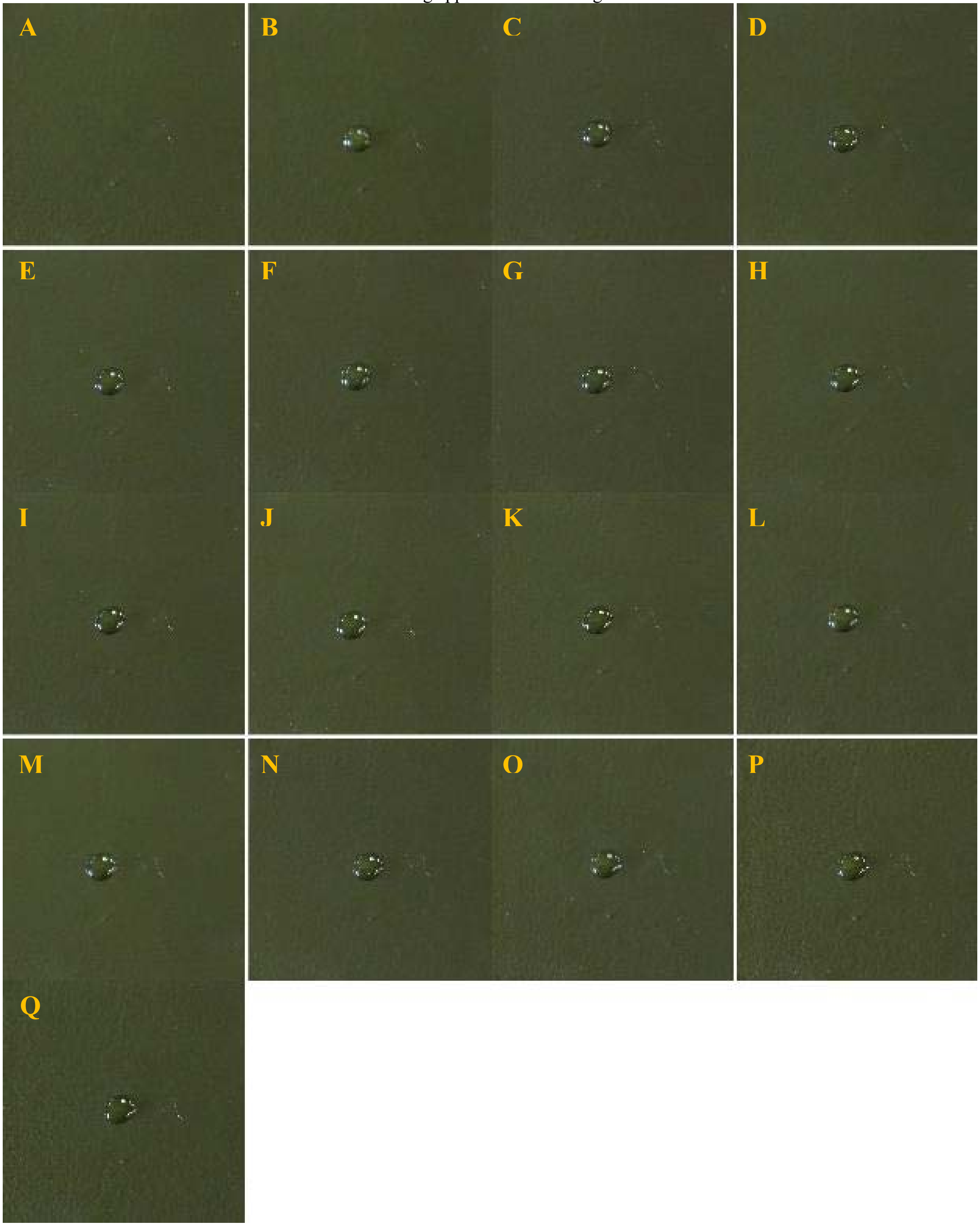
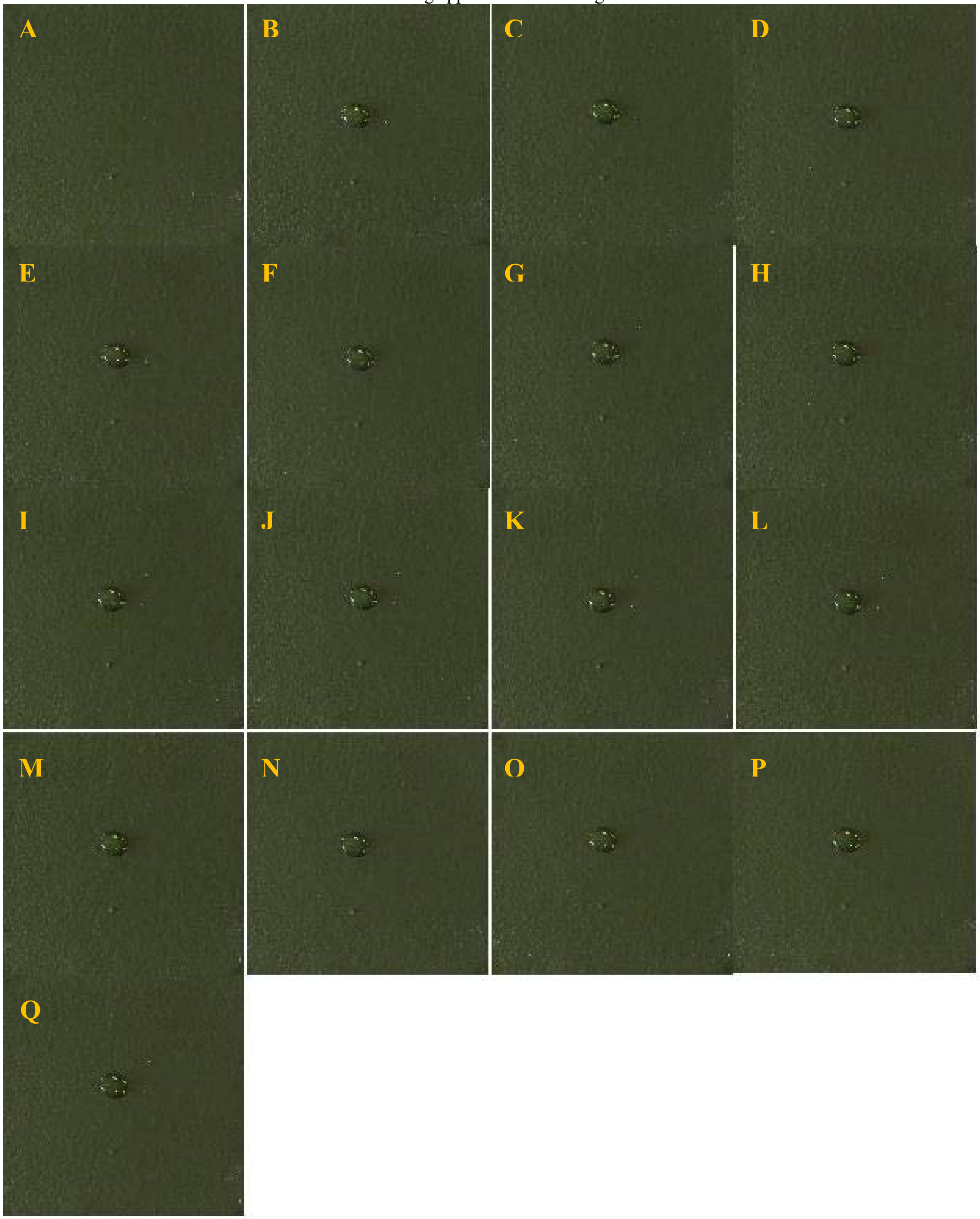


Fig. D3 — DMMP on SOCAL-ARSiO, extracted, 270 mm/min, no lubrication. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix E

AS SYNTHESIZED, 25 MM/MIN COUPON IMAGES

Fig. E1 — DFP on SOCAL-ARSiO, as synthesized, 25 mm/min, no lubrication. 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.

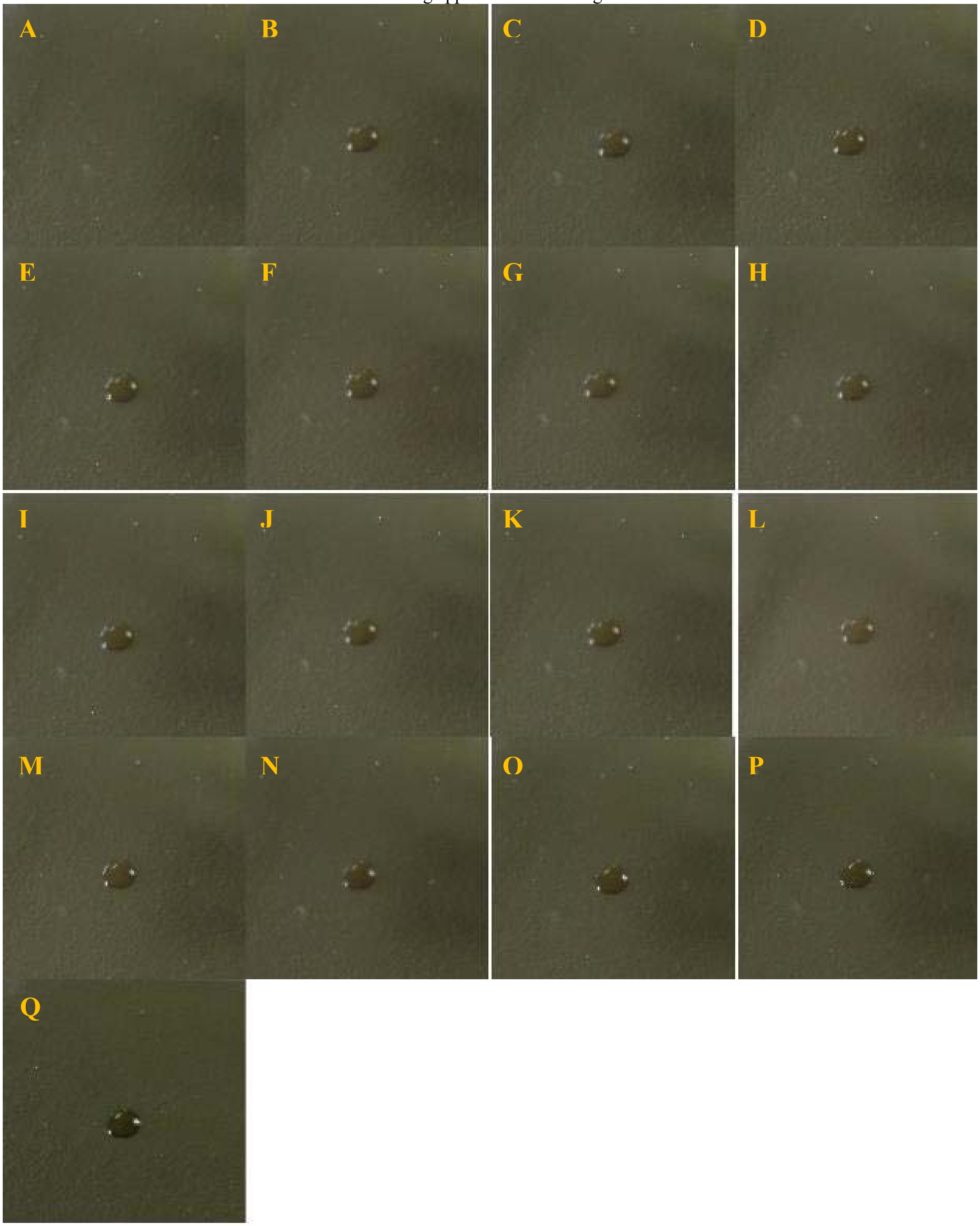


Fig. E2 — MES on SOCAL-ARSiO, as synthesized, 25 mm/min, no lubrication. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

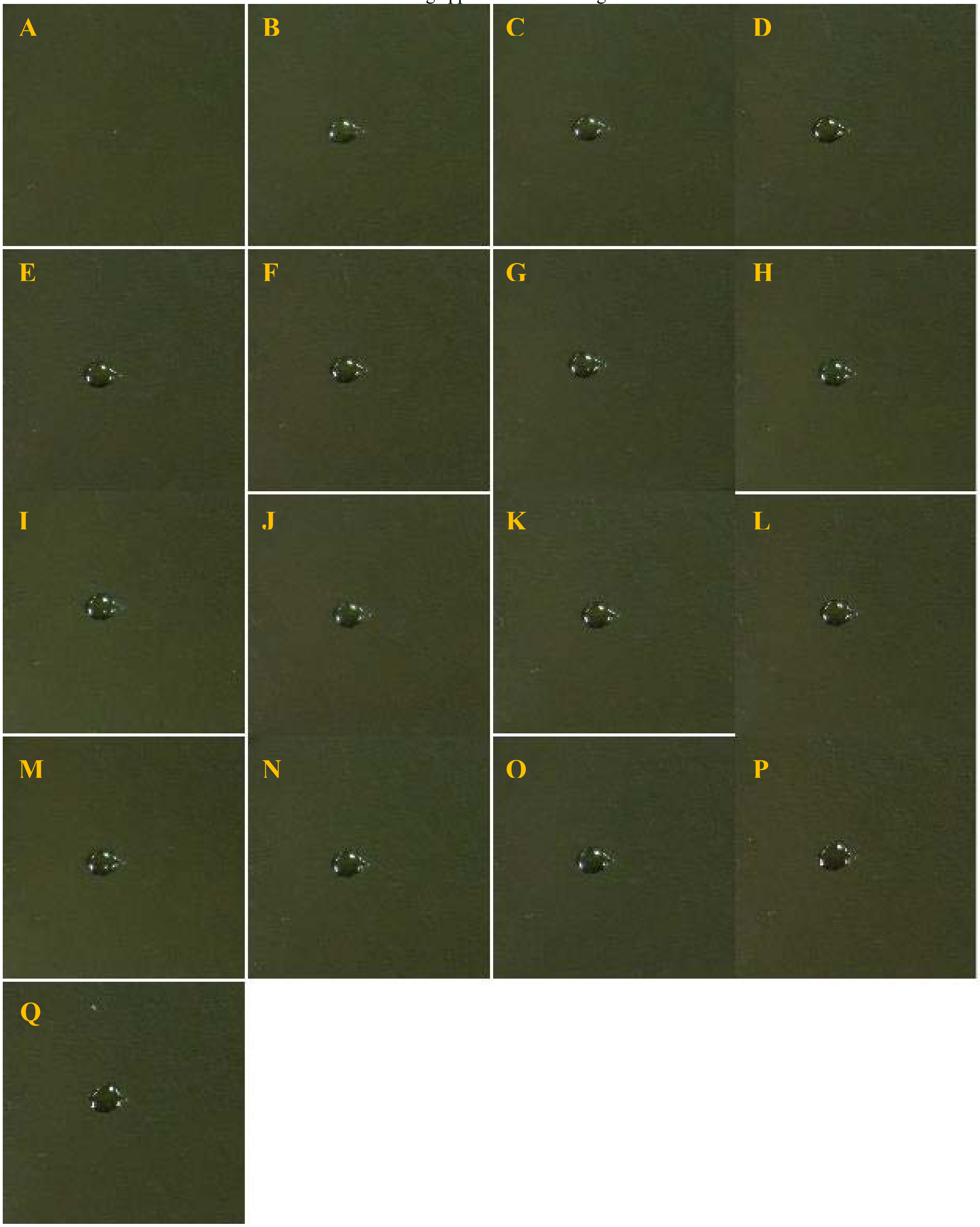
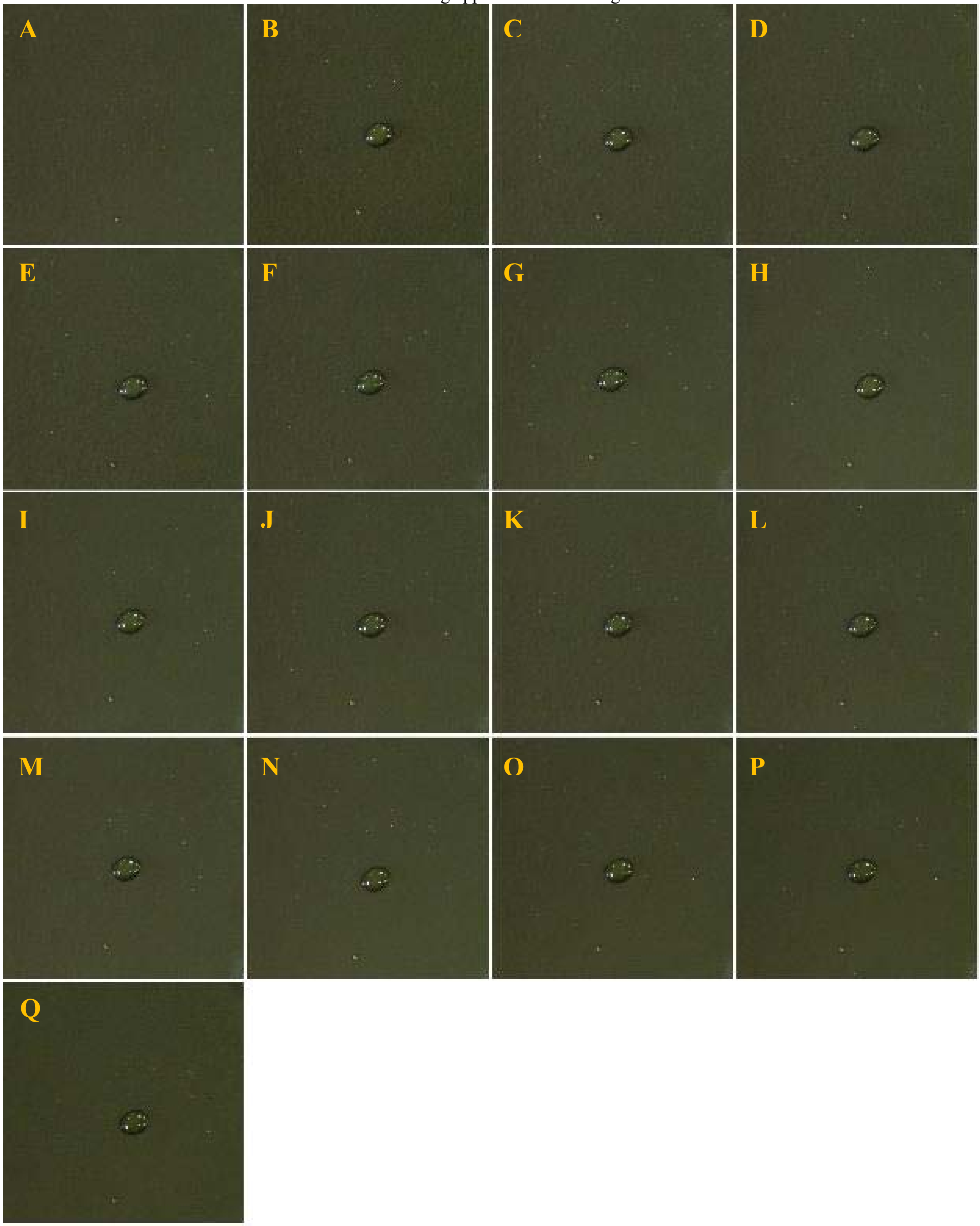


Fig. E3 — DMMP on SOCAL-ARSiO, as synthesized, 25 mm/min, no lubrication. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix F

AS SYNTHESIZED, 100 MM/MIN COUPON IMAGES

Fig. F1 — DFP on SOCAL-ARSiO, as synthesized, 100 mm/min, no lubrication. 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.

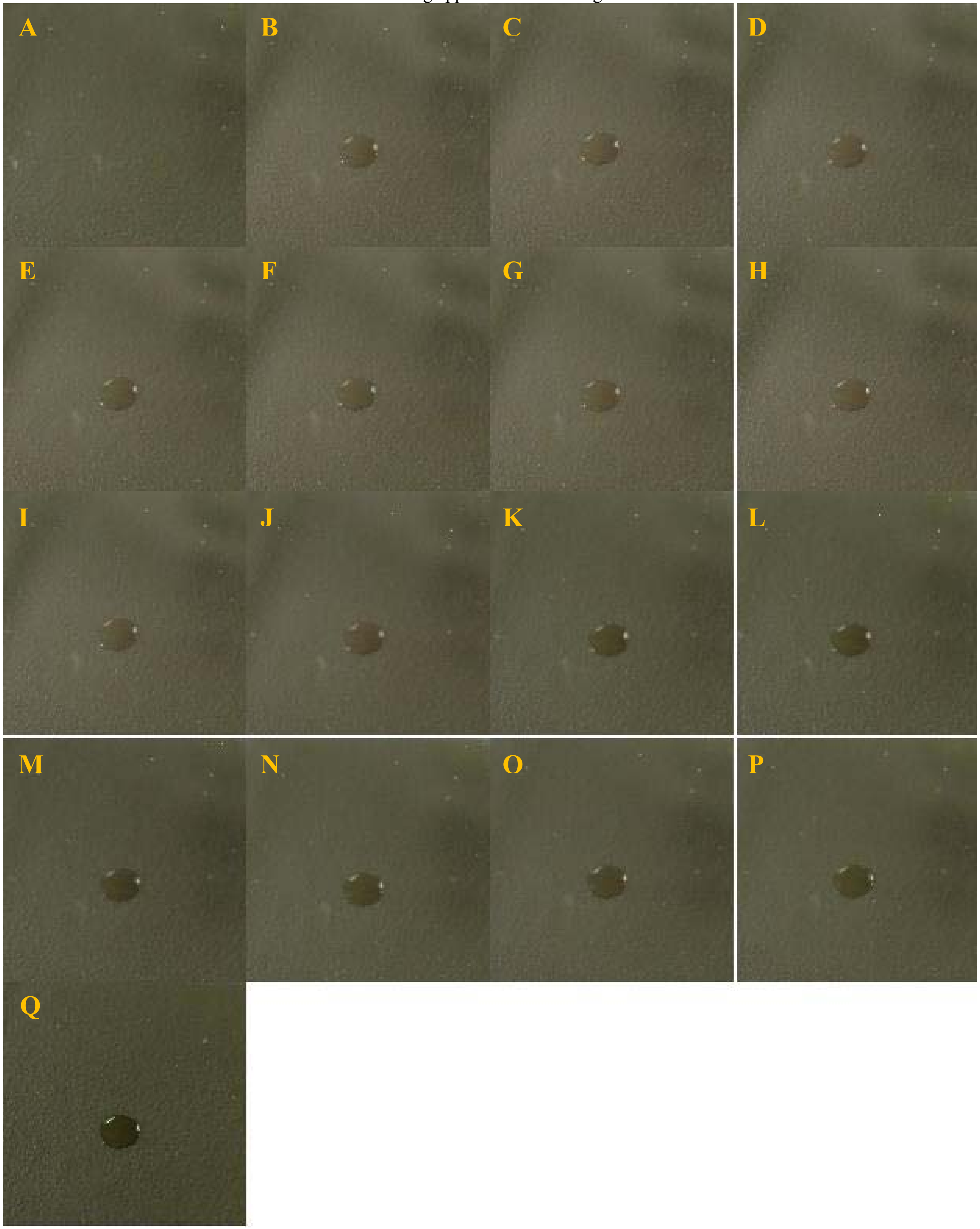


Fig. F2 — MES on SOCAL-ARSiO, as synthesized, 100 mm/min, no lubrication. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

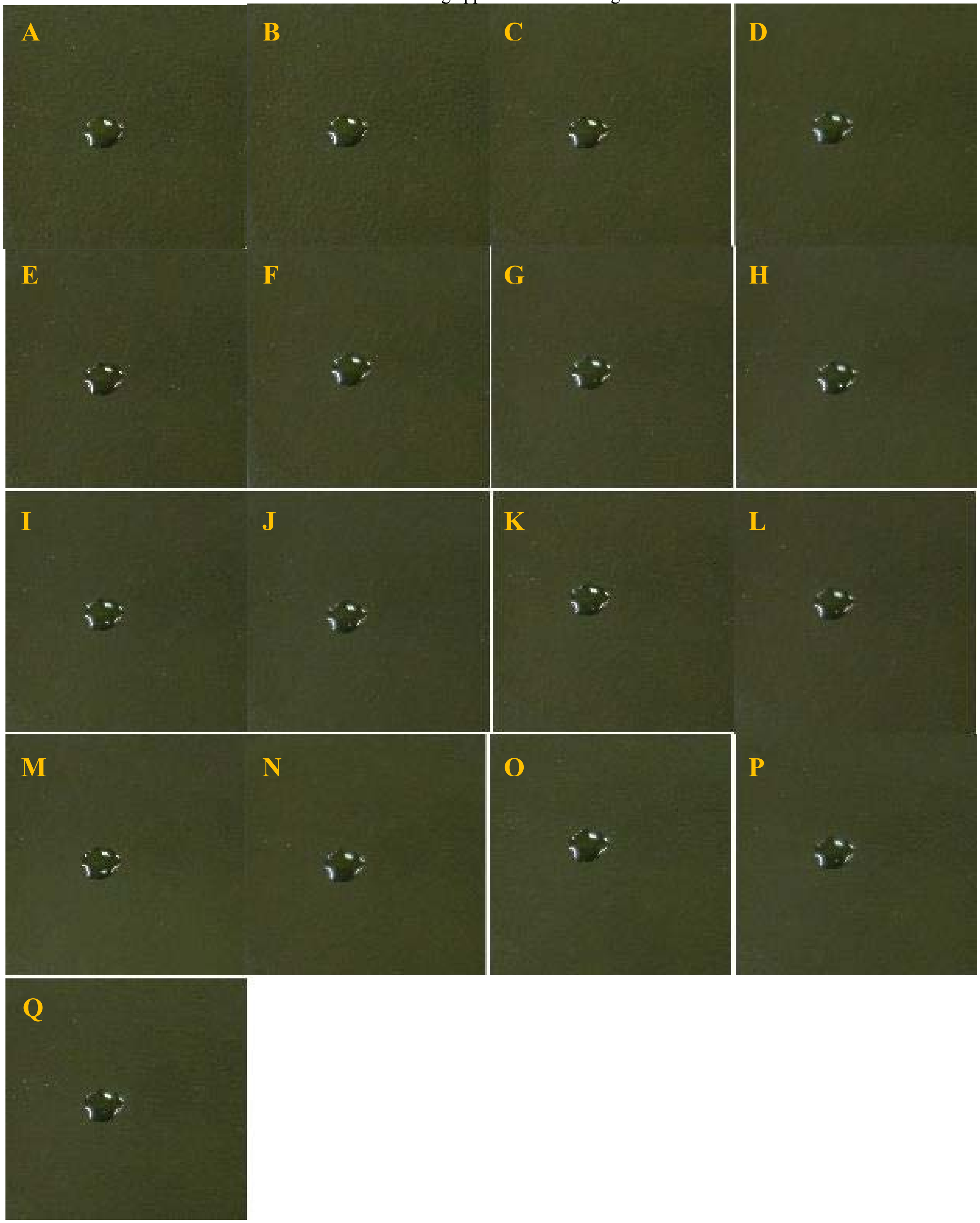
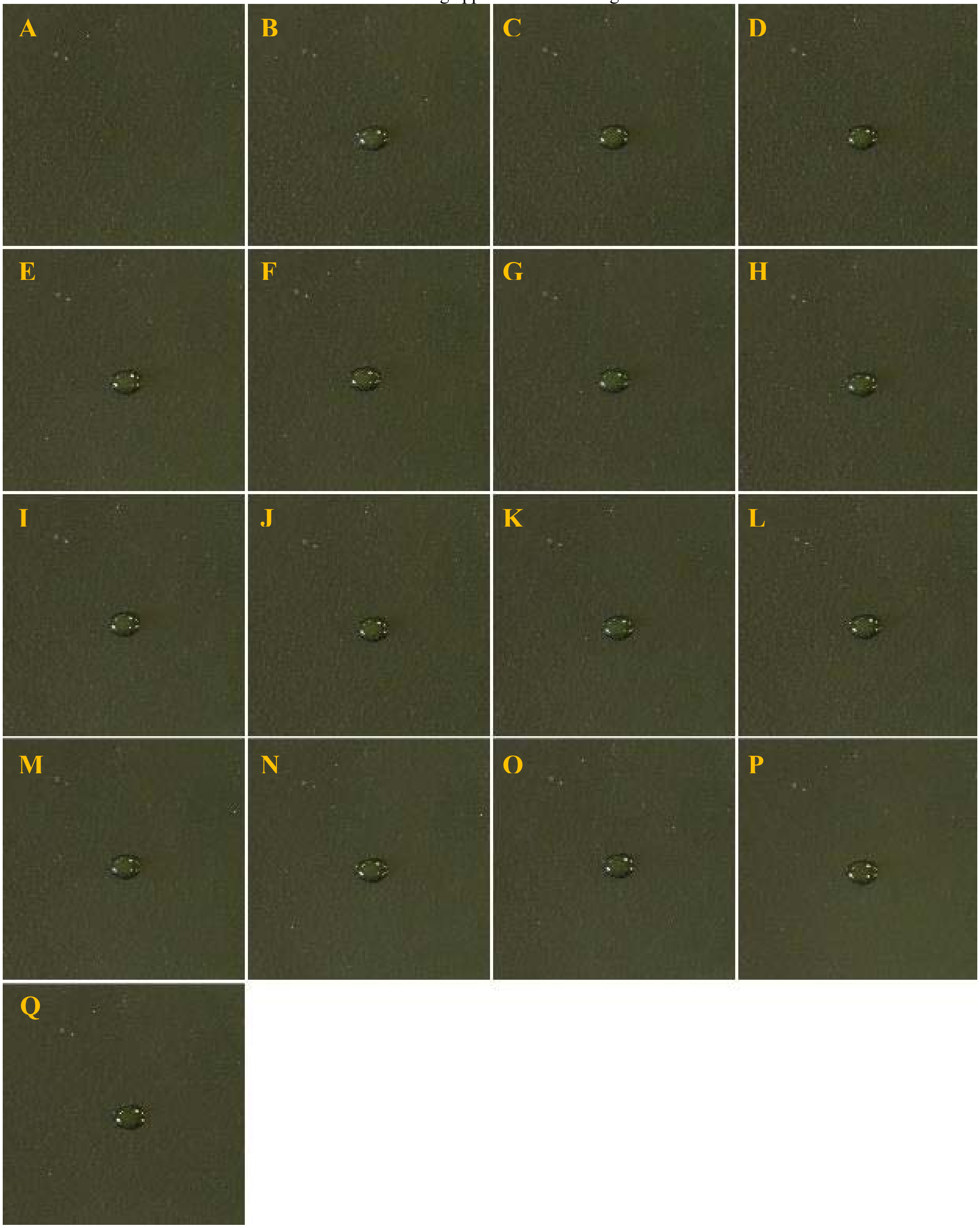


Fig. F3 — DMMP on SOCAL-ARSiO, as synthesized, 100 mm/min, no lubrication. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix G

AS SYNTHESIZED, 270 MM/MIN COUPON IMAGES

Fig. G1 — DFP on SOCAL-ARSiO, as synthesized, 270 mm/min, no lubrication. 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.

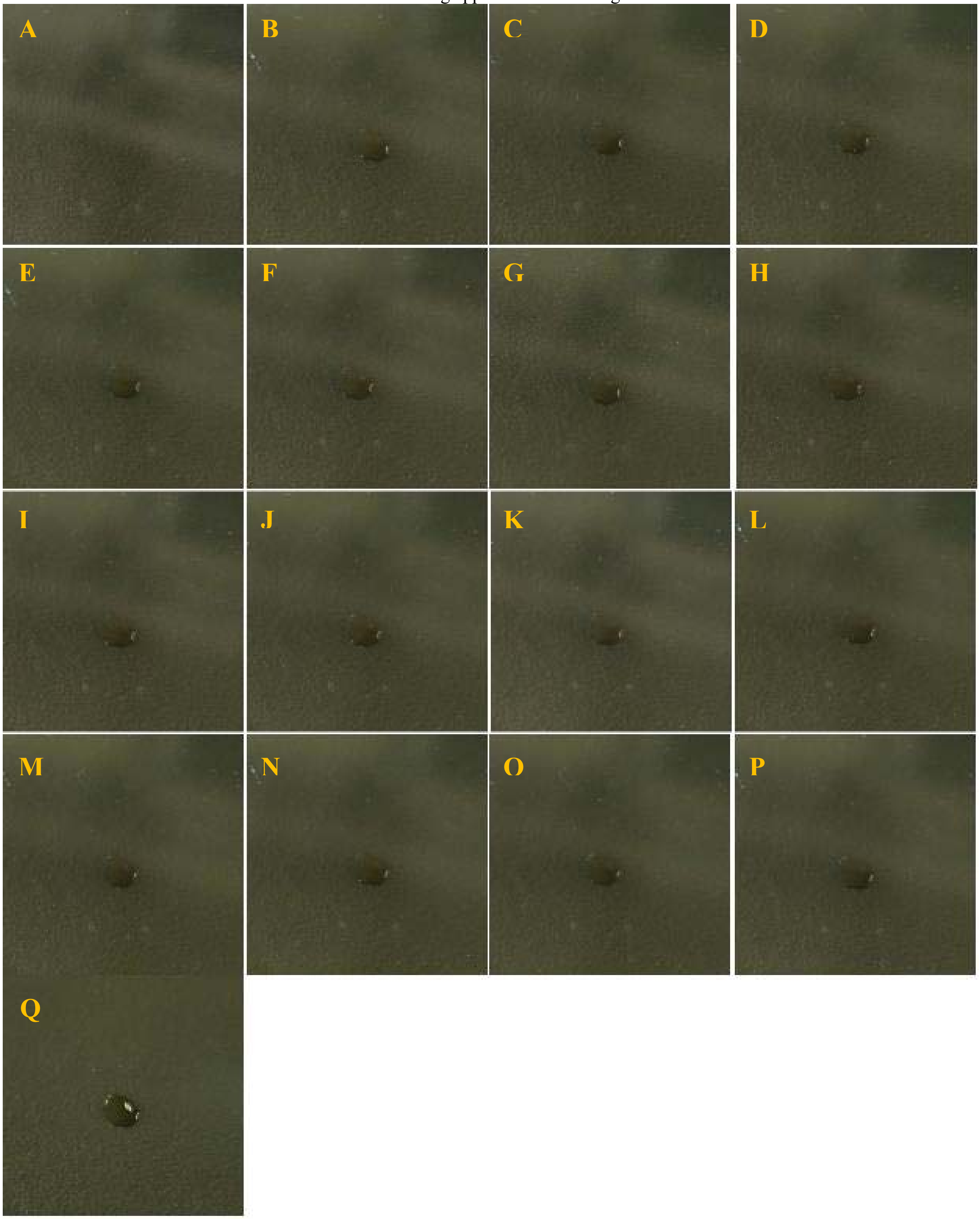


Fig. G2 — MES on SOCAL-ARSiO, as synthesized, 270 mm/min, no lubrication. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

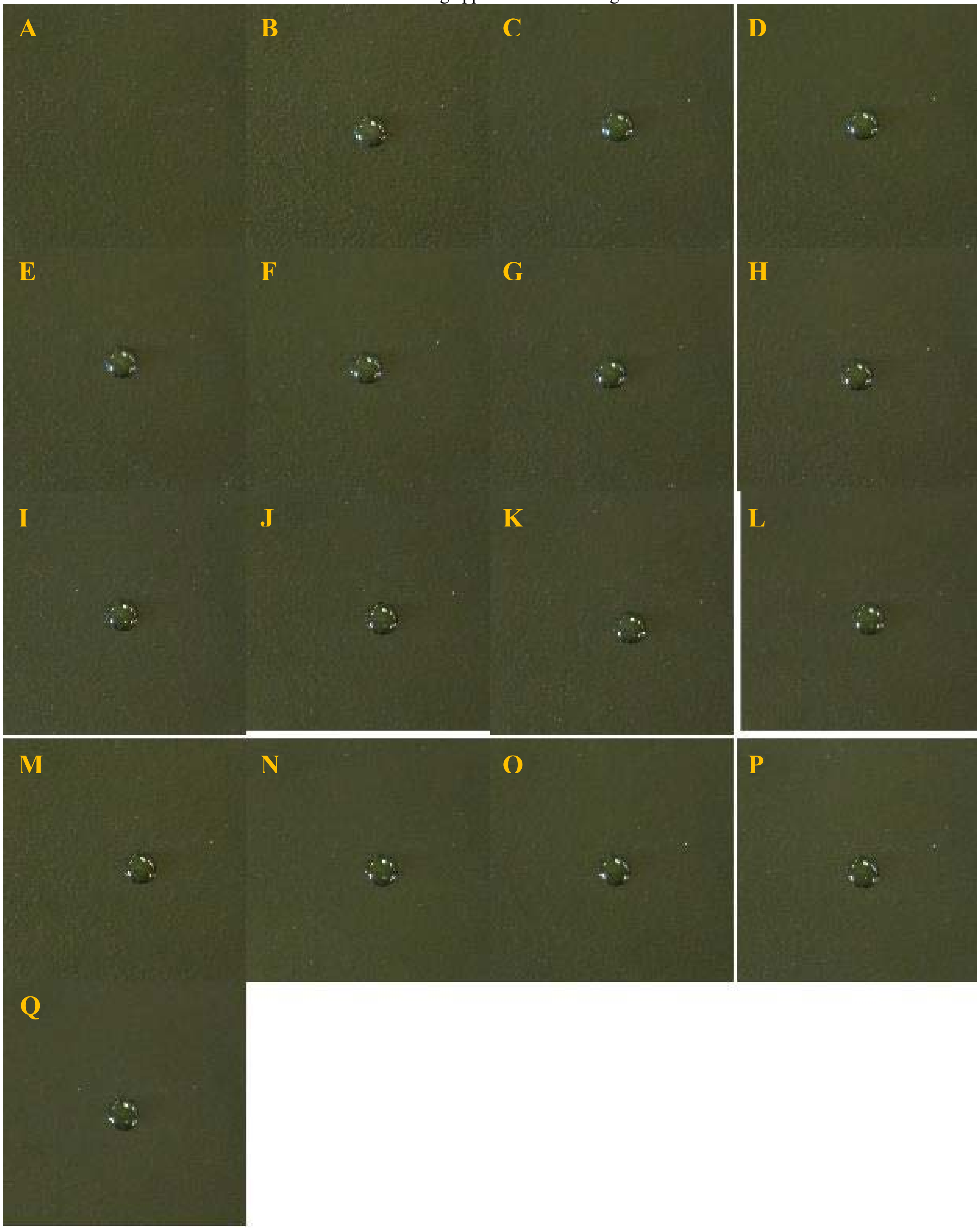
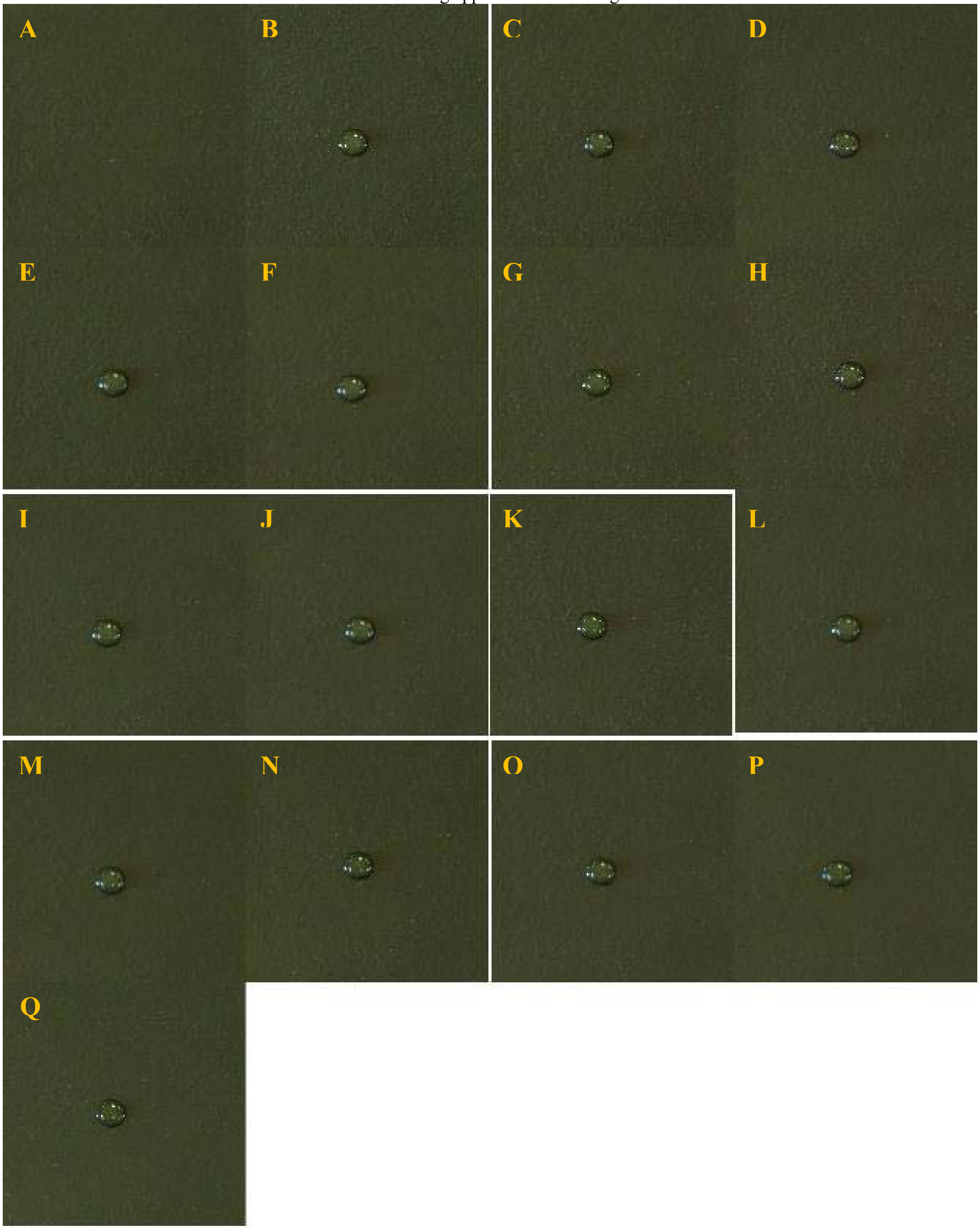


Fig. G3 — DMMP on SOCAL-ARSiO, as synthesized, 270 mm/min, no lubrication. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix H

EXTRACTED, 25 MM/MIN, PDMS OILED COUPON IMAGES

Fig. H1 — DFP on SOCAL-ARSiO, extracted, 25 mm/min, PDMS oiled. 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.

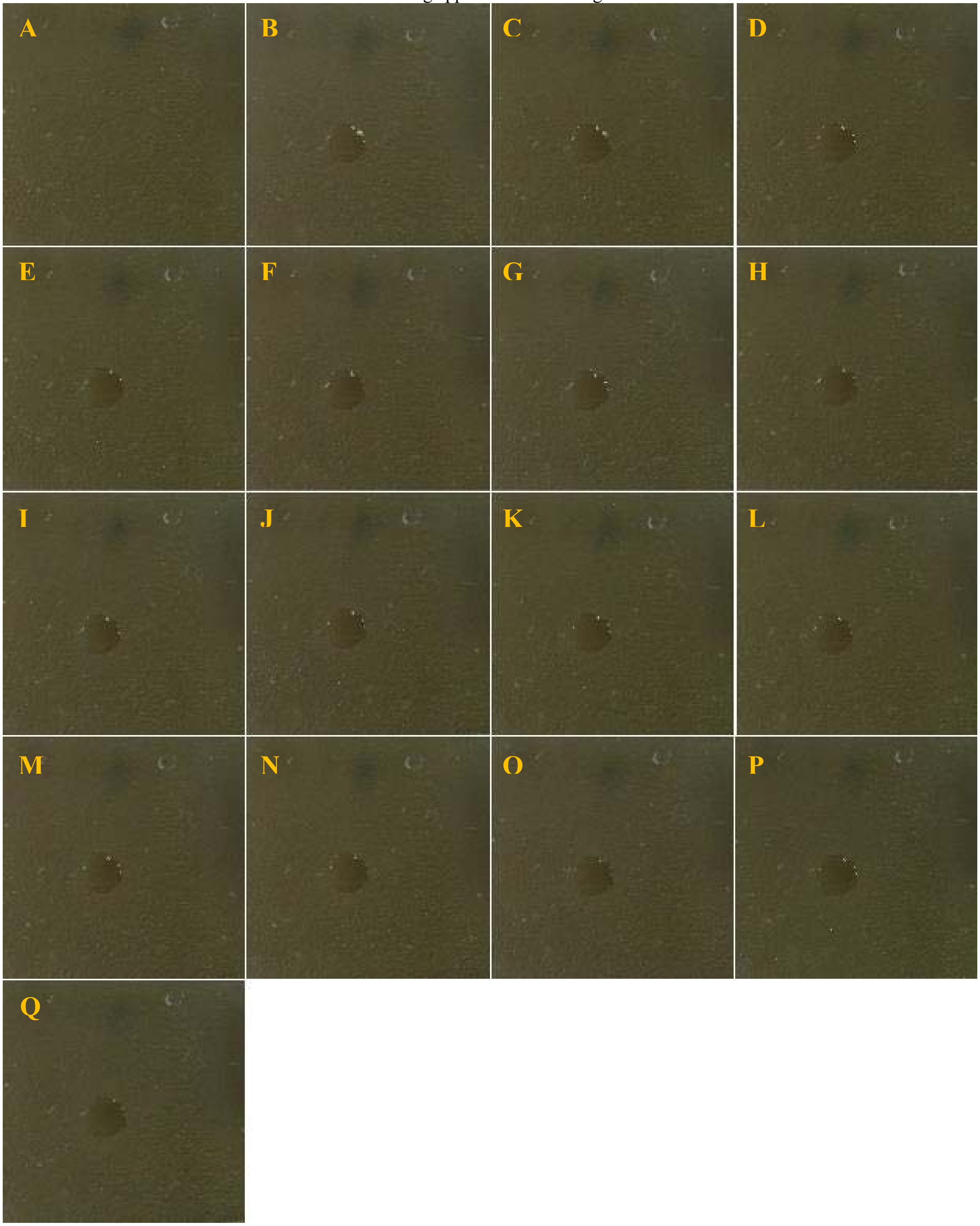


Fig. H2 — MES on SOCAL-ARSiO, extracted, 25 mm/min, PDMS oiled. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

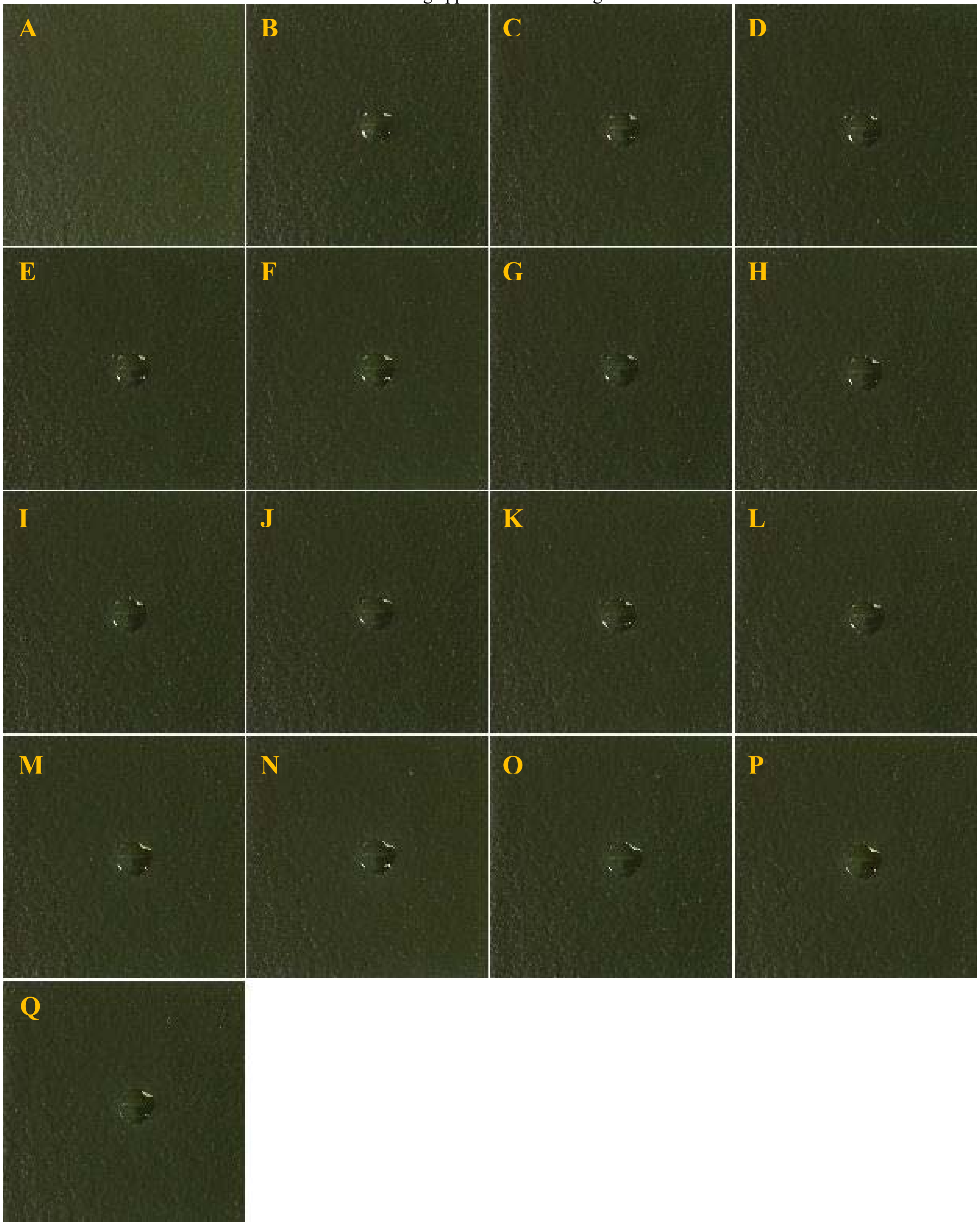
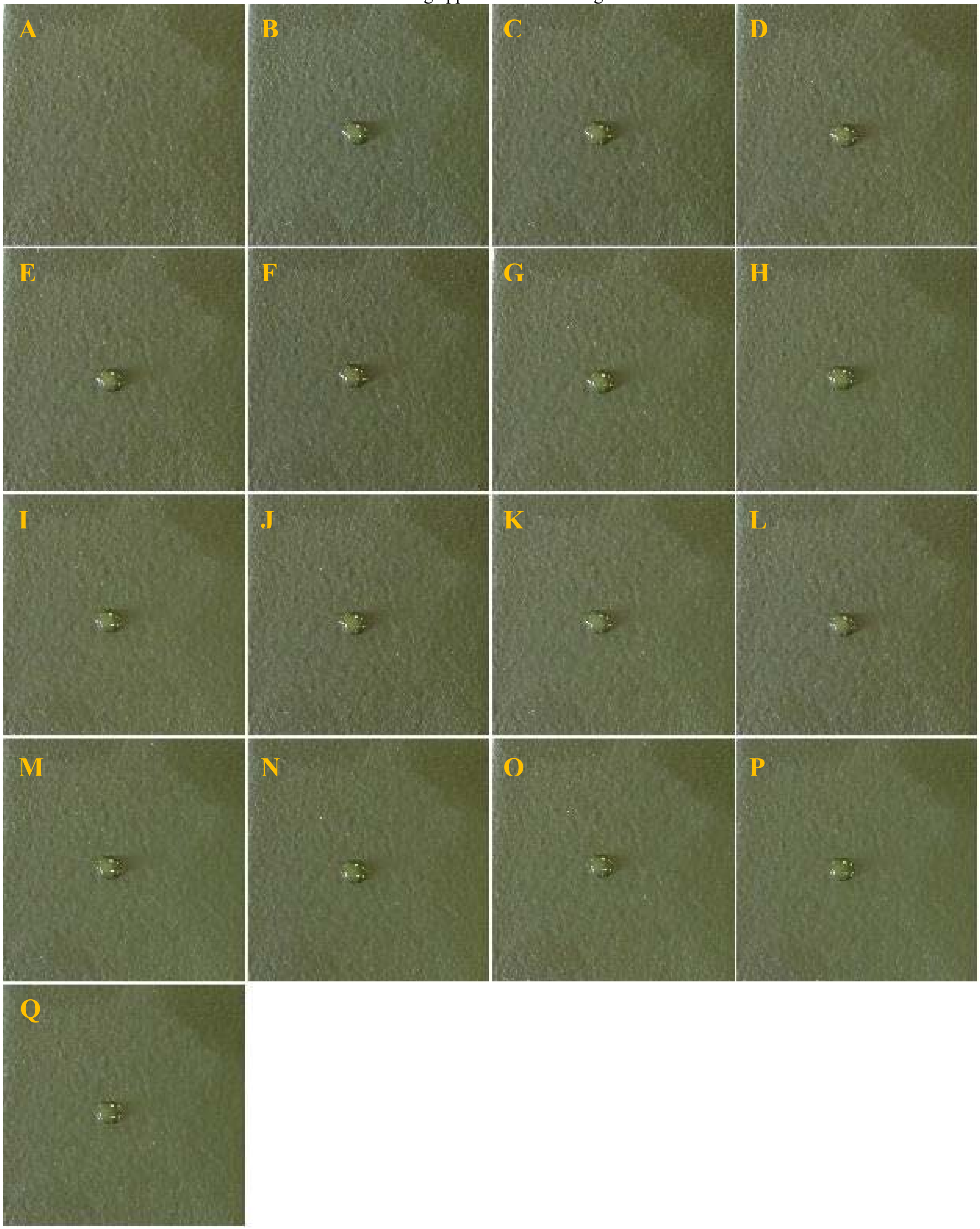


Fig. H3 — DMMP on SOCAL-ARSiO, extracted, 25 mm/min, PDMS oiled. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix I

EXTRACTED, 100 MM/MIN, PDMS OILED COUPON IMAGES

Fig. I1 — DFP on SOCAL-ARSiO, extracted, 100 mm/min, PDMS oiled. 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.

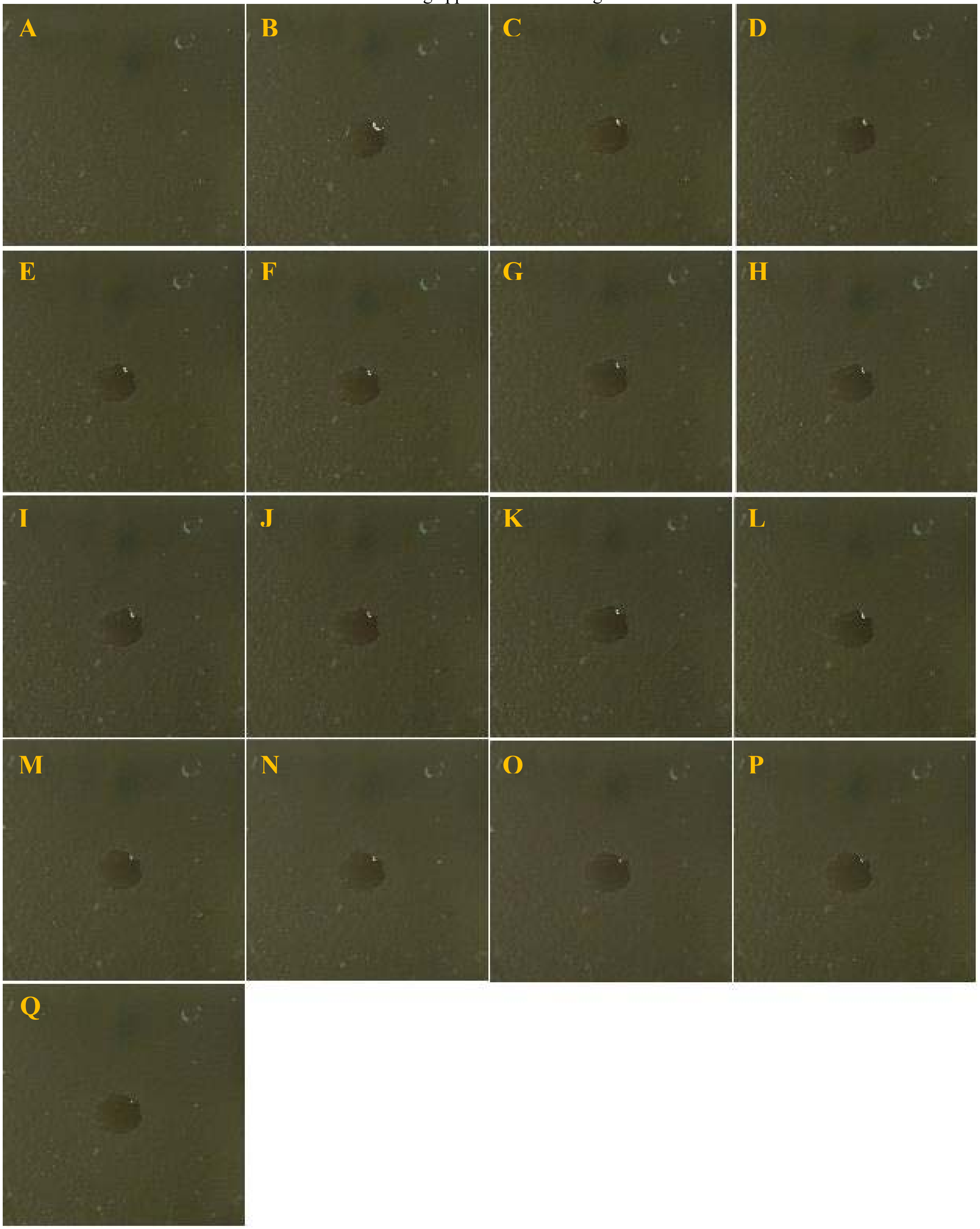


Fig. I2 — MES on SOCAL-ARSiO, extracted, 100 mm/min, PDMS oiled. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

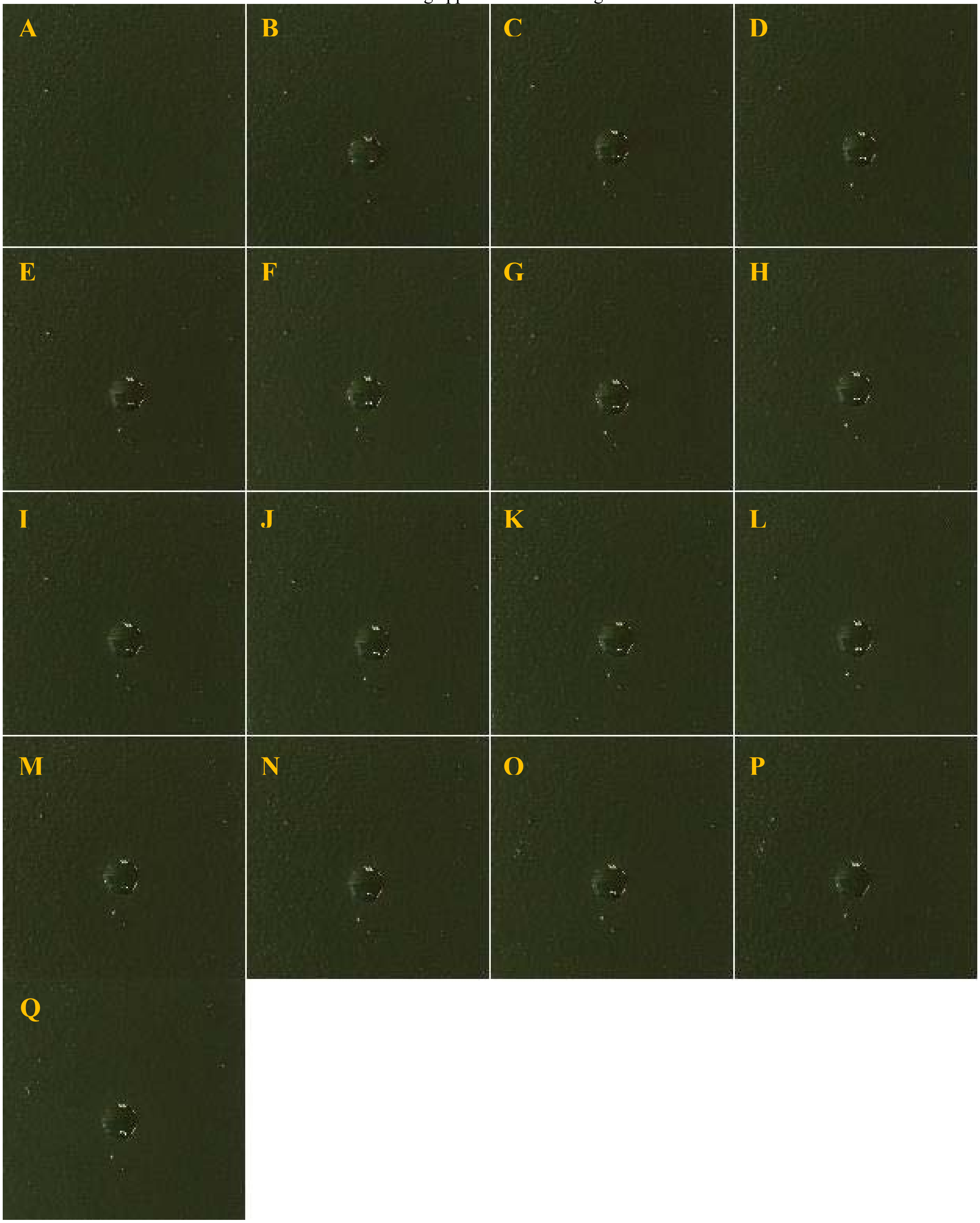
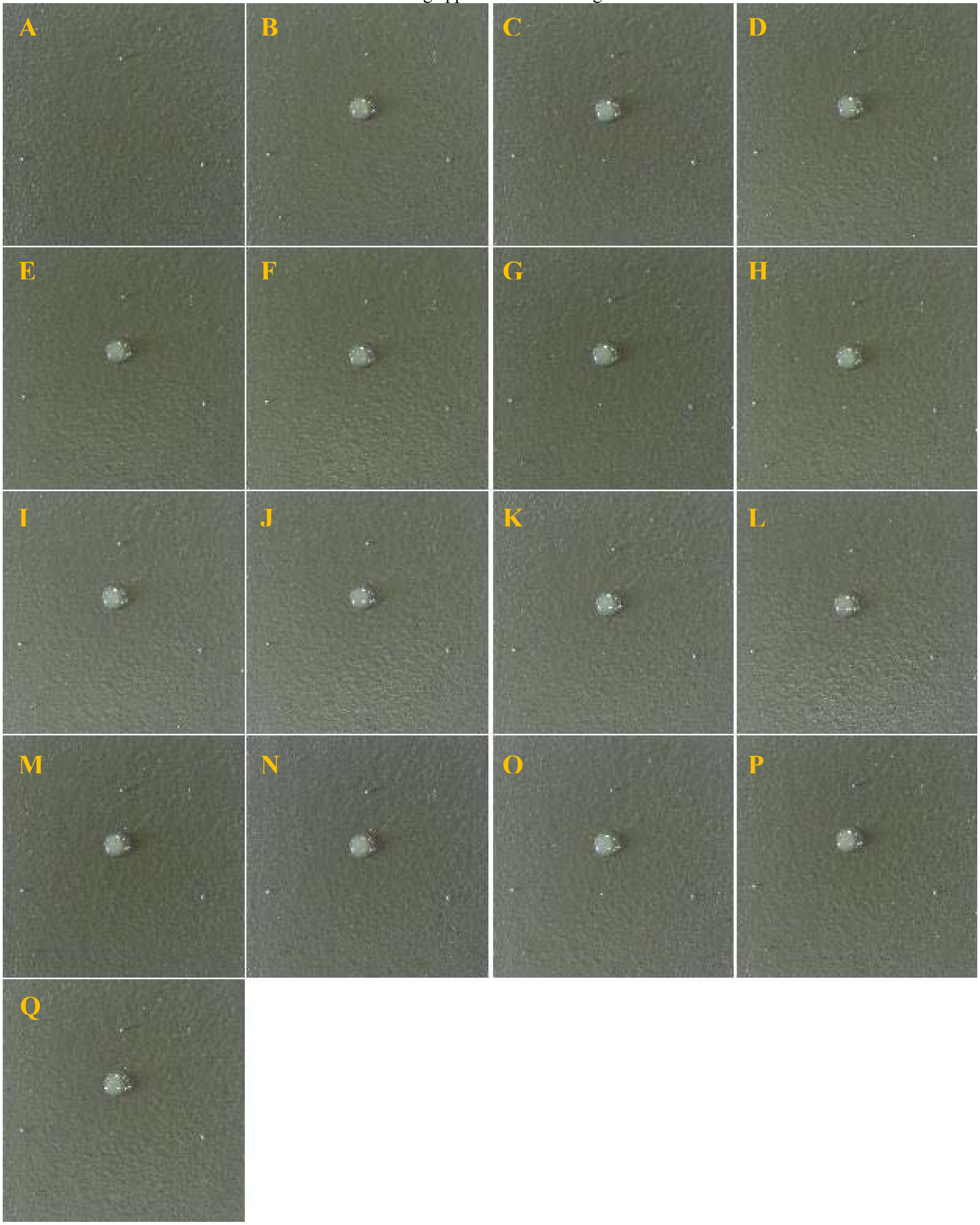


Fig. I3 — DMMP on SOCAL-ARSiO, extracted, 100 mm/min, PDMS oiled. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix J

EXTRACTED, 270 MM/MIN, PDMS OILED COUPON IMAGES

Fig. J1 — DFP on SOCAL-ARSiO, extracted, 270 mm/min, PDMS oiled. 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.

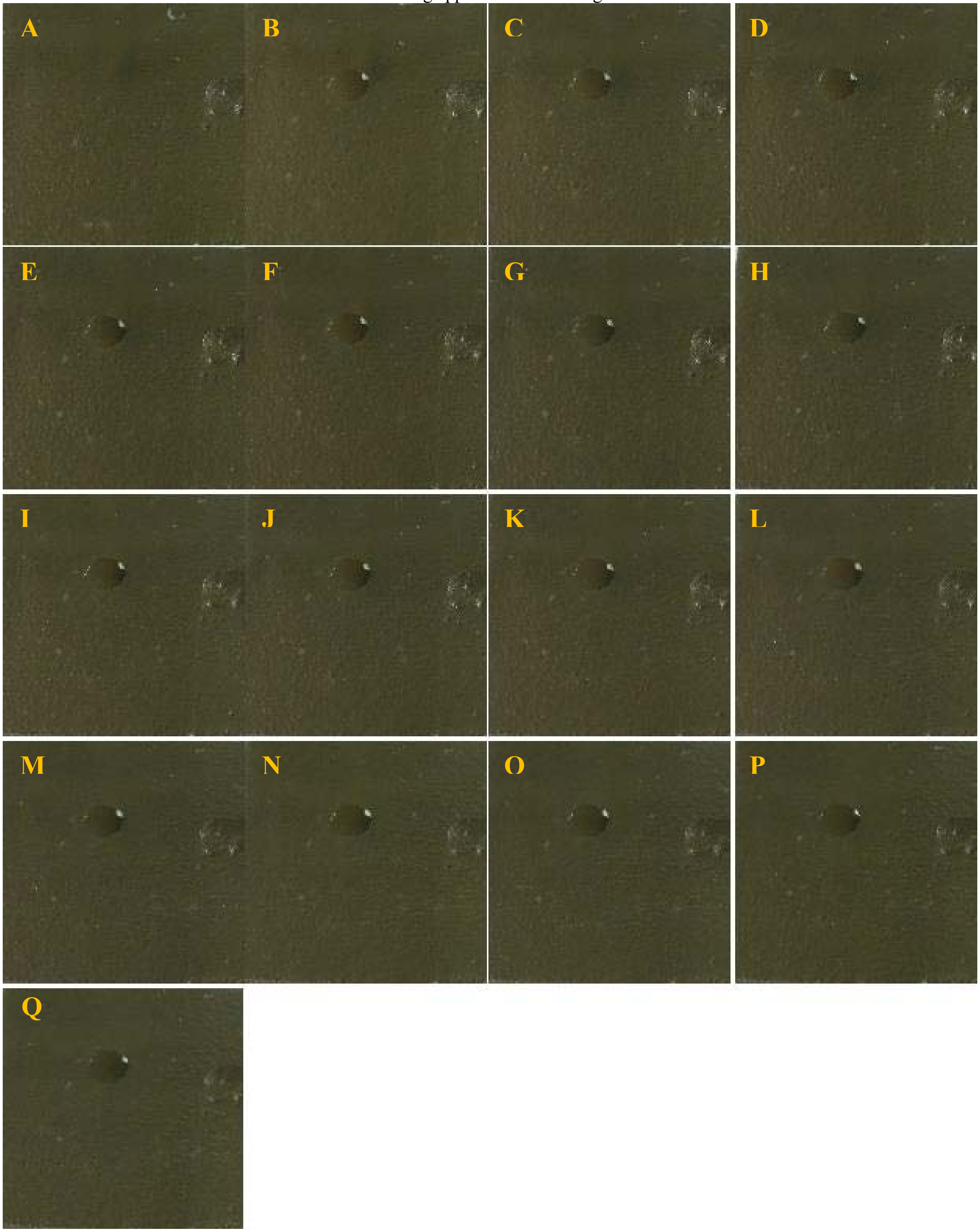


Fig. J2 — MES on SOCAL-ARSiO, extracted, 270 mm/min, PDMS oiled. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

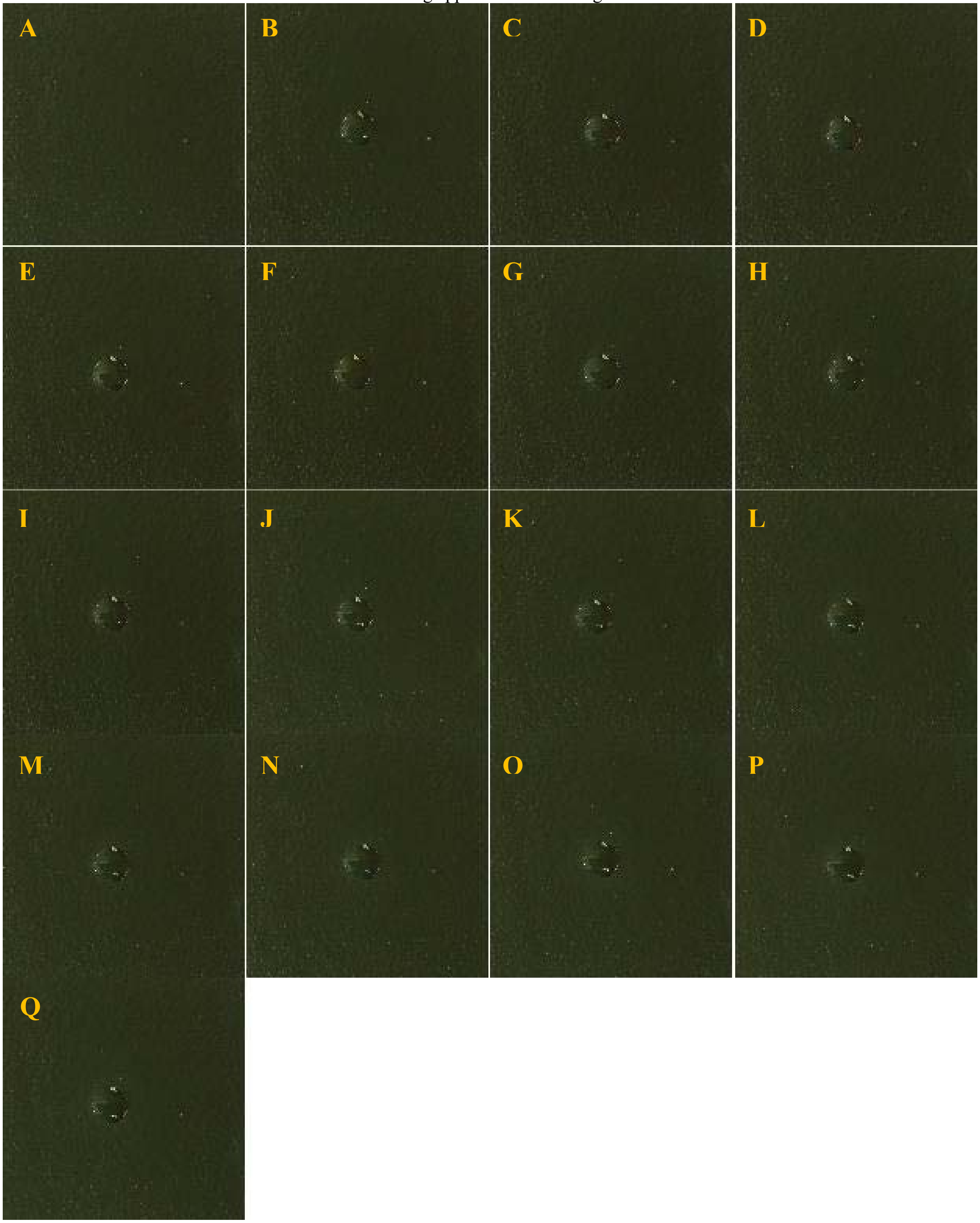
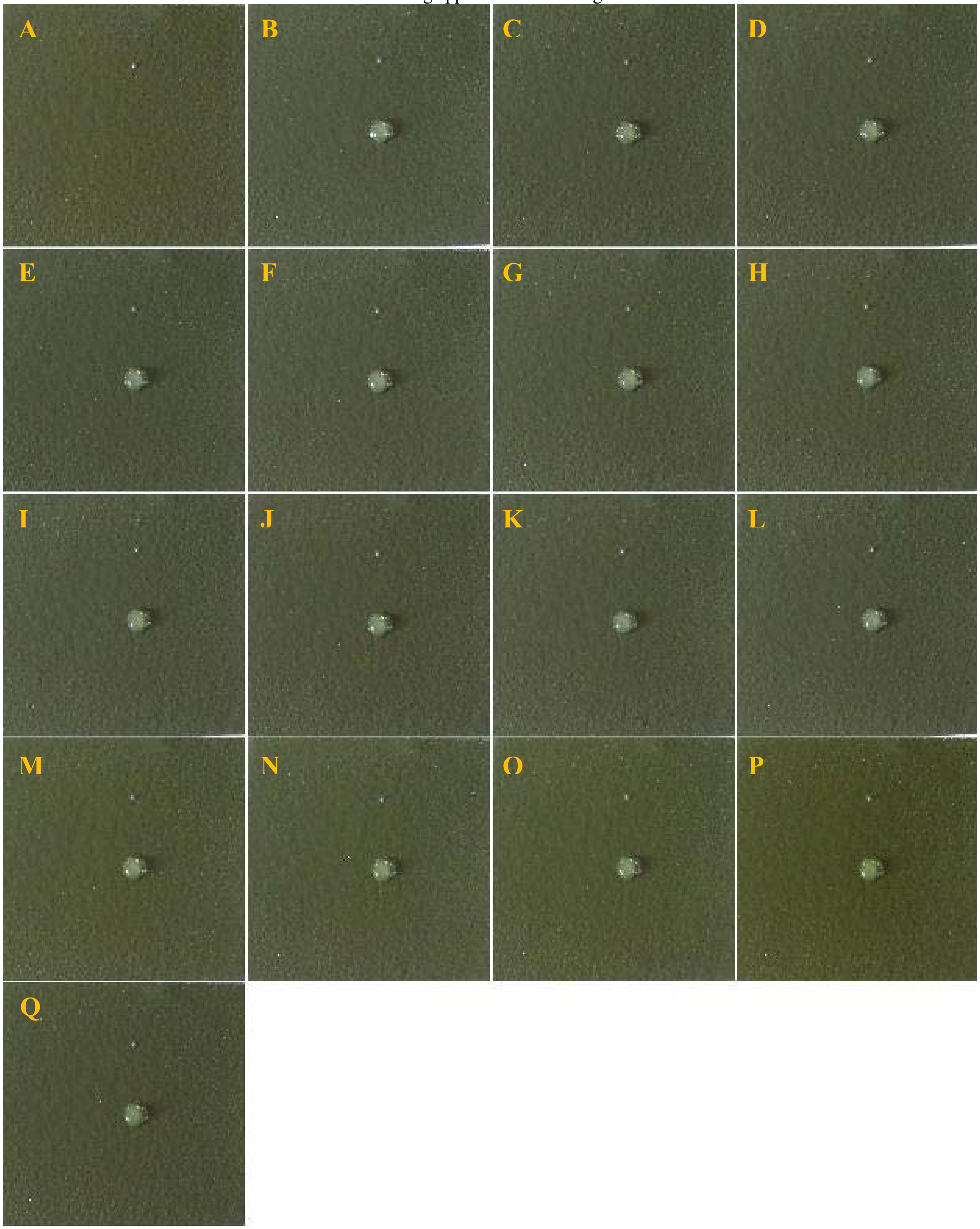


Fig. J3 — DMMP on SOCAL-ARSiO, extracted, 270 mm/min, PDMS oiled. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix K

AS SYNTHESIZED, 25 MM/MIN, PDMS OILED COUPON IMAGES

Fig. K1 — DFP on SOCAL-ARSiO, as synthesized, 25 mm/min, PDMS oiled. 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.

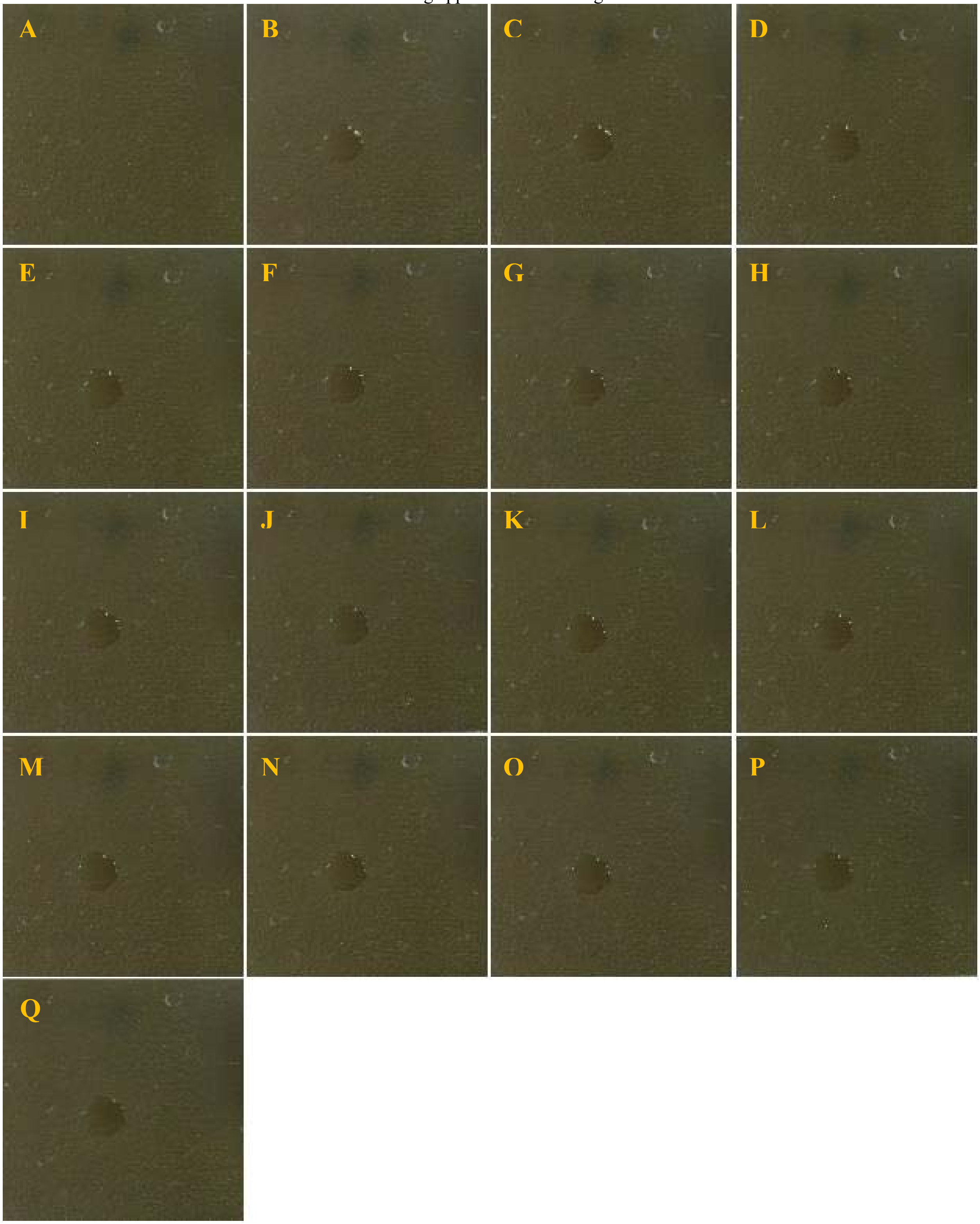


Fig. K2 — MES on SOCAL-ARSiO, as synthesized, 25 mm/min, PDMS oiled. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

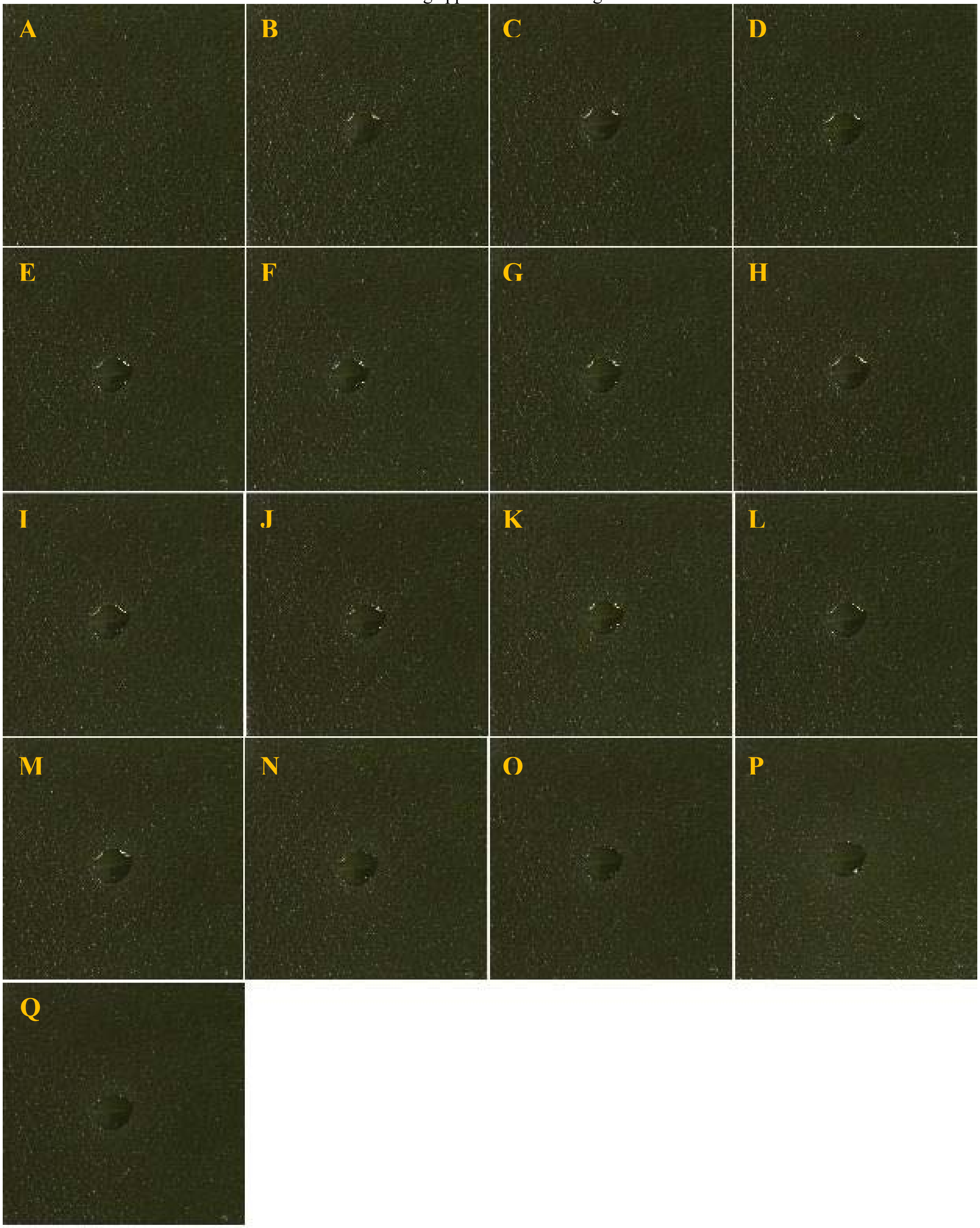
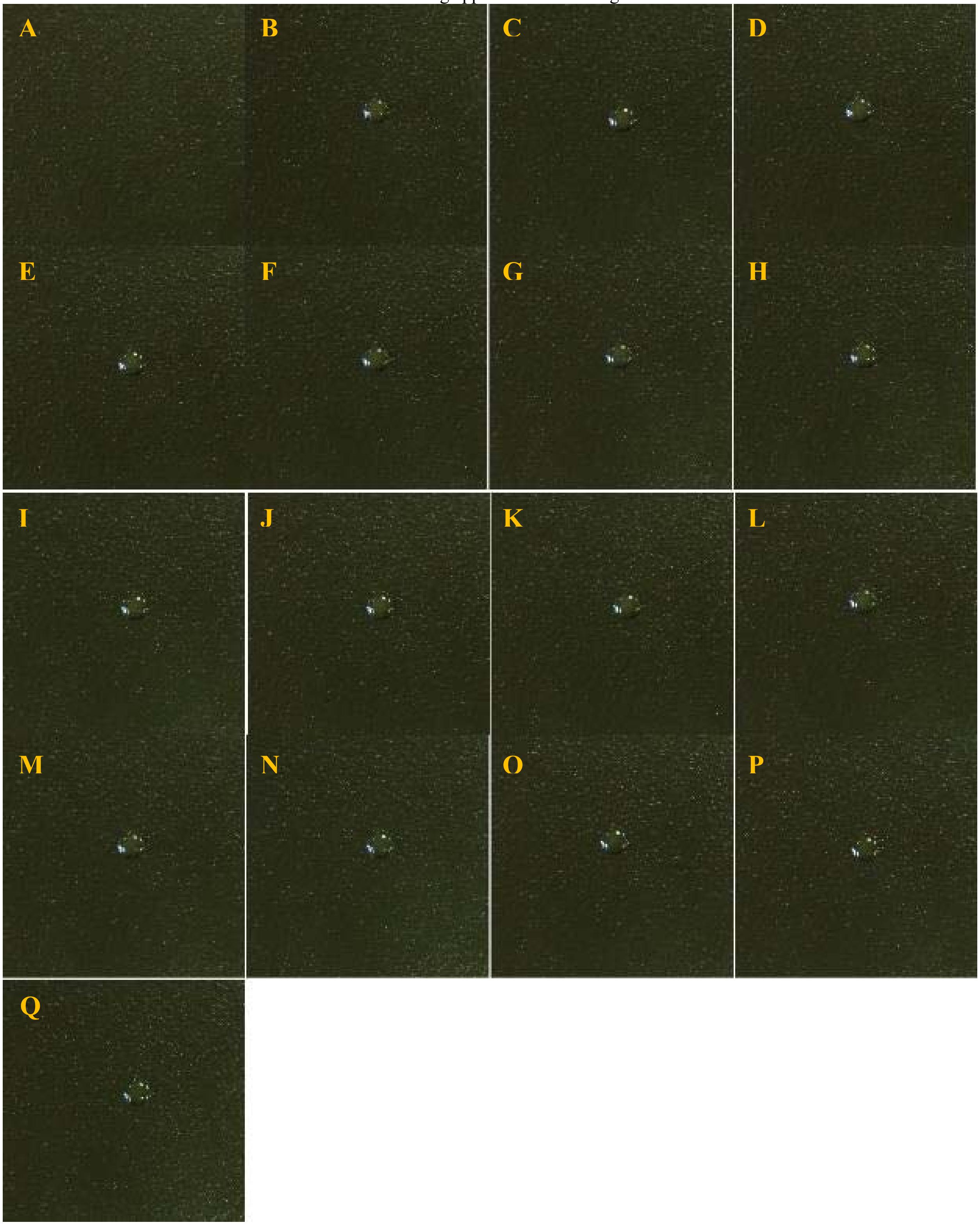


Fig. K3 — DMMP on SOCAL-ARSiO, as synthesized, 25 mm/min, PDMS oiled. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix L

AS SYNTHESIZED, 100 MM/MIN, PDMS OILED COUPON IMAGES

Fig. L1 — DFP on SOCAL-ARSiO, as synthesized, 100 mm/min, PDMS oiled. 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.

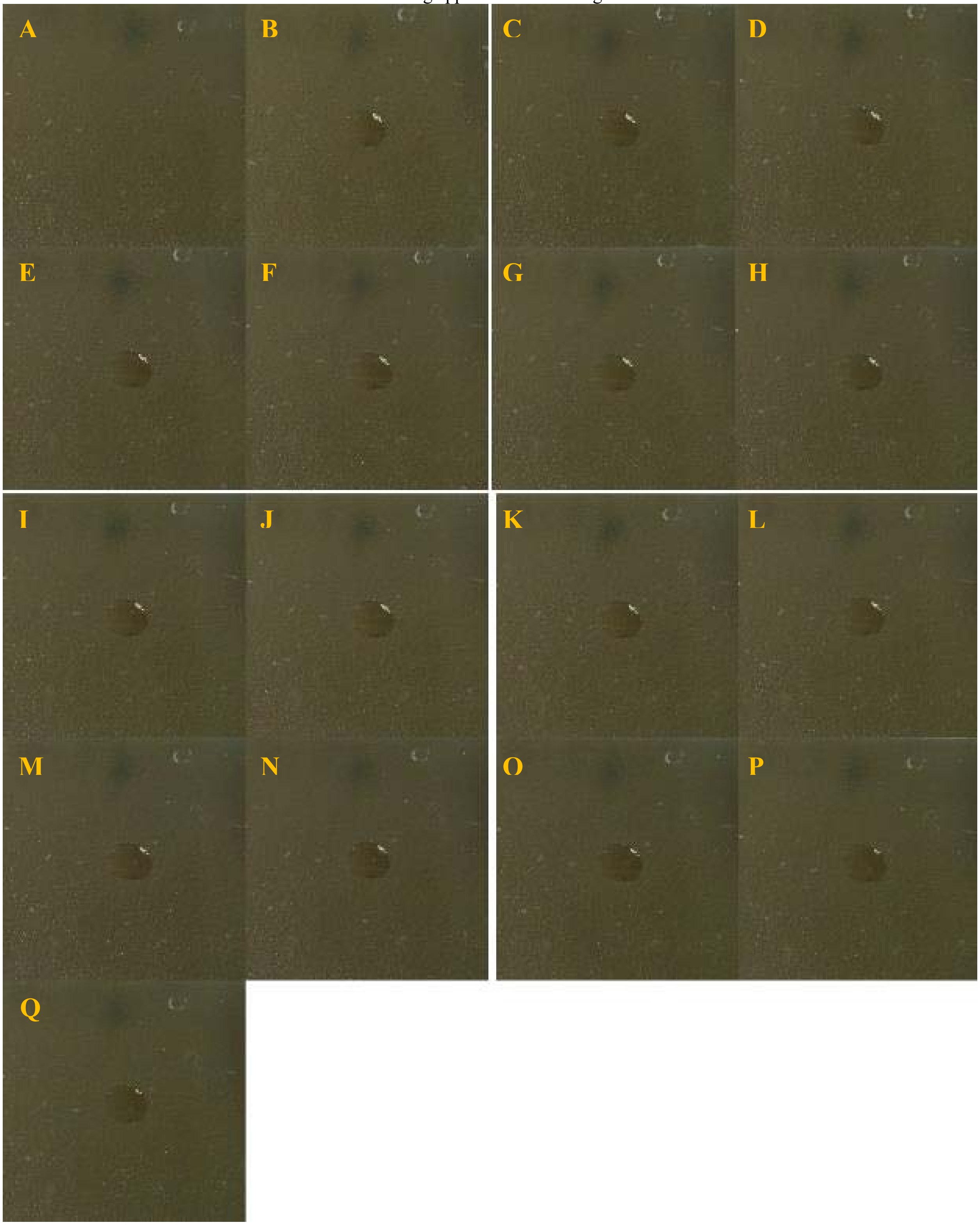


Fig. L2 — MES on SOCAL-ARSiO, as synthesized, 100 mm/min, PDMS oiled. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

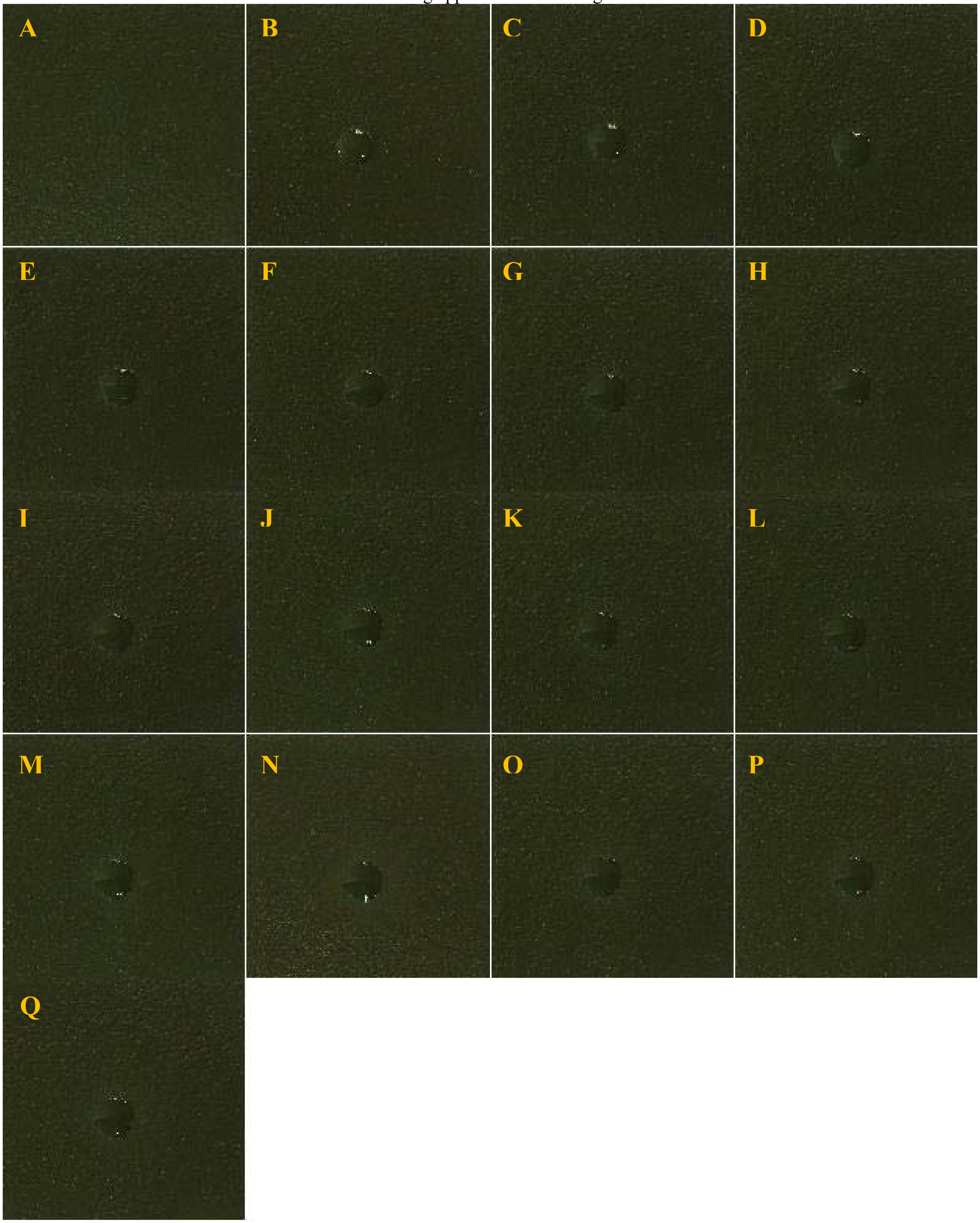
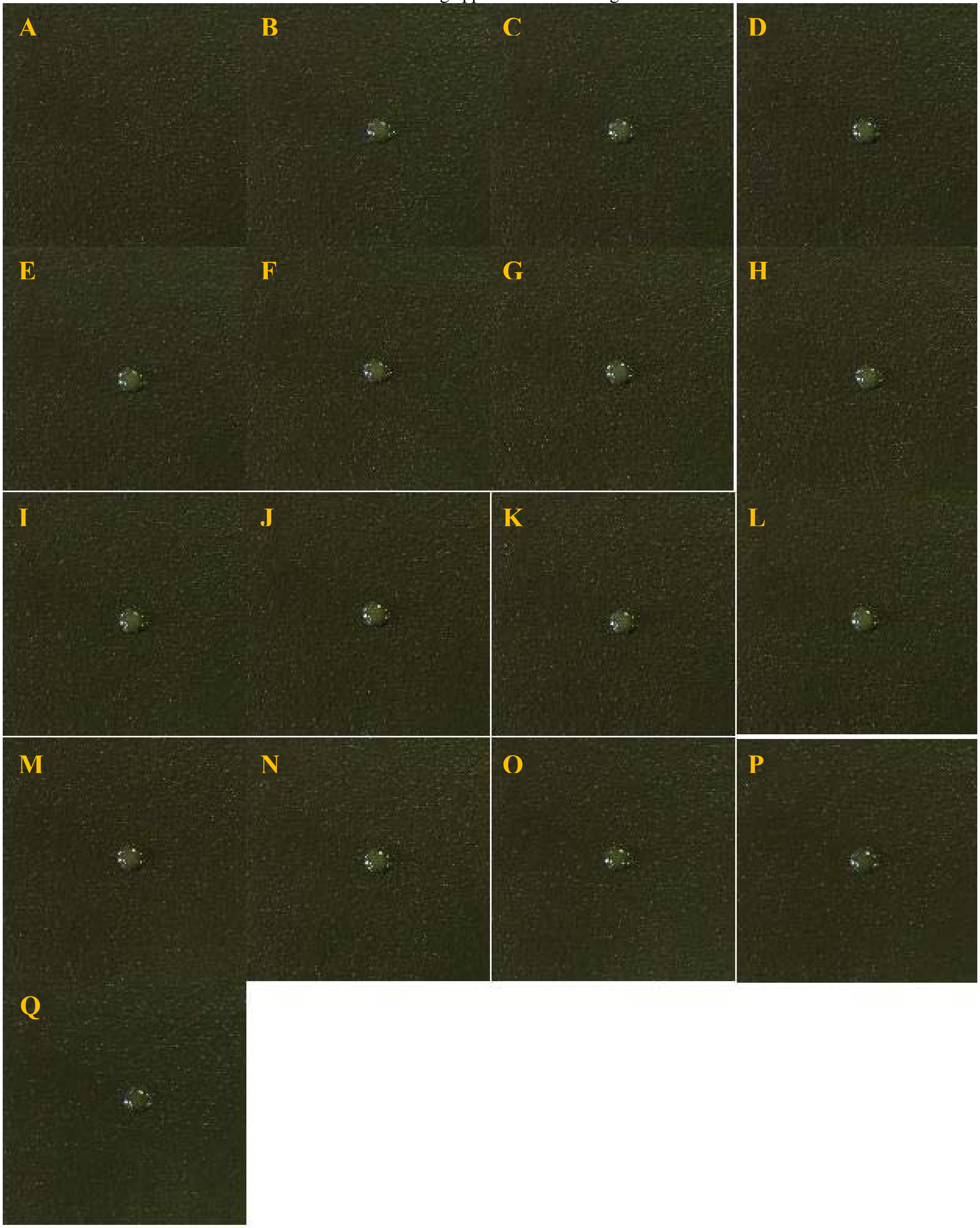


Fig. L3 — DMMP on SOCAL-ARSiO, as synthesized, 100 mm/min, PDMS oiled. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix M

AS SYNTHESIZED, 270 MM/MIN, PDMS OILED COUPON IMAGES

Fig. M1 — DFP on SOCAL-ARSiO, as synthesized, 270 mm/min, PDMS oiled. 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.

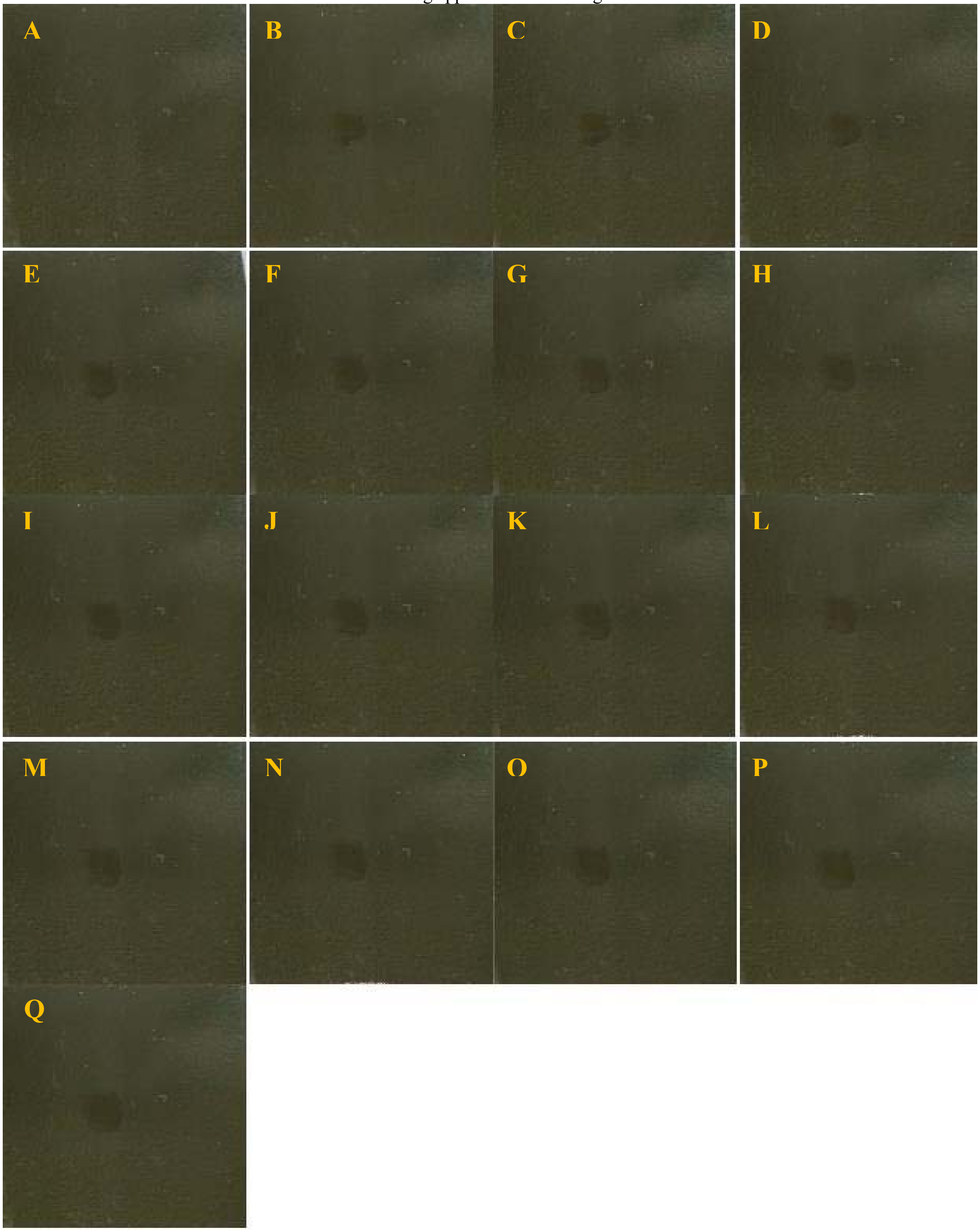


Fig. M2 — MES on SOCAL-ARSiO, as synthesized, 270 mm/min, PDMS oiled. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

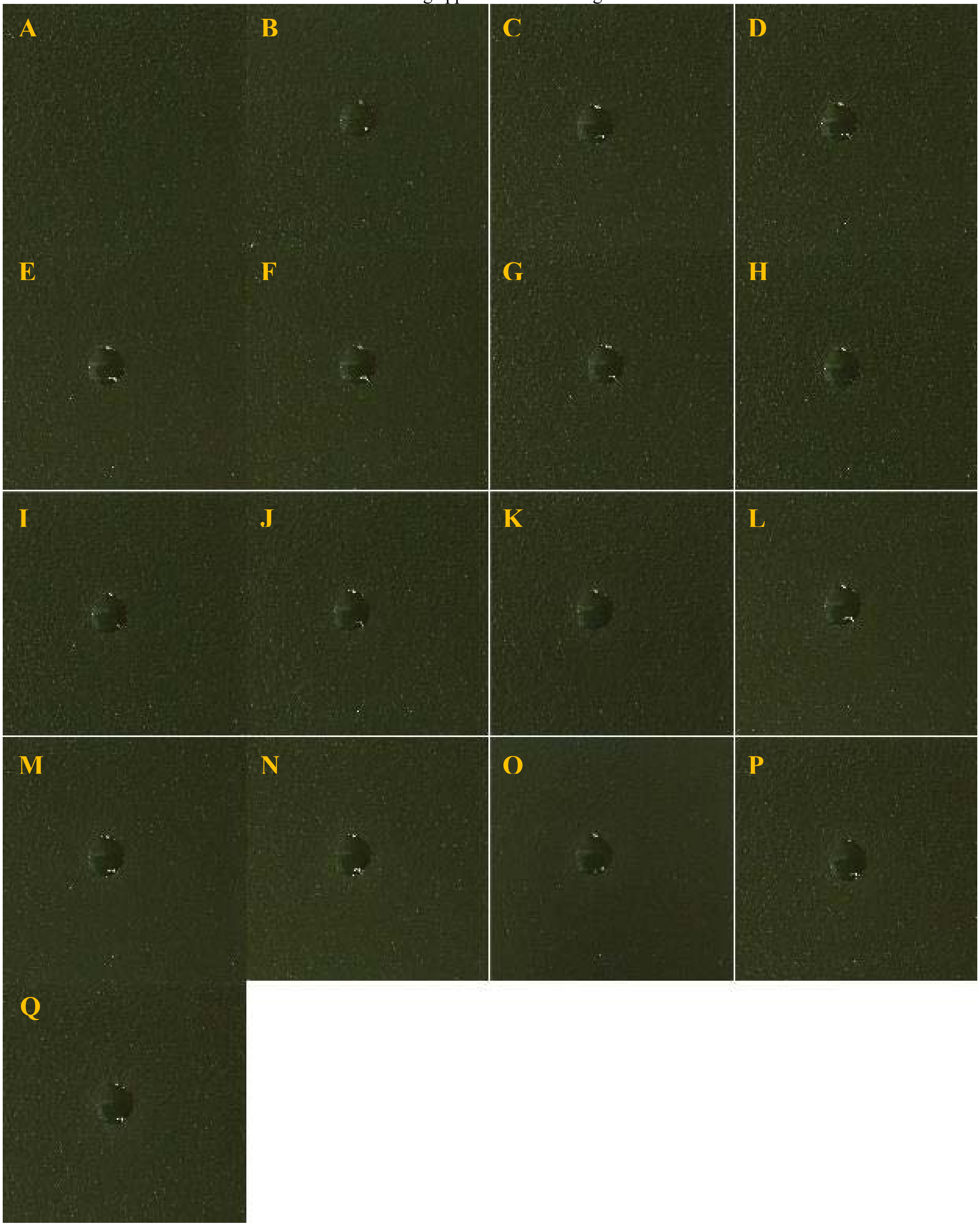


Fig. M3 — DMMP on SOCAL-ARSiO, as synthesized, 270 mm/min, PDMS oiled. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.