Naval Research Laboratory
Washington, DC 20375-5320

NRL/6306/MR—2022/11

Bioinspired Surface Treatments for Improved Decontamination: Cyanoacrylate Coatings II

ANTHONY P. MALANOSKI

The Biological and Bio-Inspired Advanced Materials Special Projects Group
Material Sciences Technology Division

BRANDY J. WHITE

Laboratory for the Study of Molecular Interfacial Interactions
Center for Bio/Molecular Science & Engineering

BRIAN J. MELDE

Laboratory for the Study of Molecular Interfacial Interactions
Center for Bio/Molecular Science & Engineering

MARTIN H. MOORE

Laboratory for the Study of Molecular Interfacial Interactions
Center for Bio/Molecular Science & Engineering

January 1, 2023

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
01-01-2023

2. REPORT TYPE
NRL Memorandum Report

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE

Bioinspired Surface Treatments for Improved Decontamination: Cyanoacrylate Coatings II

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
1C75

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Research Laboratory
4555 Overlook Avenue, SW
Washington, DC 20375-5320

8. PERFORMING ORGANIZATION REPORT NUMBER

NRL/6306/MR—2022/11

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Defence 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

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 top coat applications based on an approach adapted from published literature. The coatings are use a mixture of perfluorohexyltrichlorosilane (PFTS) and either n-butyl 2-cyanoacrylate or ethyl 2-cyanoacrylate. The approach can be used to produce multi-re-entrant surfaces on fabrics. Here, the materials were deposited on polyurethane paint coated aluminum coupons; the method is not expected to produce texture on the surfaces. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphonate, diisopropyl fluorophosphate, and 2-chloroethyl ethyl sulfide following treatment of contaminated surfaces with a soapy water solution is reported. Wetting behaviors and target droplet diffusion on the surfaces are also discussed.

15. SUBJECT TERMS

Coatings Decontamination
Paint

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Anthony Malanoski
U	U	U	U	72	**19b. TELEPHONE NUMBER** *(include area code)* (202) 404-5432

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

This page intentionally left blank.

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). This report details results for evaluation of top coat applications based on an approach adapted from published literature. The coatings are use a mixture of perfluorohexyltrichlorosilane (PFTS) and either *n*-butyl 2-cyanoacrylate or ethyl 2-cyanoacrylate. The approach can be used to produce multi-re-entrant surfaces on fabrics. Here, the materials were deposited on polyurethane paint coated aluminum coupons; the method is not expected to produce texture on the surfaces. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphonate, diisopropyl fluorophosphate, and 2-chloroethyl ethyl sulfide following treatment of contaminated surfaces with a soapy water solution is reported along with droplet diffusion on the surfaces and wetting angles.

This page intentionally left blank.

BIOINSPIRED SURFACE TREATMENTS FOR IMPROVED DECONTAMINATION: CYANOACRYLATE COATINGS

INTRODUCTION

The DoD Chemical and Biological Defense Program (CBDP) seeks to provide protection of forces in a contaminated environment including contamination avoidance, individual protection, collective protection, and decontamination. In January 2015, the Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) began an effort funded through the Defense Threat Reduction Agency (DTRA, CB10125) intended to evaluate top-coat type treatments suitable for application to painted surfaces for reduction of chemical threat agent retention 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 type of identified technology.

A recent publication described multi-re-entrant, hierarchically structured coatings based on fluorosilanes and cyanoacrylates.[1] The coatings can be applied using spray or immersion techniques. The coatings are described as transparent, robust, mechanically durable, and self-healing. They offer repellence to liquids, including those with low surface tension. The hierarchical structures are organized across local domains and can be applied to a wide range of support materials including fabrics. While described for liquid repellence with a focus on anti-ice coatings, these characteristics may also offer advantages to the application under consideration here.

A previous study evaluated two types of coating; PFTS-BCA used perfluorohexyltrichlorosilane (PFTS) with *n*-butyl 2-cyanoacrylate while PFTS-ECA used PFTS with ethyl 2-cyanoacrylate.[2] These acrylate derivatives are used in medical grade (BCA) and other adhesive products. This study focuses on variations in the syntheses of PFTS-ECA coatings and the use of a secondary spray coating after initial dip –coating. The initial coatings deposition method used only a dip-coating process that was not expected to produce the textures described for other deposition methods.[1] The use of spray coating was explored to determine the impact of such an application method. It is one of the application methods that can be used for real applications and as such the effect of altering the application method for a coating from the methodology used in initial testing to spray coating needed to be measured. These coatings represent a system that performed reasonably well, had more variations to explore for improvement of performance, and could be adapted to being applied via a spray coating technique.

For the complete evaluated systems, aluminum coupons were coated with a polyurethane paint system. The coatings were applied to this support material following an accelerated cure process. Materials were evaluated using standard approaches including measurement of sessile, sliding, and shedding contact angles and quantification of retention for the simulant compounds. The coatings had little impact on the visible characteristics of the coupons (Figure 1).

Manuscript approved December 19, 2022.

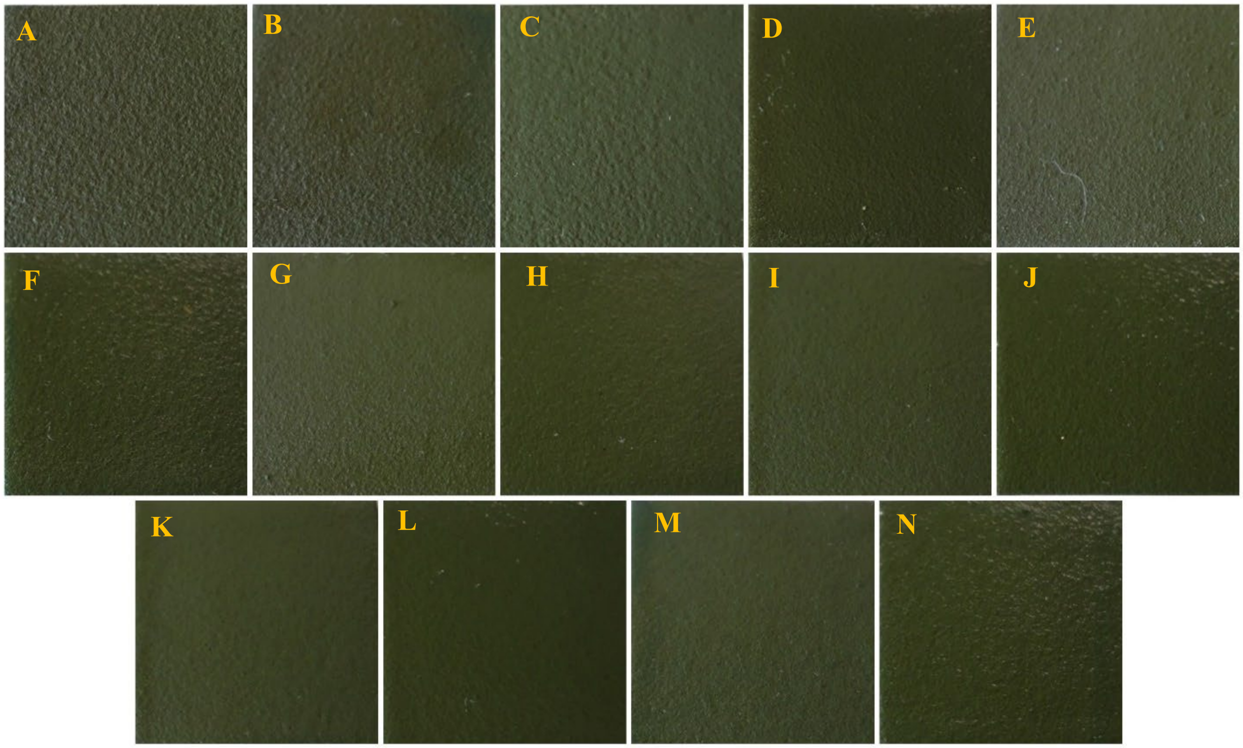


Fig. 1 — Images of a painted coupon with PFTS (Dip) (A), PFTS (Spray) (B), PFTS-TEOS (dip) (C), PFTS-TEOS (Spray) (D), PFTS-ECA (Dip, V.low) (E), PFTS-ECA (Spray,V.low) (F), PFTS-ECA (Dip, low) (G), PFTS-ECA (Spray, low) (H), PFTS-ECA (Dip, Med) (I), PFTS-ECA (Spray, Med) (J), PFTS-ECA (Dip, High) (K), PFTS-ECA (Spray,High) (L), PFTS-ECA (Dip, V. high) (M), and PFTS-ECA (Spray,V.high) (N).

METHODS

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

Simulant exposure and evaluation methods were based on the tests developed by Edgewood Chemical Biological Center referred to as Chemical Agent Resistance Method (CARM).[3] Standard target exposures utilized a challenge level of 10 g/m^2. The painted coupons were 0.00101 m^2; the 10 g/m^2 target challenge was applied to the surfaces as two equally sized neat droplets. Following application of the target, coupons were aged 1 h prior to use of a gentle stream of air to expel target from the surface. Samples were then rinsed with soapy water (0.59 g/L Alconox in deionized water). The rinsed coupons were soaked in isopropanol for 30 min to extract remaining target; this isopropanol extract was analyzed by the appropriate chromatography method to determine target retention on the surface.

For analysis of paraoxon, methyl salicylate (MES), diisopropyl fluorophosphate (DFP), dimethyl methylphosphonate (DMMP), and 2-chloroethyl ethyl sulfide (CEES), gas chromatography-mass spectrometry (GC-MS) was accomplished using a Shimadzu GCMS-QP2010 with AOC-20 auto-injector equipped with a Restex Rtx-5 (30 m x 0.25 mm ID x 0.25 μm df) cross bond 5% diphenyl 95% dimethyl polysiloxane column. A GC injection temperature of 200°C was used with a 1:1 split ratio at a flow rate of 3.6 mL/min at 69.4 kPa. The oven gradient ramped from 50°C (1 min hold time) to 180°C at 15°C/min and then to 300°C at 20°C/min where it was held for 5 min.

Coating Synthesis.

Synthesis of the cyanoacrylate coatings was adapted from a published report.[1] For original ECA coating, painted coupons were rinsed with 2-propanol and dried at 65 ºC. Coupons were then soaked (5 min) in 20 wt % PFTS (nonafluorohexyltrichlorosilane) in dichloropentafluoropropane, with ~10 mg/mL ECA (ethyl 2-cyanoacrylate). Coated substrates were cured at 70 ºC for 2 h.

Some coupons were subjected to coverage with TEOS before the PFTS/ECA mixture was used to coat the surface using the following procedure. A sol was prepared from 184 mL 2-propanol, 6 mL tetraethyl orthosilicate (TEOS), and 10 mL NH4OH (~ 30% in H2O reagent) at RT. It was mixed briefly and divided into 2 separate 240 mL PFA jars. 4 painted Al coupons were immersed in each jar, leaning vertically against inside walls, for 10 min at RT. Soaked coupons were then heated in an oven at 65 ℃ for 30 min. The procedure was repeated twice, for a total of 3 cycles of immersion and heating, with coupons left in the oven at 65 ℃ over-night for the final curing step.

For all coupon variants prepared in the current study, the following procedure was used. Each variant used different amounts of PFTS and ECA as listed in table 1. In a 120 mL PFA jar, the quantities of PFTS and ECA for the particular variant was dissolved in 20 g solvent with magnetic stirring at RT for 30 min. painted Al coupons or TEOS/paint coupons were immersed in the solution for 5 min each at RT. They were stored in Fluoroware and heated in an oven at 70 °C for 3 h.

Table 1 – Dip coating: Quantities of PFTS, ECA, and solvent for each variant

Coupon	PFTS	ECA	Solvent
PFTS (Dip)	5 g	0 g	20 g
PFTS-TEOS (Dip)	5 g	0 g	20 g
PFTS (Dip,Very Low)	5 g	0.05 g	20 g
PFTS (Dip,Low)	5 g	0.1 g	20 g
PFTS (Dip, Medium)	5 g	0.119 g	20 g
PFTS (Dip, Hi)	5 g	0.15 g	20 g
PFTS (Dip,Very Hi)	5 g	0.16 g	20 g

Some of each coating was then given a spray coating using the following procedure. Each variant used different amounts of PFTS and ECA as listed in table 2. In a 120 mL PFA jar, the quantities of PFTS and ECA for the particular variant was dissolved in 40 g solvent with magnetic stirring at RT for 30 min. Dip-coated PFTS/paint or dip-coated PFTS-TEOS/paint substrates prepared with the quantities of the same labeled variant type were set in an open shallow cardboard box with double-sided tape. They were spray-coated with the prepared solution, using a Paasche airbrush for 2 min at ~ 40-50 psi at a distance ~ 20 cm. The coated substrates were stored in Fluoroware and heated in an oven at 70 °C for 3 h.

Table 2 – Spray coating: Quantities of PFTS, ECA, and solvent for each variant

Coupon	PFTS	ECA	Solvent
PFTS (Spray)	10 g	0 g	40 g
PFTS-TEOS (Spray)	10 g	0 g	40 g
PFTS (Spray,Very Low)	10 g	0.1 g	40 g
PFTS (Spray,Low)	10 g	0.2 g	40 g
PFTS (Spray, Medium)	10 g	0.238 g	40 g
PFTS (Spray, Hi)	10 g	0.3 g	40 g
PFTS (Spray,Very Hi)	10 g	0.32 g	40 g

RESULTS

Analysis of the support surface in the absence of additional coatings provides a point of comparison for evaluating the benefits of the surface treatment. Each table includes data on the relevant support material, a painted aluminum coupon, as well as that for a Fomblin Y oiled painted aluminum coupon. The fluorinated oil reduces the surface energy of the coupons (Table 3 and Figure 2). Application of the PFTS-ECA coating variants significantly reduced the surface energy of the painted coupon, increasing contact angles for water and ethylene glycol. The original PFTS-ECA formulation has the lowest observed surface energy with a higher ethylene glycol contact angle and a similar water contact angle. Variants had surface energies mostly between the low of the original and that observed for Fomblin Y coated surfaces with contact angles trending higher but still lower than that seen for original PFTS-ECA sample. Sliding behaviors were not observed on any of the coupons. While shedding was observed for the oiled coupon, it was not observed on any of the PFTS coatings. Spray coated samples tended to have higher surface energies. For three of the variants, the increase was small while another two had slightly larger differences and the final two cases saw a much larger increase in surface energy between dip coating and spray coating.

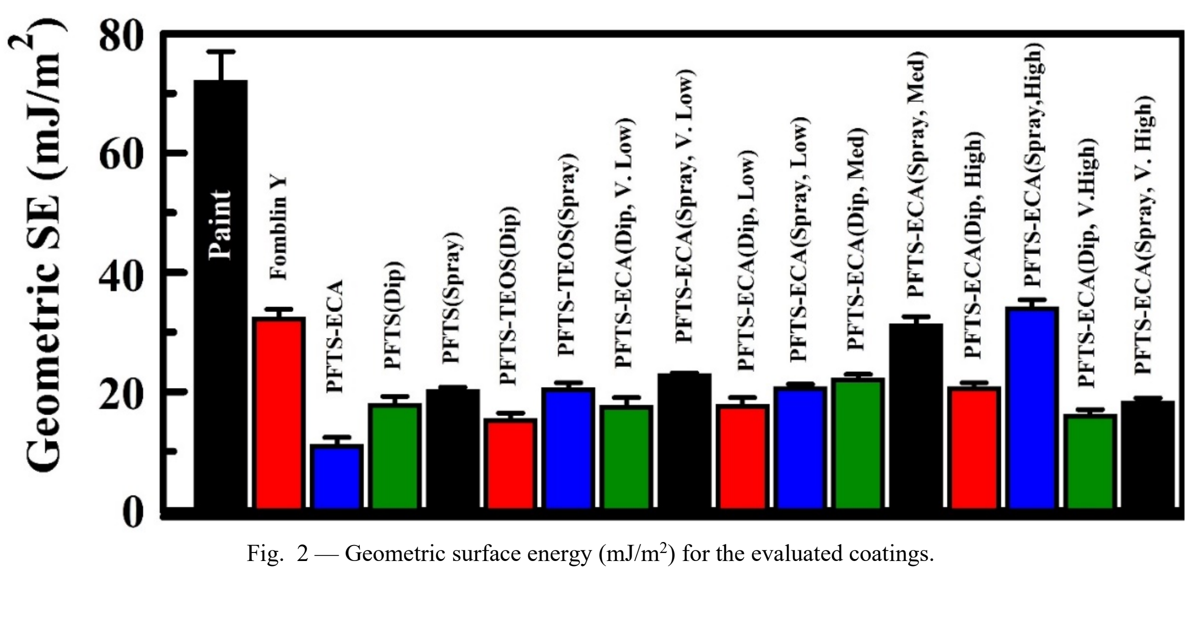


Fig. 2 — Geometric surface energy (mJ/m^2) for the evaluated coatings.

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

Coupon	**Liquid**	**Sessile Angle**	**Sliding Angle**	**Shedding Angle**	**Geometric Surface Energy (mJ/m²)**
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	
PFTS-ECA[4]	water	104.8 ± 1.7	>60	>60	10.8 ± 1.5
	ethylene glycol	96.6 ± 2.1	>60	>60	
	n-heptane	--	--	--	
PFTS (Dip)	water	95.0 ± 0.99	>60	>60	17.7 ± 1.5
	ethylene glycol	86.6 ± 1.4	>60	>60	
	n-heptane	--	--	--	
PFTS (Spray)	water	93.7 ± 0.40	>60	>60	20.0 ± 0.74
	ethylene glycol	74.0 ± 0.94	>60	>60	
	n-heptane	--	--	--	
PFTS-TEOS (Dip)	water	95.1 ± 1.6	>60	>60	15.2 ± 1.2
	ethylene glycol	86.8 ± 1.7	>60	>60	
	n-heptane	--	--	--	
PFTS-TEOS (Spray)	water	94.8 ± 0.93	>60	>60	20.3 ± 1.2
	ethylene glycol	79.6 ± 0.86	>60	>60	
	n-heptane	--	--	--	
PFTS-ECA (Dip, V. Low)	water	92.9 ± 1.4	>60	>60	17.4 ± 1.6
	ethylene glycol	85.7 ± 1.9	>60	>60	
	n-heptane	--	--	--	
PFTS-ECA (Spray, V. Low)	water	92.3 ± 0.46	>60	>60	22.7 ± 0.42
	ethylene glycol	69.1 ± 0.44	>60	>60	
	n-heptane	--	--	--	
PFTS-ECA (Dip, Low)	water	98.3 ± 2.3	>60	>60	17.5 ± 1.5
	ethylene glycol	79.5 ± 1.3	>60	>60	
	n-heptane	--	--	--	
PFTS-TEOS (Spray, Low)	water	89.2 ± 2.5	>60	>60	20.5 ± 0.73
	ethylene glycol	72.2 ± 0.87	>60	>60	
	n-heptane	--	--	--	
PFTS-ECA (Dip, Medium)	water	103.1 ± 1.0	>60	>60	21.9 ± 1.0
	ethylene glycol	78.7 ± 0.42	>60	>60	
	n-heptane	--	--	--	
PFTS-ECA (Spray, Medium)	water	98.6 ± 0.98	>60	>60	31.0 ± 1.6
	ethylene glycol	68.4± 0.60	>60	>60	
	n-heptane	--	--	--	
PFTS-ECA (Dip, High)	water	91.7 ± 1.2	>60	>60	20.5 ± 1.0
	ethylene glycol	72.7 ± 1.3	>60	>60	
	n-heptane	--	--	--	
PFTS-ECA (Spray, High)	water	94.2 ± 0.83	>60	>60	33.9 ± 1.5
	ethylene glycol	63.3 ± 0.51	>60	>60	
	n-heptane	--	--	--	
PFTS-ECA (Dip, Very High)	water	96.6 ± 0.80	>60	>60	15.9 ± 1.1
	ethylene glycol	87.7 ± 1.3	>60	>60	
	n-heptane	--	--	--	
PFTS-TEOS (Spray, Very High)	water	92.1 ± 0.46	>60	>60	18.1 ± 0.82
	ethylene glycol	78.1 ± 2.1	>60	>60	
	n-heptane	--	--	--	

The tendency of droplets to spread across the surfaces was also evaluated (Figure 3 and 4; Appendices A through D). 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, 6, 7, and 8). 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. Similar behavior is noted for the Fomblin Y oiled coupons. DMMP and MES did not spread for any of the variants of PFTS-ECA or coated coupons tested. DFP spread was slowed on the coatings as compared to the painted surface. The fastest spread was noted for the original formulation with other variants coming close to the same behavior while other ones had a significantly slower spreading of the DFP droplet. For some of the dip coated samples, it may be possible that some initial spreading occurred and the droplets then reached some sort of equilibrium. It is difficult to confirm whether that is the case or that the droplet spread was too slow to accurately measure in the current experiment. No further testing was done to resolve whether the spread is very slow or had ceased after some initial relaxation. Initial droplet sizes for DFP were also smaller than those noted for the painted or oiled surfaces.

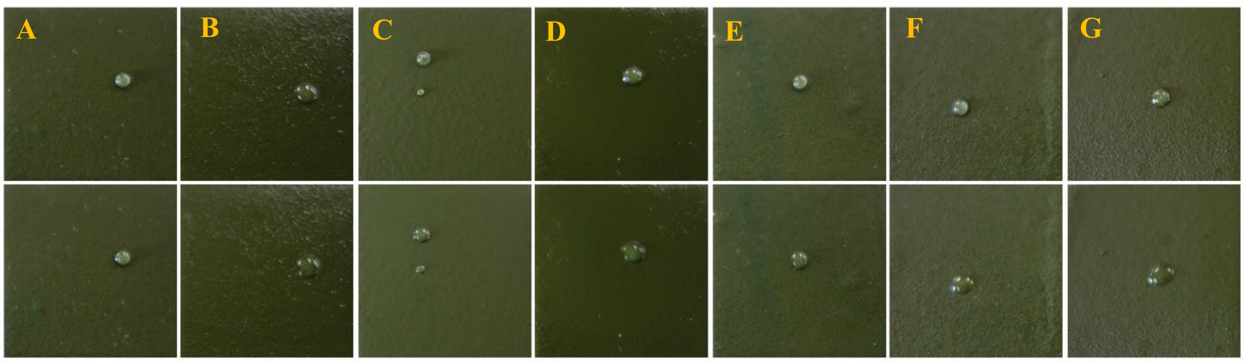


Fig. 3 — Images of coupons immediately following MES deposition (top) and images of the coupons at 30 min following deposition (bottom): PFTS (Dip) coupon (A), PFTS (Spray) coupon (B), PFTS-TEOS (dip) coupon (C), PFTS-TEOS (Spray) coupon (D), PFTS-ECA (Dip, V.low) coupon (E), PFTS-ECA (Spray,V.low) coupon (F), and PFTS-ECA (Dip, low) coupon (G).

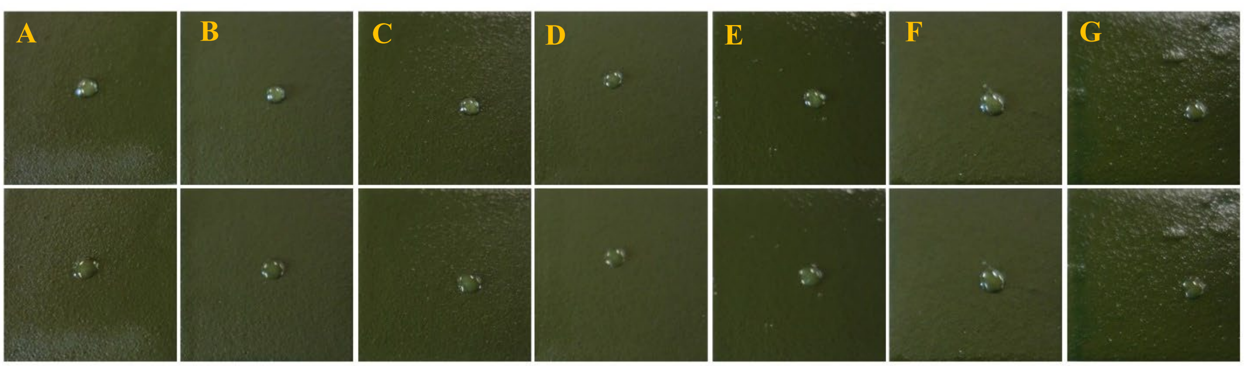


Fig. 4 — Images of coupons immediately following MES deposition (top) and images of the coupons at 30 min following deposition (bottom): PFTS-ECA (Spray, low) coupon (A), PFTS-ECA (Dip, Med) coupon (B), PFTS-ECA (Spray, Med) coupon (C), PFTS-ECA (Dip, High) coupon (D), PFTS-ECA (Spray,High) coupon (E), PFTS-ECA (Dip, V. high) coupon (F), and PFTS-ECA (Spray,V.high) coupon (G).

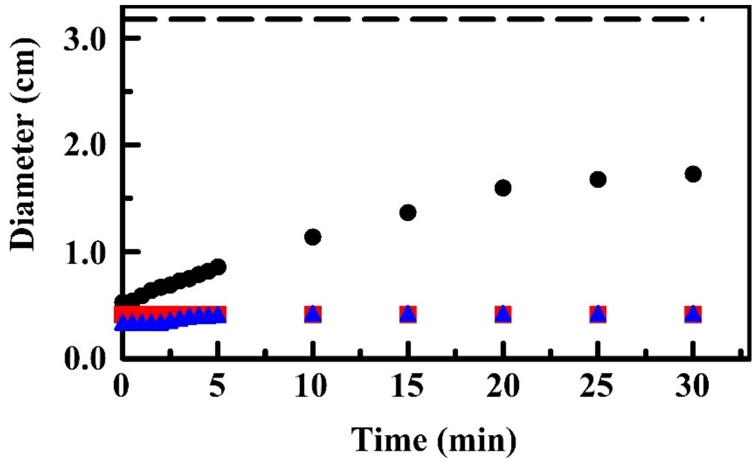


Fig. 5 — Droplet diameters over time following exposure to DFP (black), MES (red), and DMMP (blue) for a painted coupon with initial ECA variant

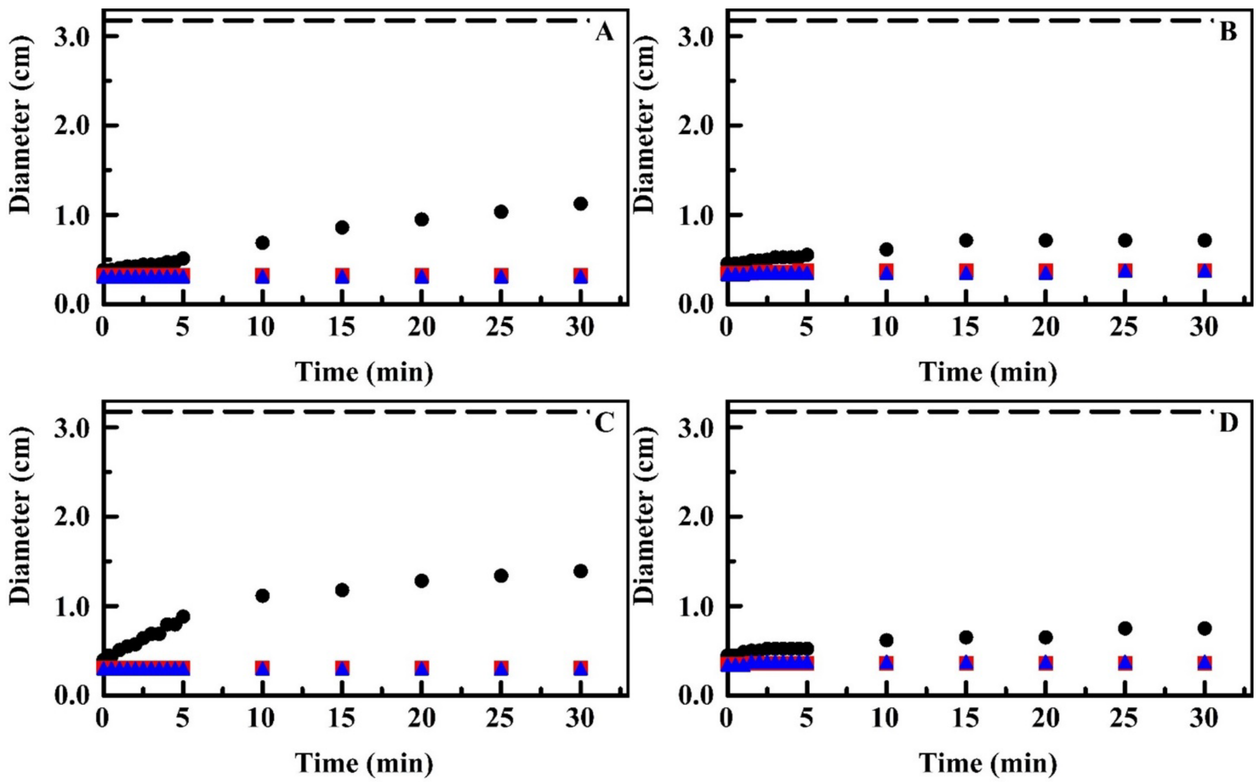


Fig. 6 — Droplet diameters over time following exposure to DFP (black), MES (red), and DMMP (blue) for a PFTS (Dip) coupon (A), PFTS (Spray) coupon (B), PFTS-TEOS (dip) coupon (C), and PFTS-TEOS (Spray) coupon (D).

The coupons were subjected to several cycles of simulant exposure (10 g/m^2), aging, washing, and drying over a period of one week. Some change in appearance was noted following DFP exposures, but no changes in performance were noted for the cycled samples. When the soapy water process was employed (Figure 9 and 10; Table 4), retention of all targets was less for the Fomblin Y lubricated paint treatments than for the paint only surfaces. All PFTS-ECA variants provided lower retention for all four targets considered under this study than that noted for the oiled surface. These materials also offer lower retention of all targets than the Fomblin Y oiled paint. Retention of all targets was approximately 4% of the 10 g/m^2 applied challenge. It was not uniform and different variants had poorer performance for some targets. There was no consistent pattern but an overall observation is that poorer performance was seen for DFP for these coatings.

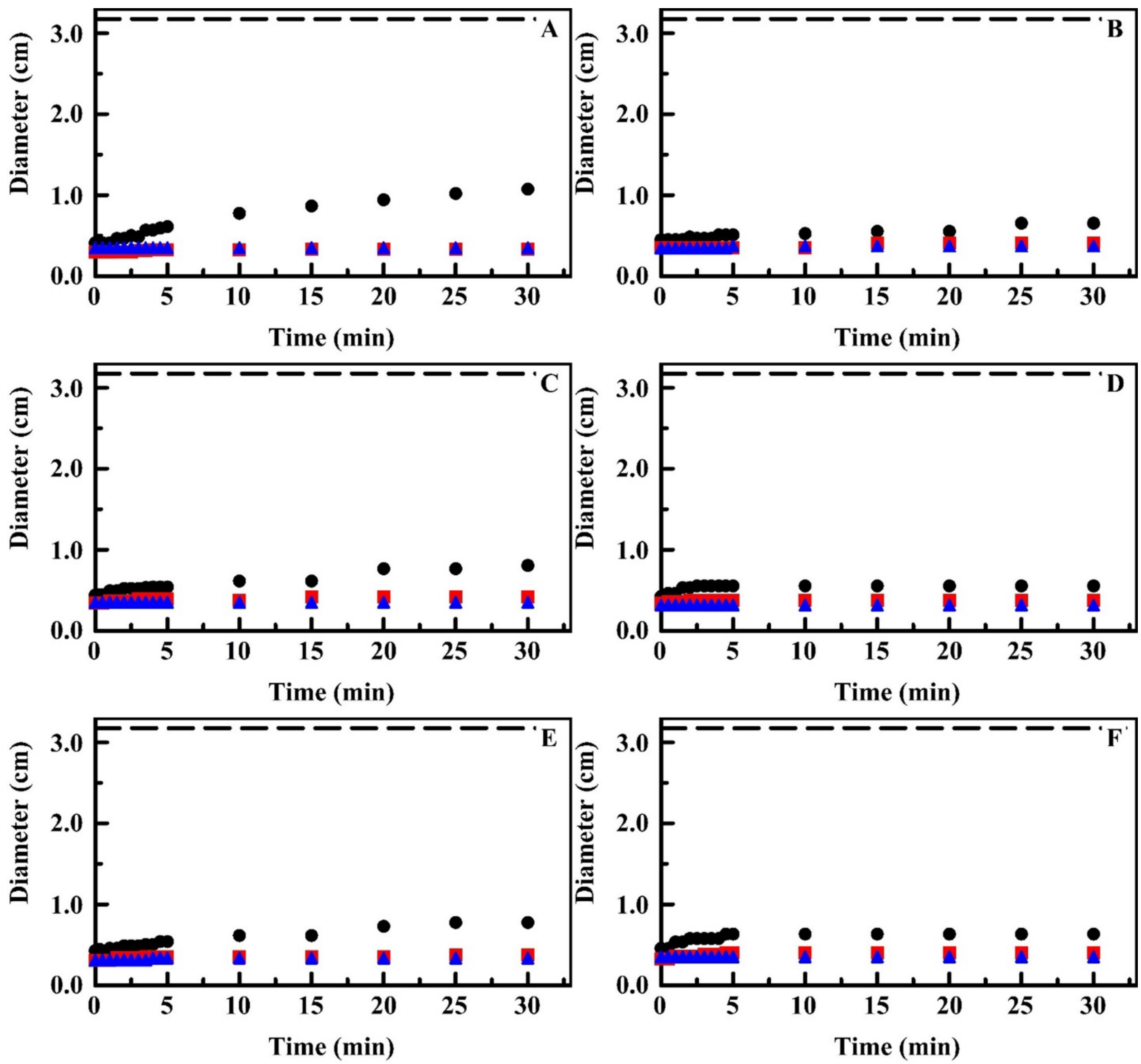


Fig. 7 — Droplet diameters over time following exposure to DFP (black), MES (red), and DMMP (blue) for a PFTS-ECA (Dip, V.low) coupon (A), PFTS-ECA (Spray,V.low) coupon (B), and PFTS-ECA (Dip, low) coupon (C), PFTS-ECA (Spray, low) coupon (D), PFTS-ECA (Dip, Med) coupon (E), and PFTS-ECA (Spray, Med) coupon (F).

For paint only coupons, retention was significant but was less than that of paint only coupons that were extracted with no rinsing or decontamination steps. 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 rinse steps due to agent interaction with the untreated region of the coupon; the back of these coupons is unpainted aluminum.

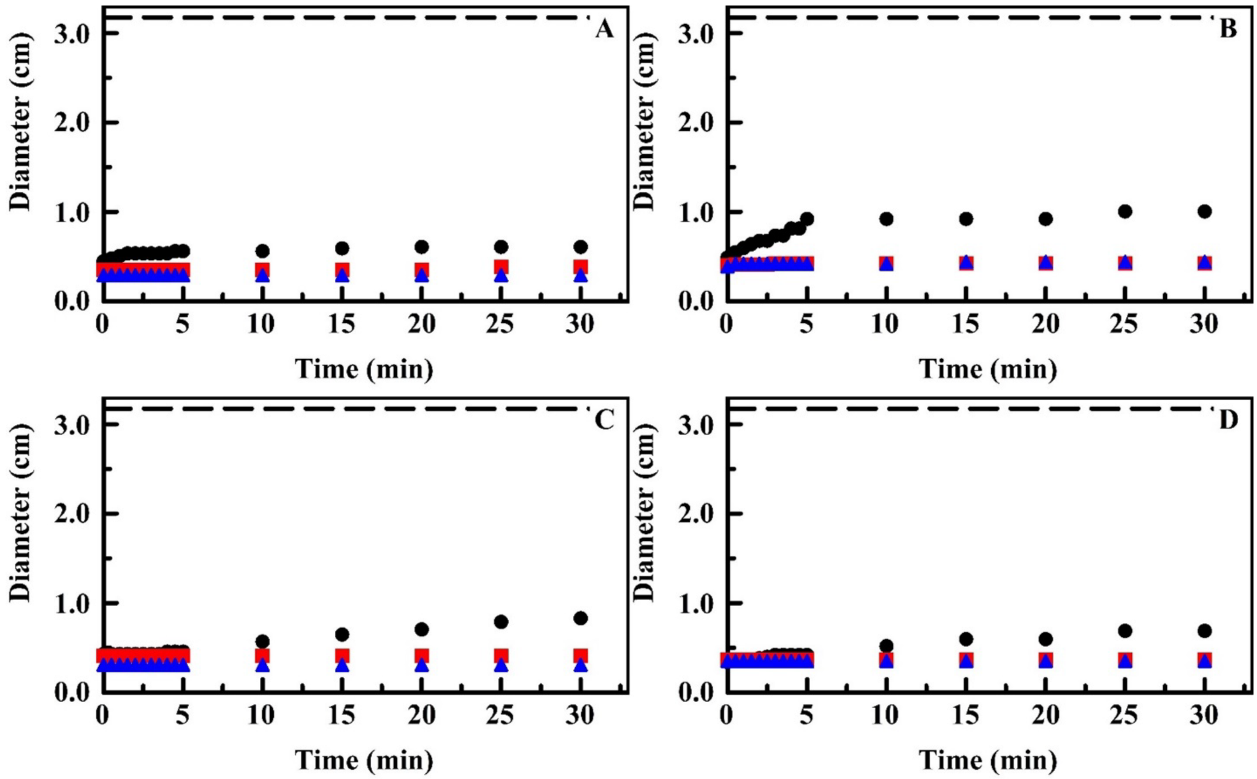


Fig. 8 — Droplet diameters over time following exposure to DFP (black), MES (red), and DMMP (blue) for a PFTS-ECA (Dip, High) coupon (A), PFTS-ECA (Spray,High) coupon (B), PFTS-ECA (Dip, V. high) coupon (C), and PFTS-ECA (Spray,V.high) coupon (D).

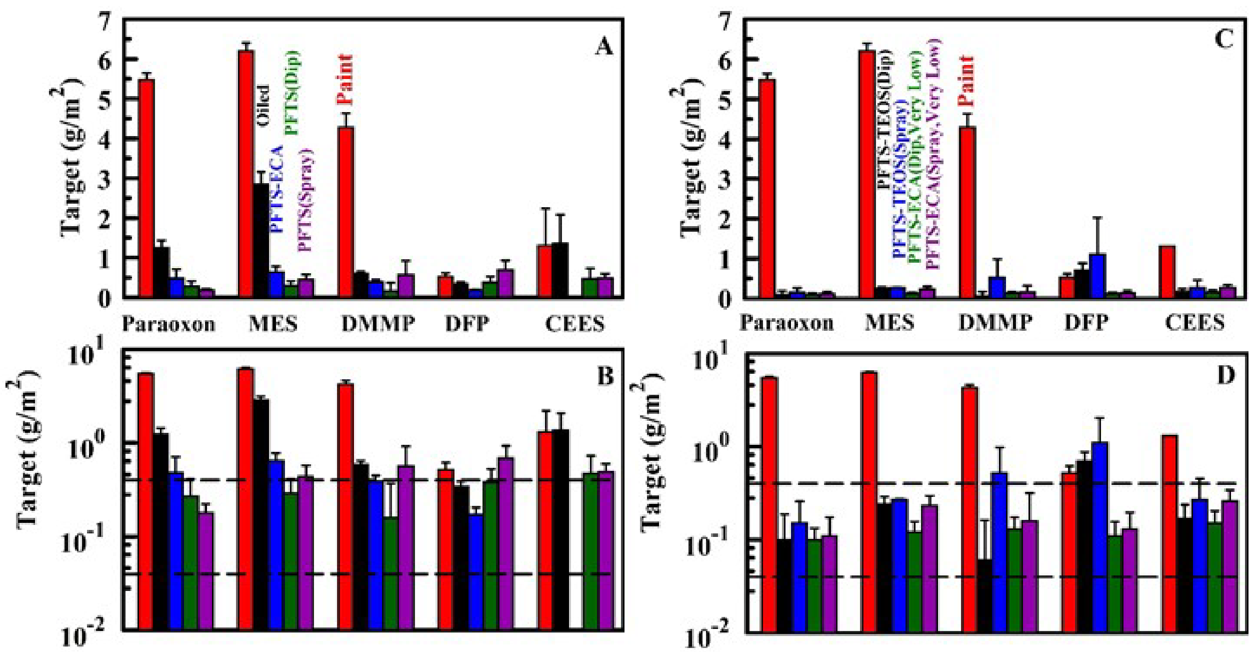


Fig. 9 — Target retention by coupons following treatment with an air stream and rinsing with soapy water: paint (red), oiled paint (black), PFTS-BCA (blue), and PFTS-ECA (green) plotted on a linear (A) and a log scale (B).

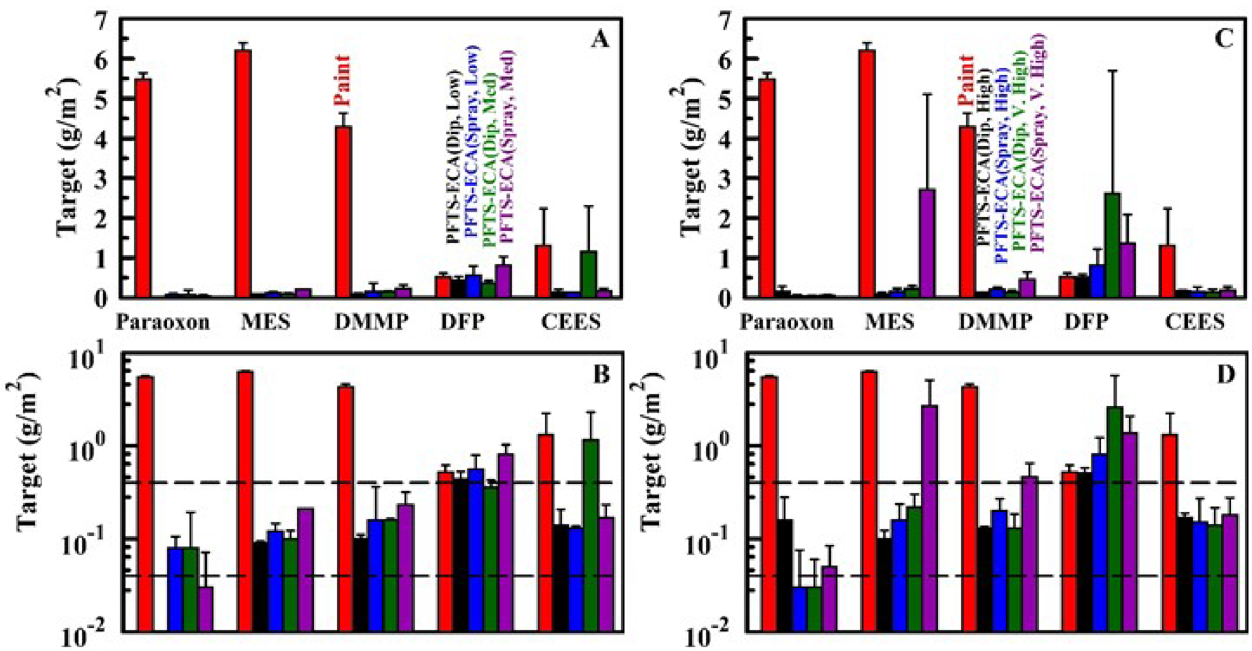


Fig. 10 — Target retention by coupons following treatment with an air stream and rinsing with soapy water: paint (red), oiled paint (black), PFTS-BCA (blue), and PFTS-ECA (green) plotted on a linear (A) and a log scale (B).

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

Coupon	Paraoxon	MES	DMMP	DFP	CEES
Paint Only	5.48	6.20	4.28	0.52	1.31
Fomblin Y Oiled Paint	1.24	2.85	0.59	0.34	1.36
PFTS-ECA	0.48	0.64	0.39	0.17	--
PFTS (Dip)	0.27	0.29	0.16	0.38	0.47
PFTS (Spray)	0.18	0.44	0.57	0.69	0.49
PFTS-TEOS (Dip)	0.10	0.24	0.06	0.70	0.17
PFTS-TEOS (Spray)	0.15	0.27	0.52	1.1	0.27
PFTS (Dip,Very Low)	0.10	0.12	0.13	0.11	0.15
PFTS (Spray, Very Low)	0.11	0.23	0.16	0.13	0.26
PFTS (Dip,Low)	ND	0.09	0.10	0.44	0.14
PFTS (Spray, Low)	0.08	0.12	0.16	0.56	0.13
PFTS (Dip, Medium)	0.08	0.10	0.16	0.36	1.15
PFTS (Spray, Medium)	0.03	0.21	0.23	0.81	0.17
PFTS (Dip, Hi)	0.16	0.10	0.13	0.51	0.17
PFTS (Spray, Hi)	0.03	0.16	0.20	0.81	0.15
PFTS (Dip,Very Hi)	0.03	0.22	0.13	2.61	0.14
PFTS (Spray, Very Hi)	0.05	2.71	0.46	1.37	0.18

-- not measured

CONCLUSIONS

The perfluorohexyltrichlorosilane-cyanoacrylate coatings provided reduction in surface energy and significantly improved performance during retention evaluations over that noted for the paint only surfaces.

Unlike many of the coatings evaluated under this effort, the coatings had little impact on the visible appearance of the painted surfaces (Figure 1 and Appendices). The use of a spray coating application method met with disappointing results. While resistance for some chemicals was not significantly affected, for several retention was much worse for the spray coat application. These results indicate that care should be taken if a coating that was tested via dip coating or other application method will then at larger scale be applied via spray coating. It may be still possible to improve performance through altering the composition of the deposition solutions. It may also be possible to use alternatives to the fluorinated component.

ACKNOWLEDGEMENTS

This research was sponsored by the Defense Threat Reduction Agency (DTRA, CB10125).

REFERENCES

1. Pan, S.J.; Guo, R.; Bjornmalm, M.; Richardson, J.J.; Li, L.; Peng, C.; Bertleff-Zieschang, N.; Xu, W.J.; Jiang, J.H.; Caruso, F. Coatings super-repellent to ultralow surface tension liquids. *Nat. Mater.* **2018**, *17*, 1040-+, doi:10.1038/s41563-018-0178-2.
2. White, B.; Malanoski, A.; Melde, B.; Moore, M. *Bioinspired Surface Treatments for Improved Decontamination: Cyanoacrylate Coatings*; NRL/MR/6930-19,9876; US Naval Research Laboratory, Washington, DC, 2019.
3. Lalain, T.; Mantooth, B.; Shue, M.; Pusey, S.; Wylie, D. *Chemical Contaminant and Decontaminant Test Methodology Source Document*; ECBC-TR-980; US Army RDEC, Edgewood Chemical Biological Center: US Army RDEC, Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, 2012.
4. White, B.; Melde, B.; Malanoski, A.; Moore, M. *Bioinspired Surface Treatments for Improved Decontamination: Cyanoacrylate Coatings*; NRL/MR/6930-19,9876; US Naval Research Laboratory, Washington, DC, 2019.

Appendix A

PFTS dip coated COUPON IMAGES

Fig. A1 — DFP on PFTS dip coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

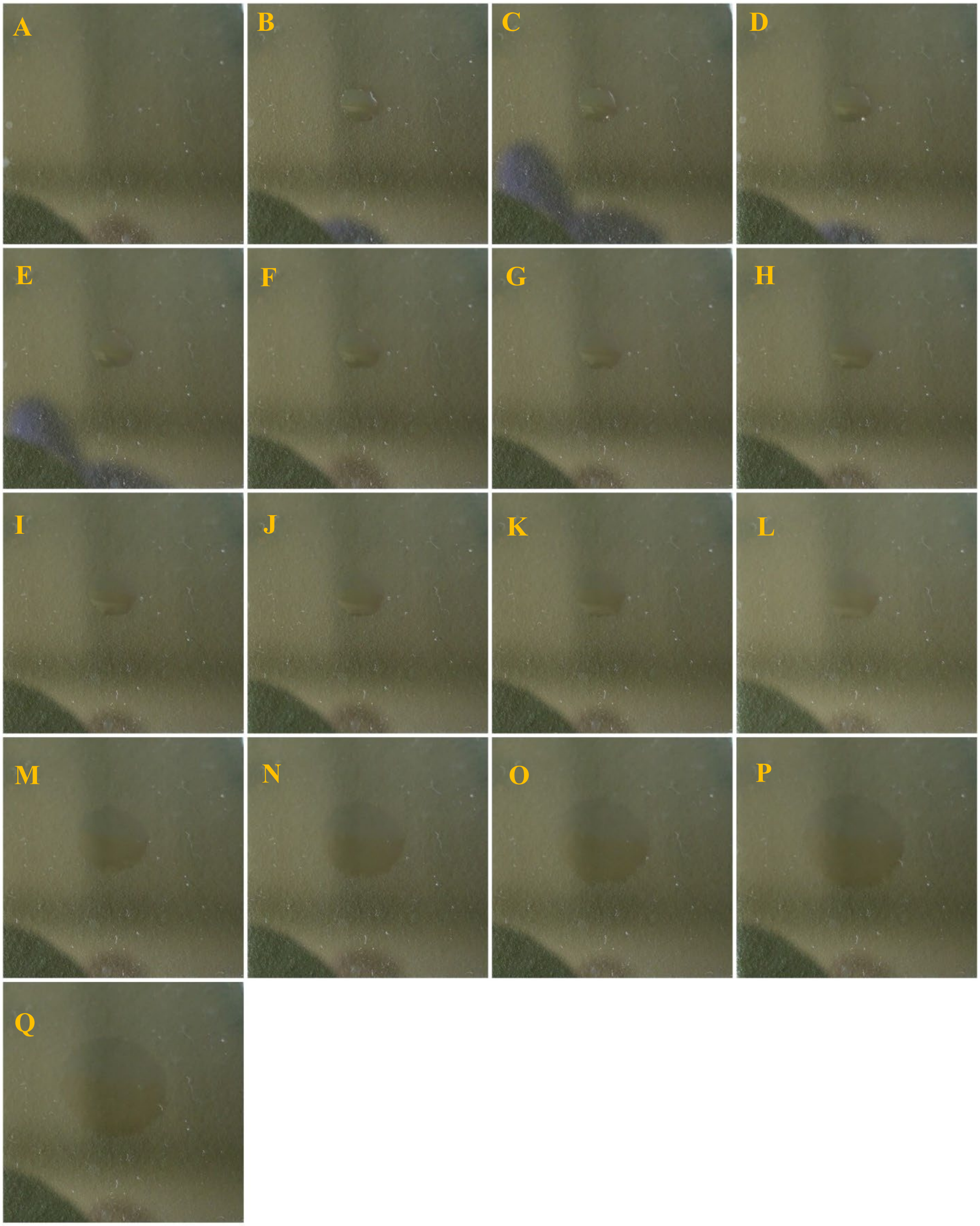


Fig. A2 — MES on PFTS dip coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

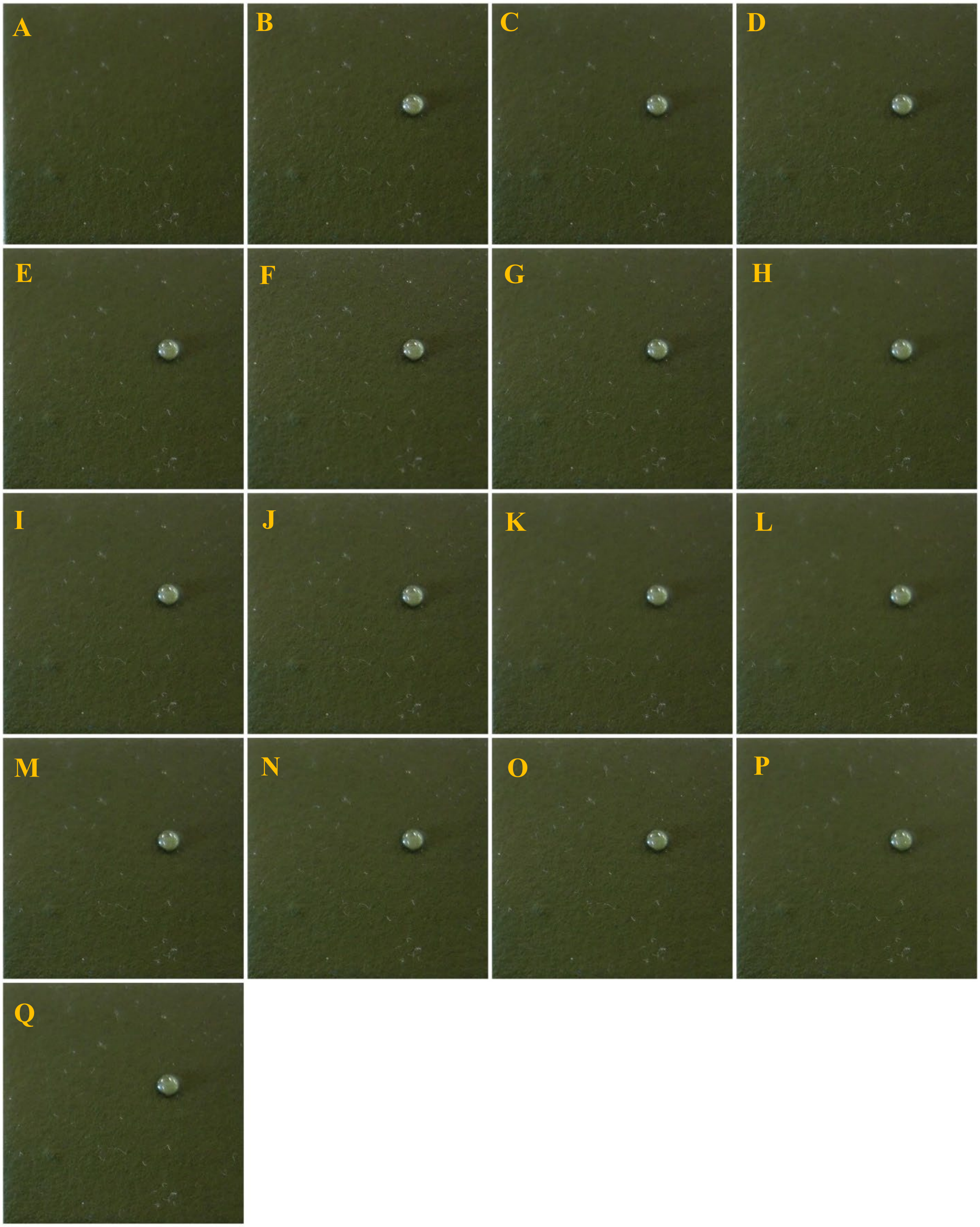
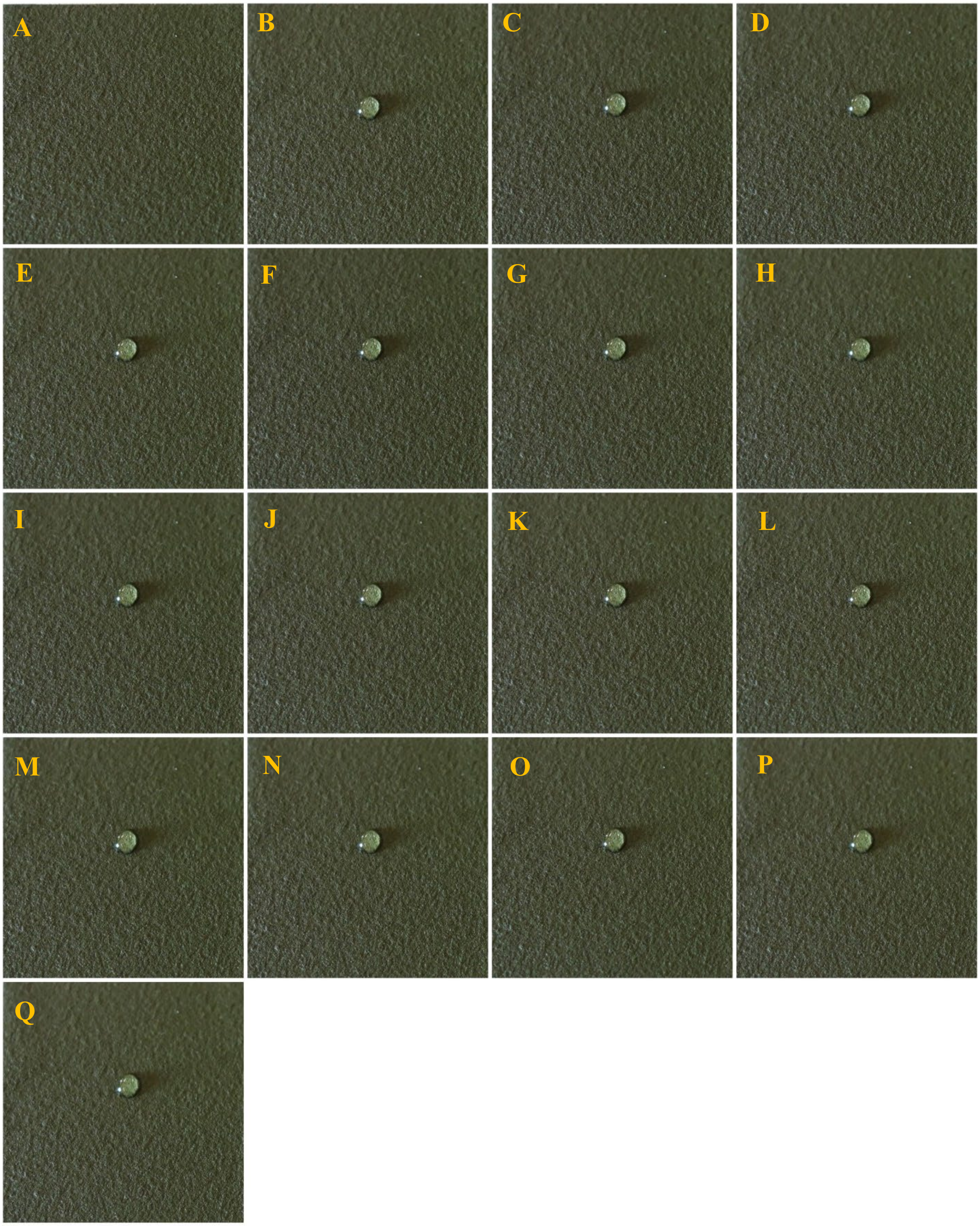


Fig. A3 — DMMP on PFTS dip coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix B

PFTS spray coated COUPON IMAGES

Fig. B1 — DFP on PFTS spray coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

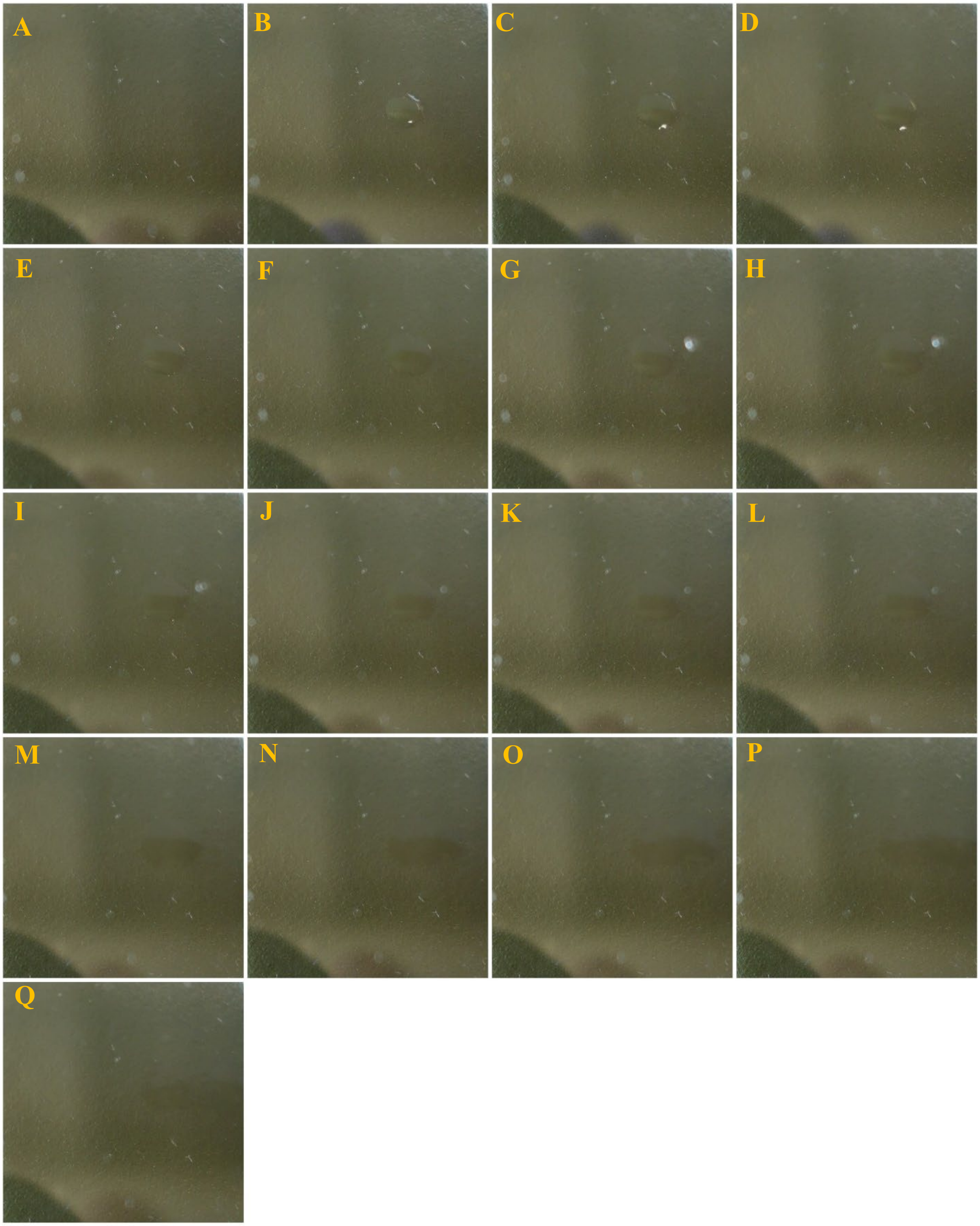


Fig. B2 — MES on PFTS spray coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

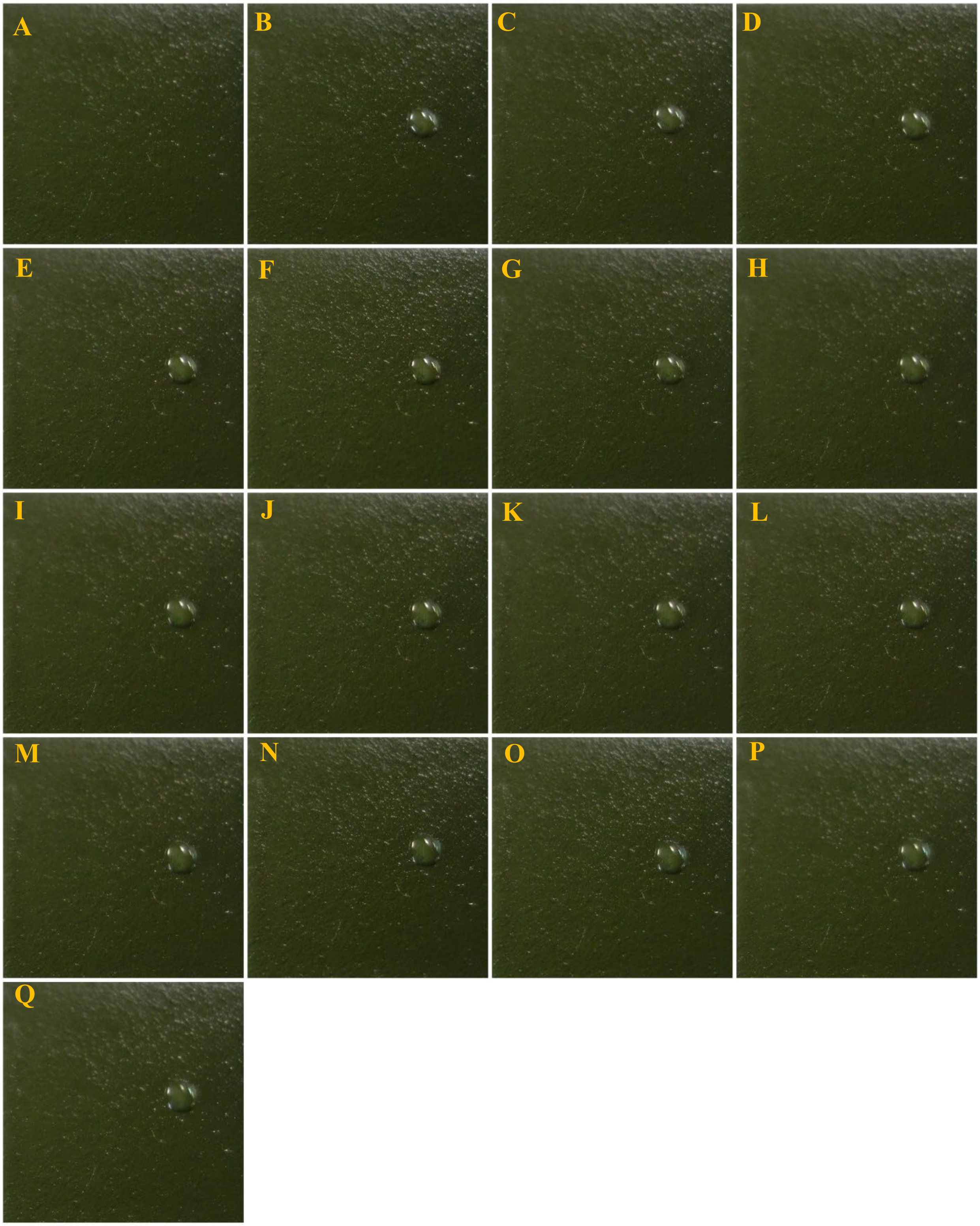
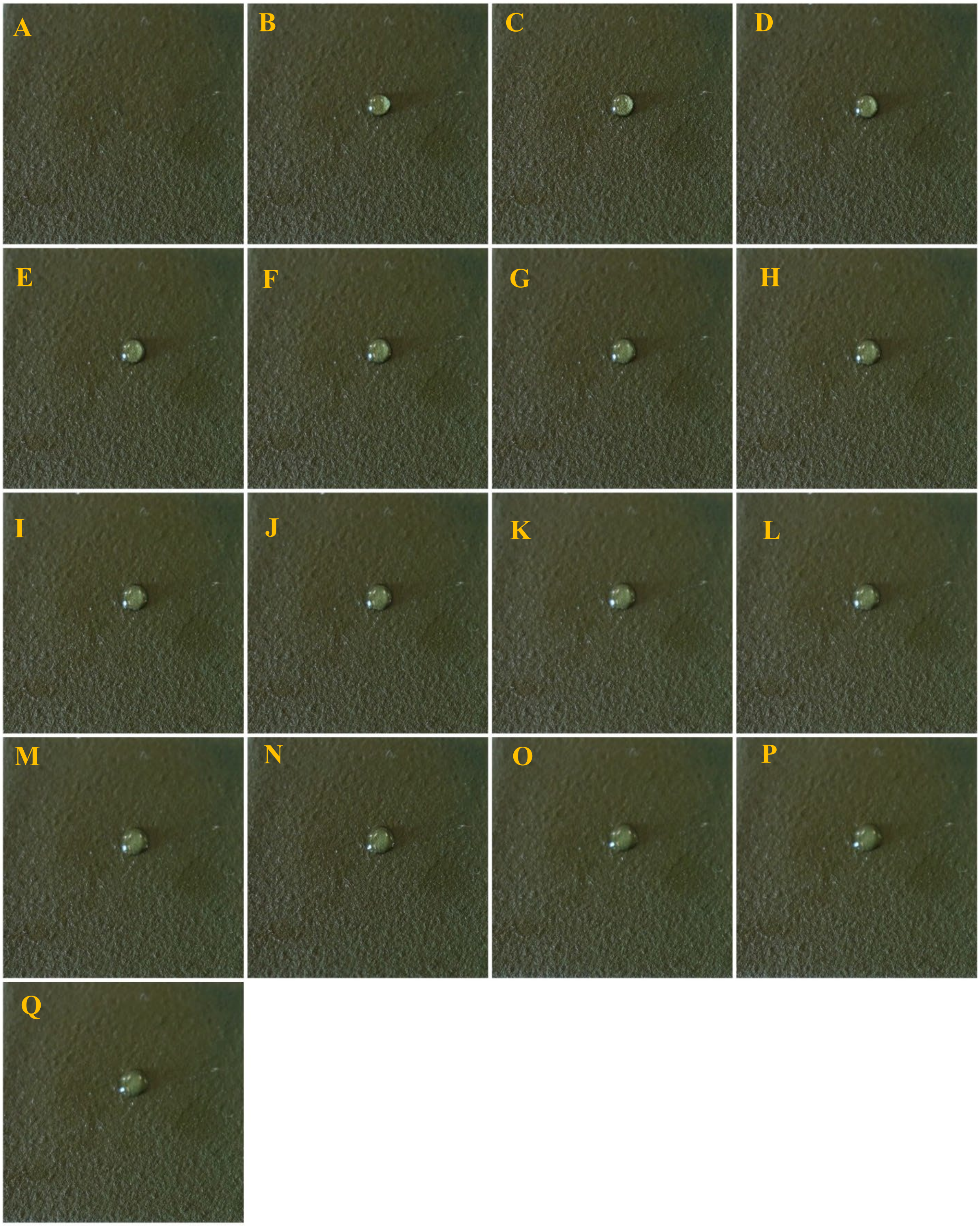


Fig. B3 — DMMP on PFTS spray coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix C

PFTS on TEOS dip coated COUPON IMAGES

Fig. C1 — DFP on PFTS on TEOS dip coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

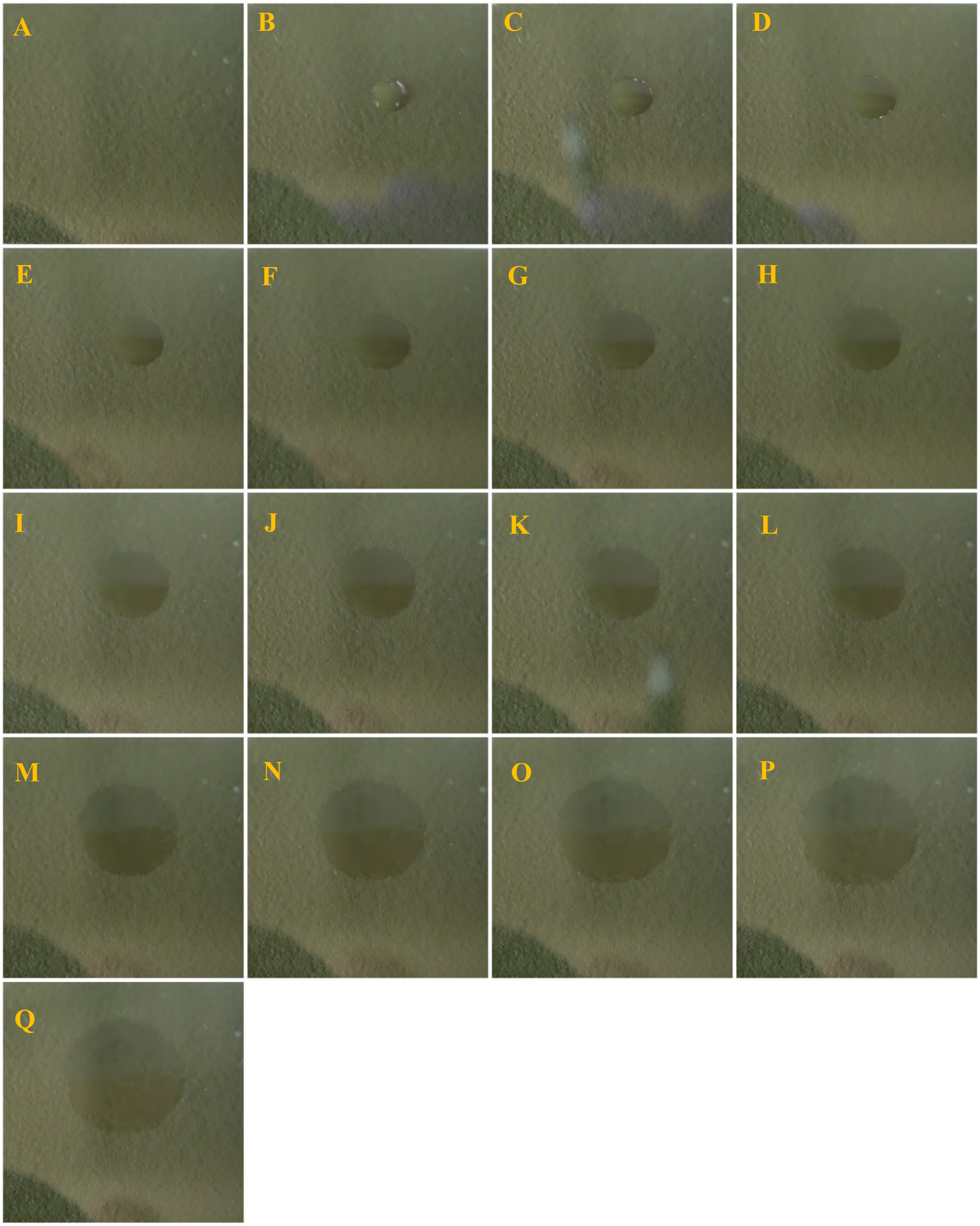


Fig. C2 — MES on PFTS on TEOS dip coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

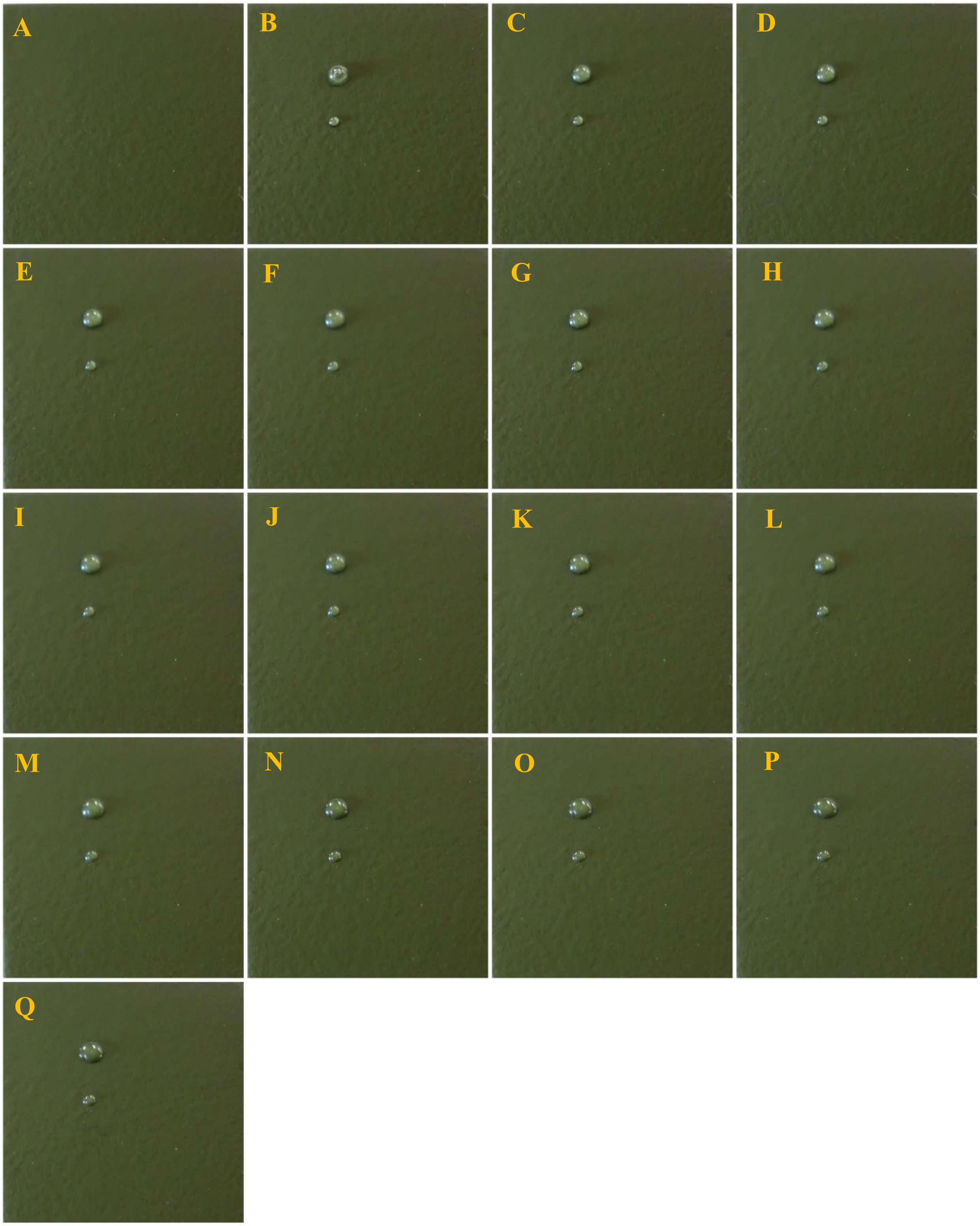
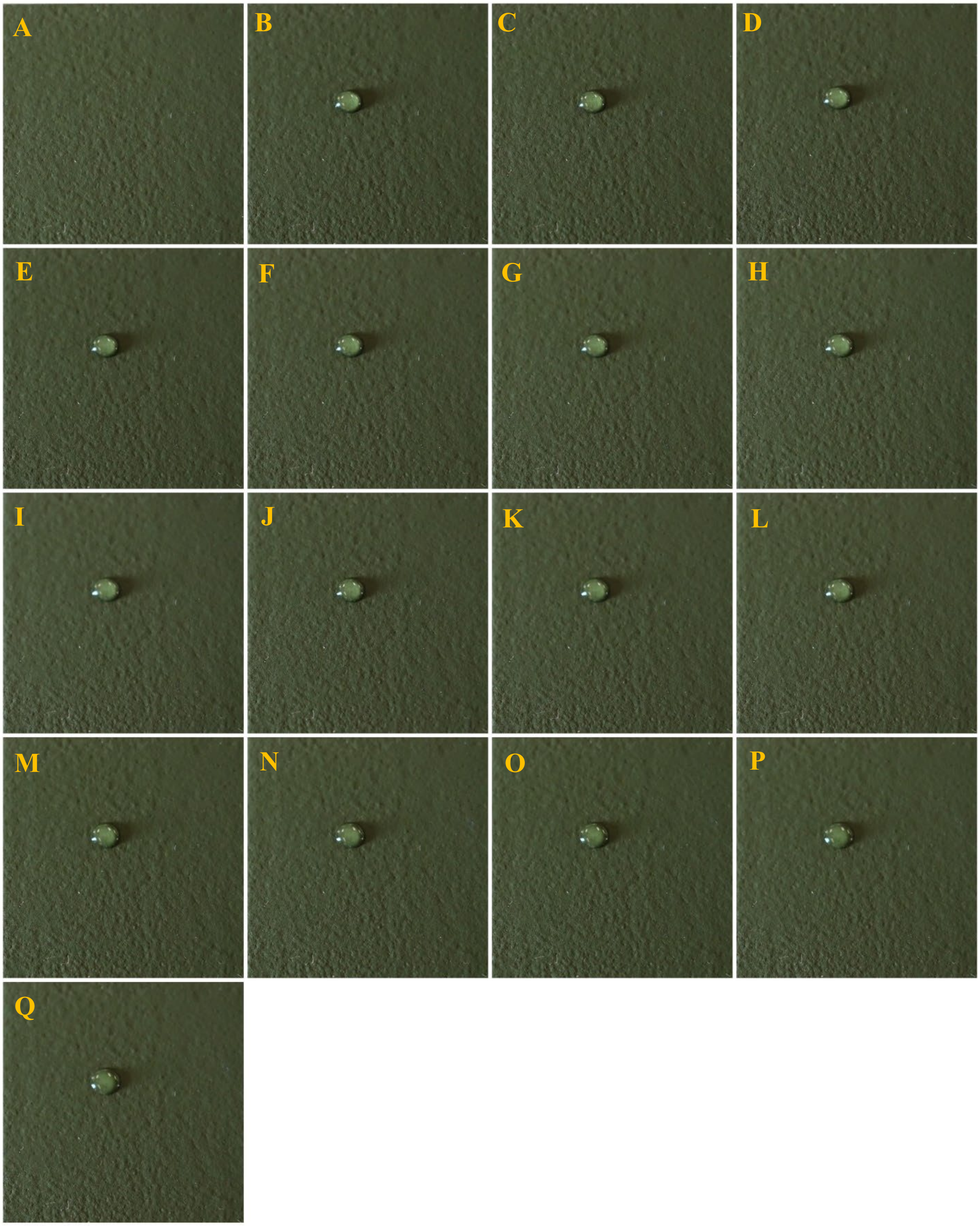


Fig. C3 — DMMP on PFTS on TEOS dip coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix D

PFTS on TEOS spray coated COUPON IMAGES

Fig. D1 — DFP on PFTS on TEOS spray coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

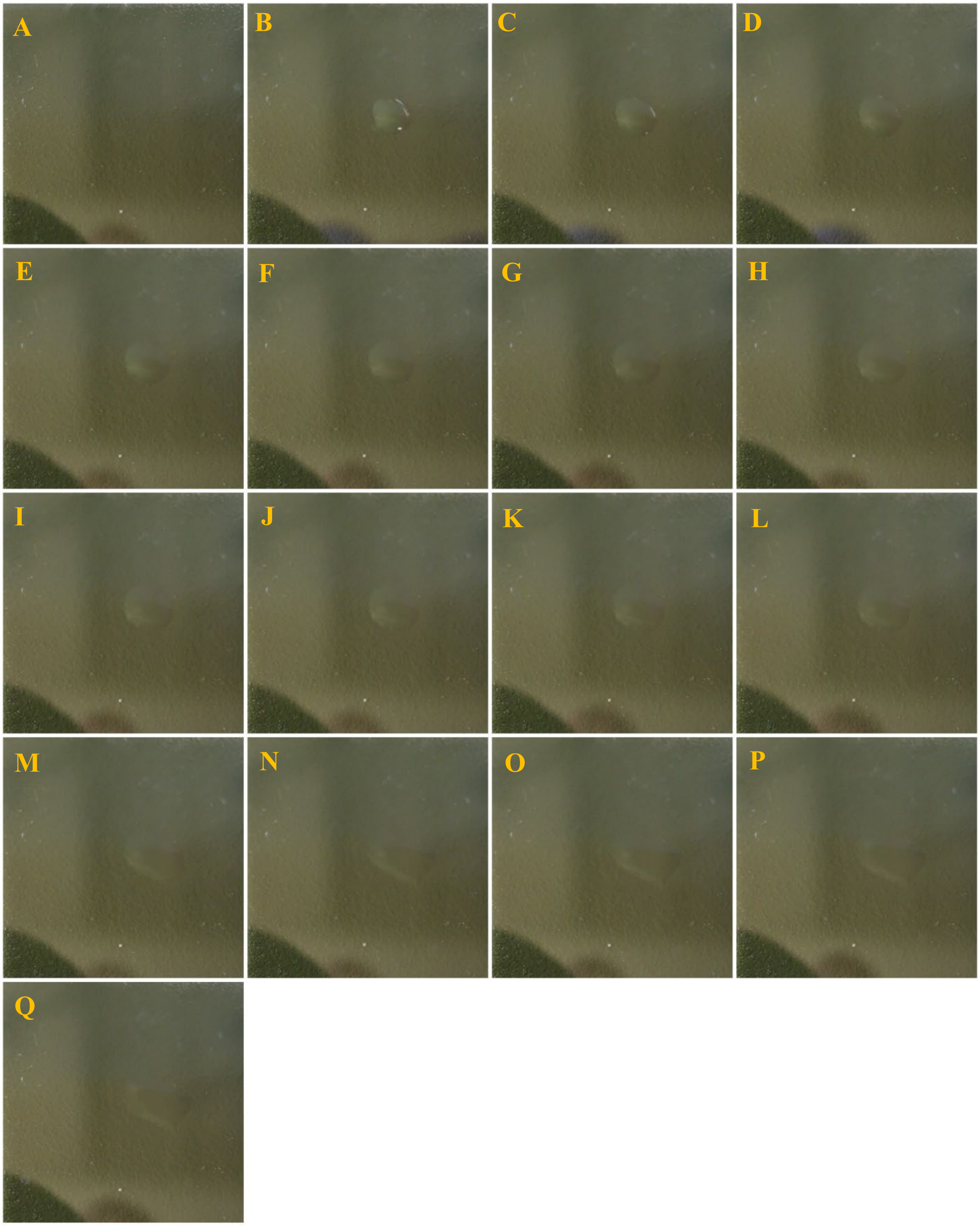


Fig. D2 — MES on PFTS on TEOS spray coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

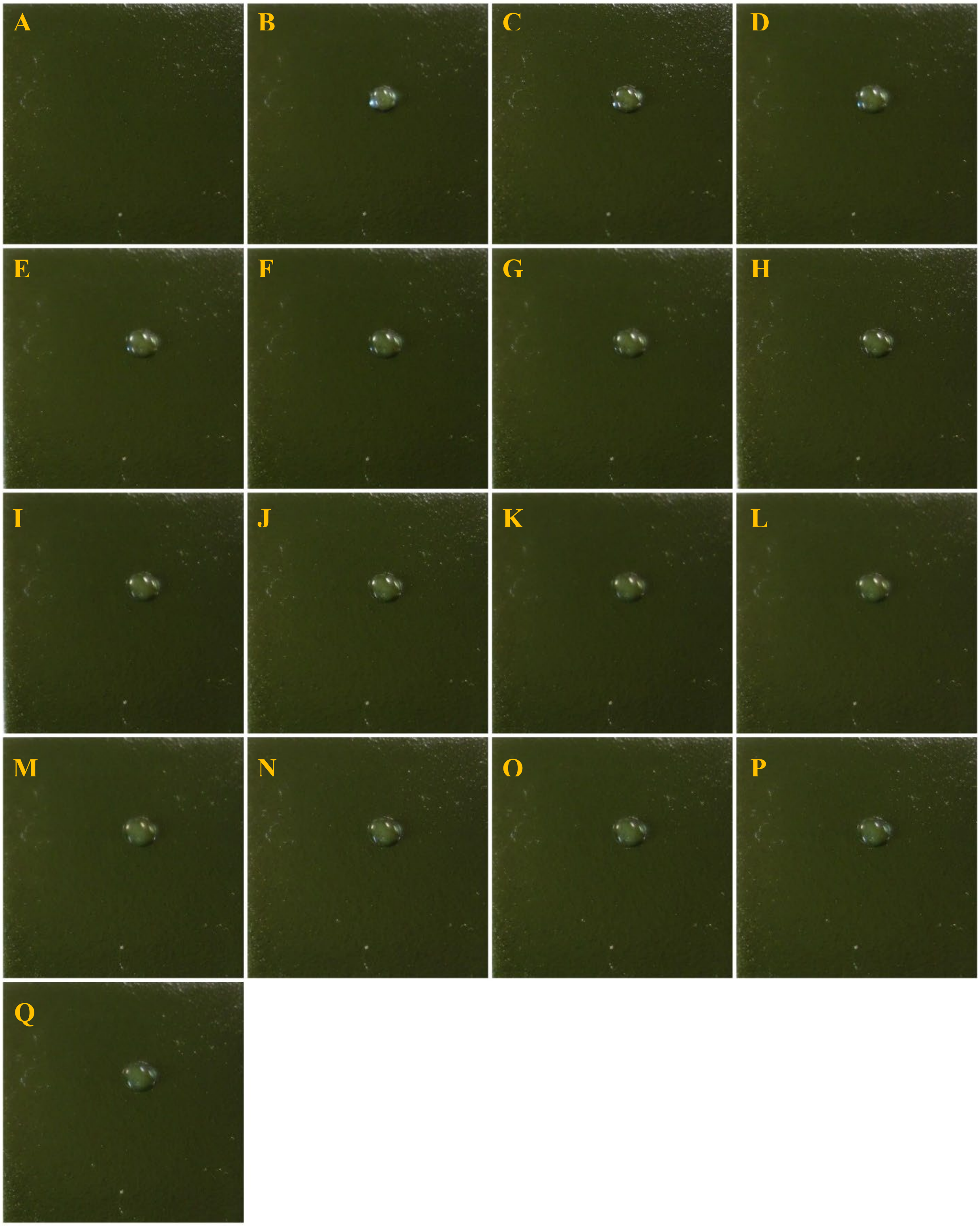
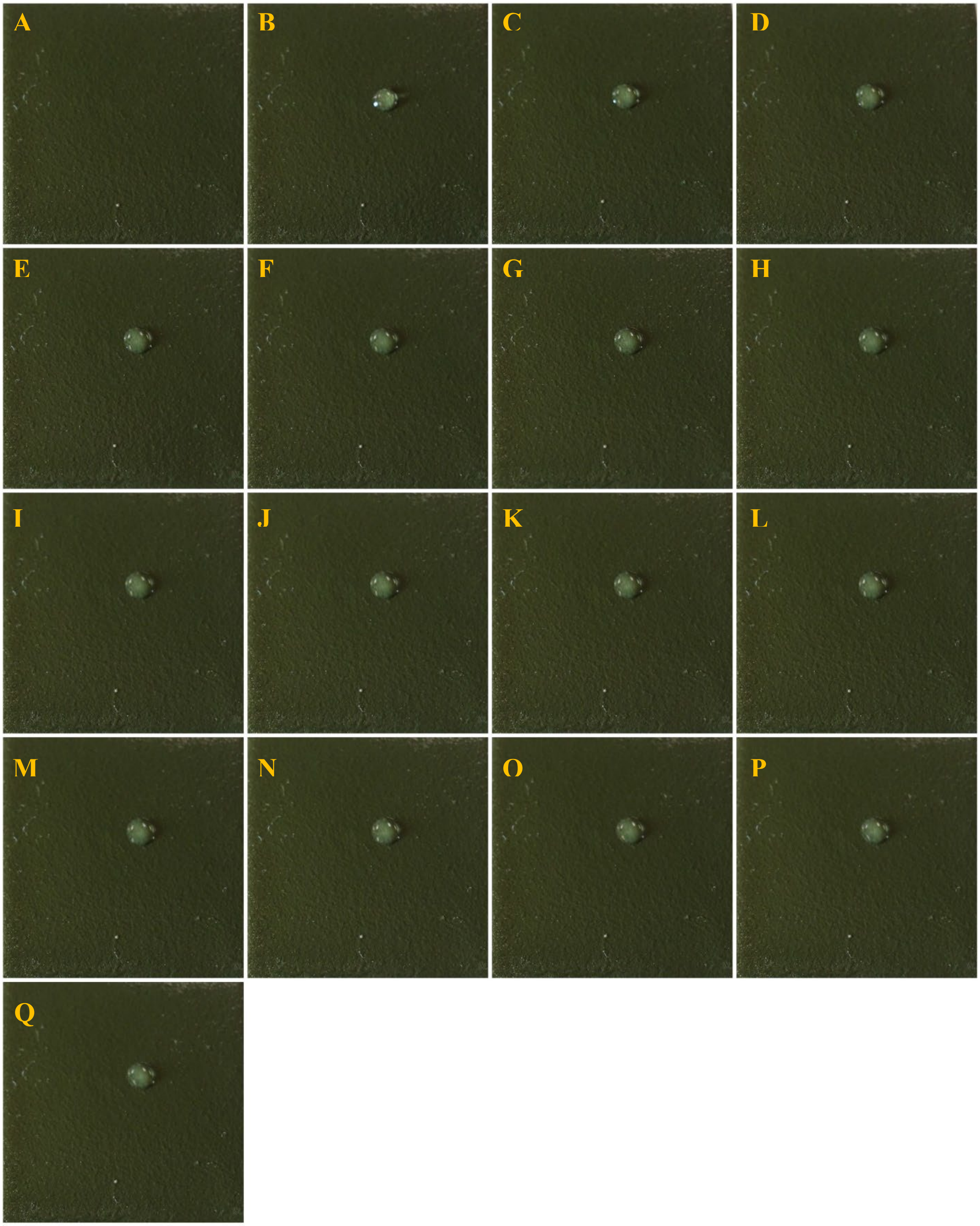


Fig. D3 — DMMP on PFTS on TEOS spray coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix E

PFTS very low ECA dip coated COUPON IMAGES

Fig. E1 — DFP on PFTS very low ECA dip coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

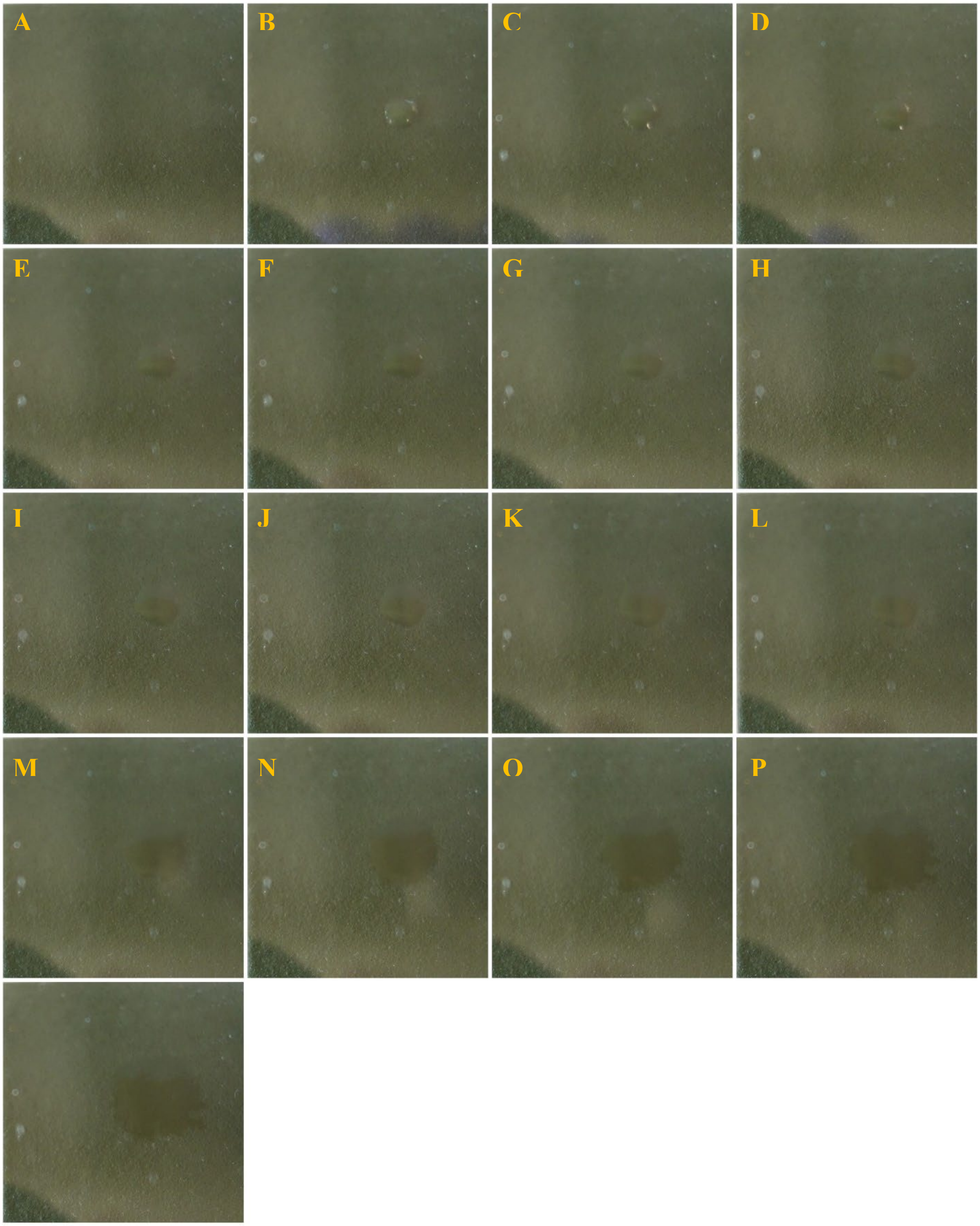


Fig. E2 — MES on PFTS very low ECA dip coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

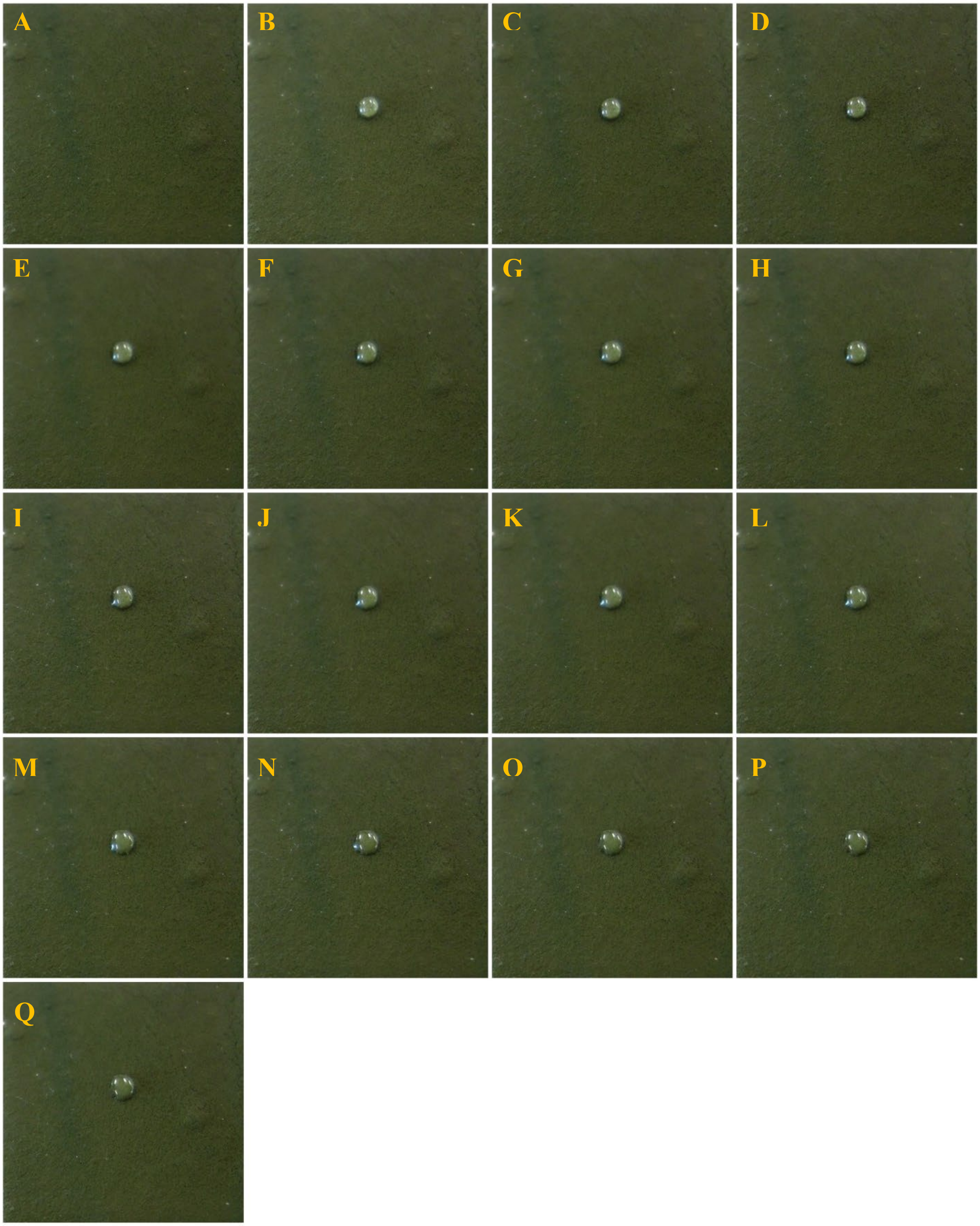
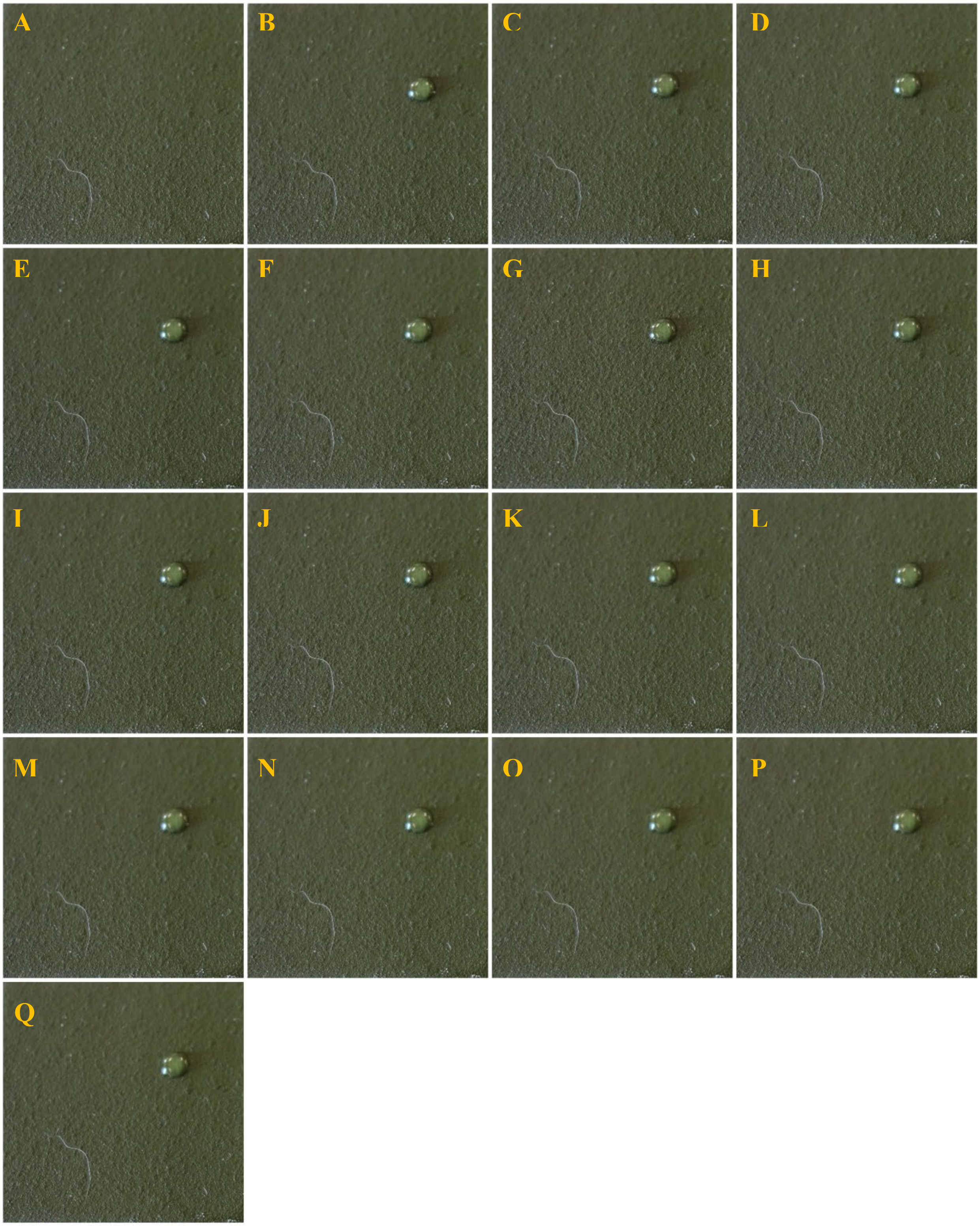


Fig. E3 — DMMP on PFTS very low ECA dip coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix F

PFTS very low ECA spray coated COUPON IMAGES

Fig. F1 — DFP on PFTS very low ECA spray coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

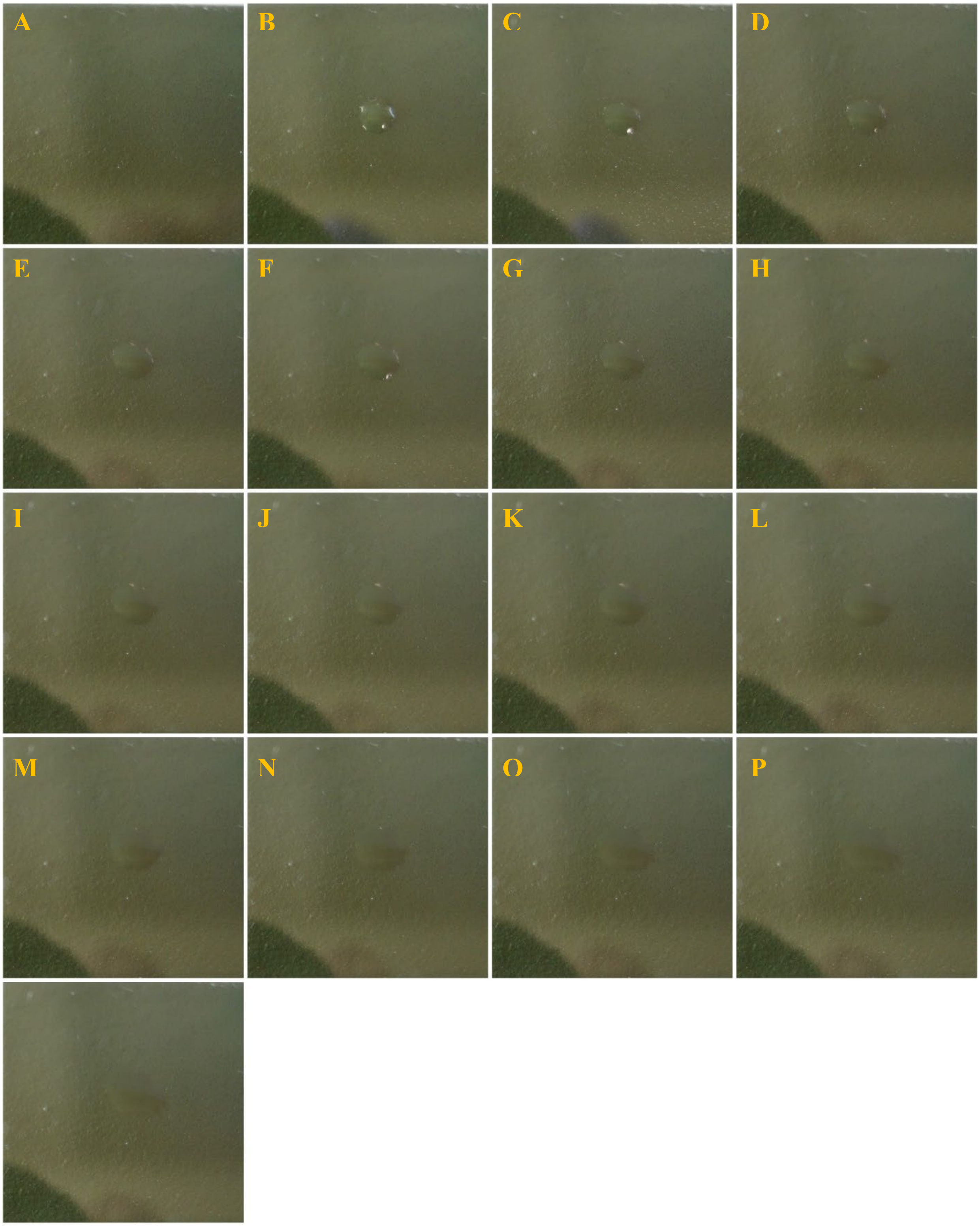


Fig. F2 — MES on PFTS very low ECA spray coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

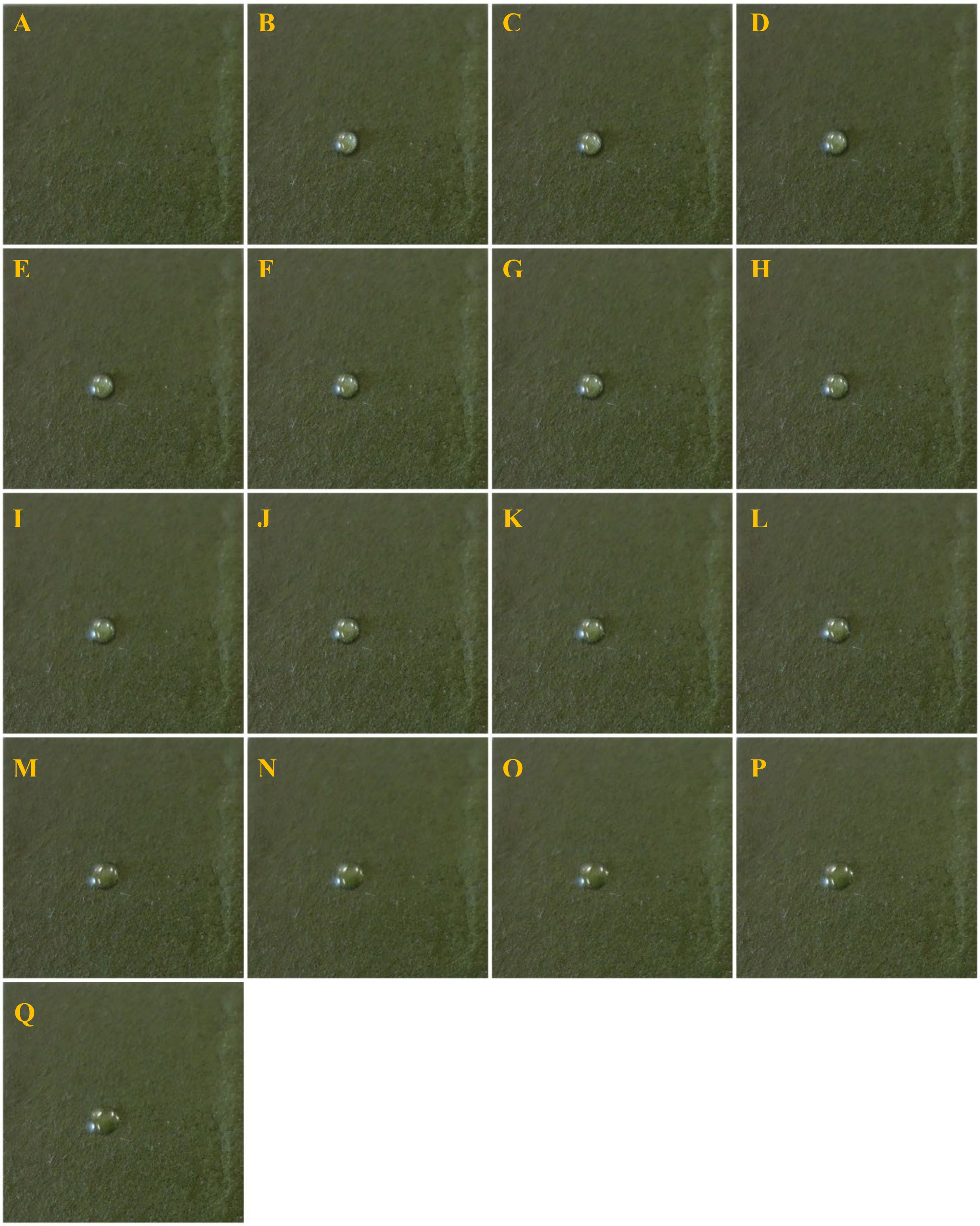
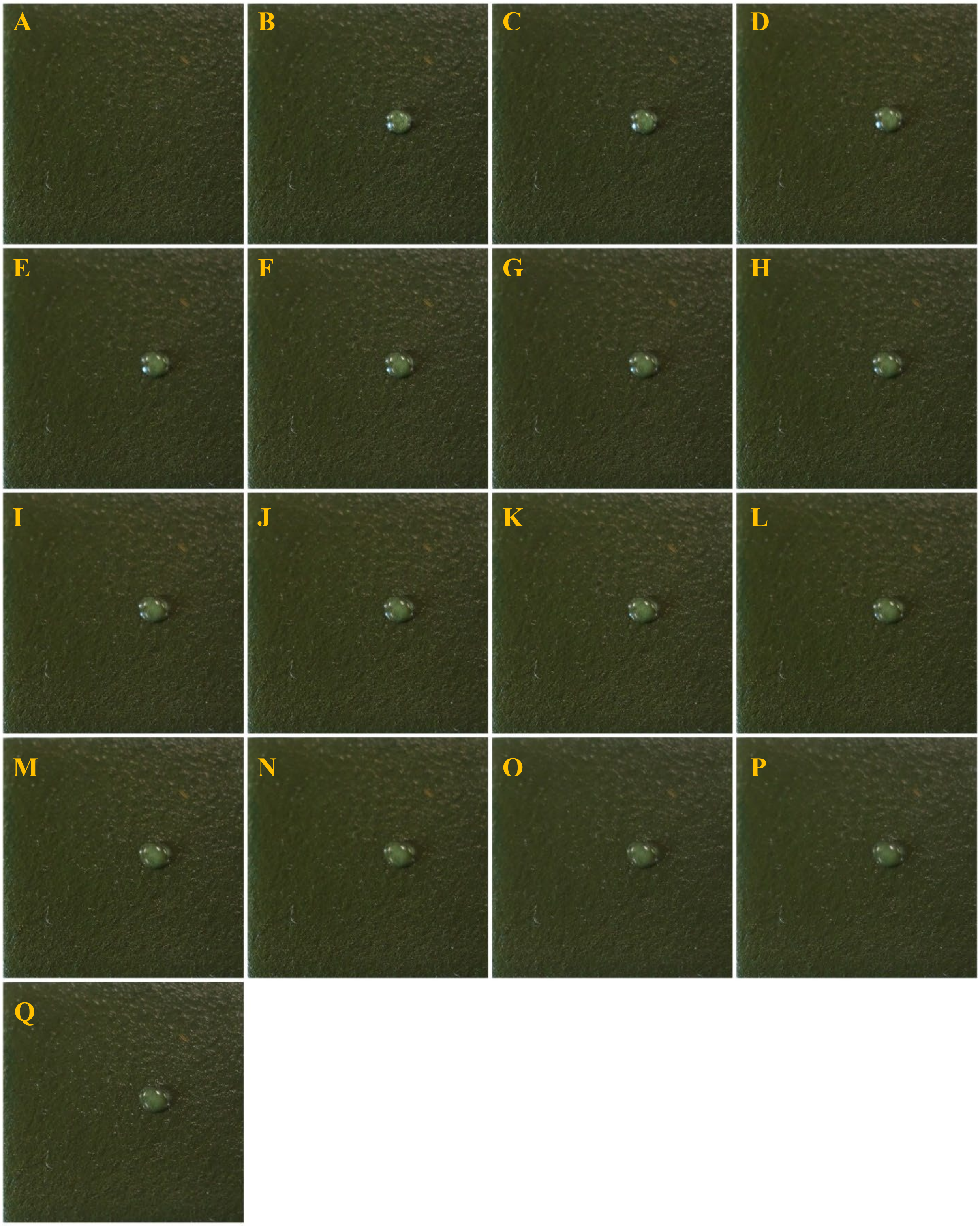


Fig. F3 — DMMP on PFTS very low ECA spray coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix G

PFTS low ECA dip coated COUPON IMAGES

Fig. G1 — DFP on PFTS low ECA dip coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

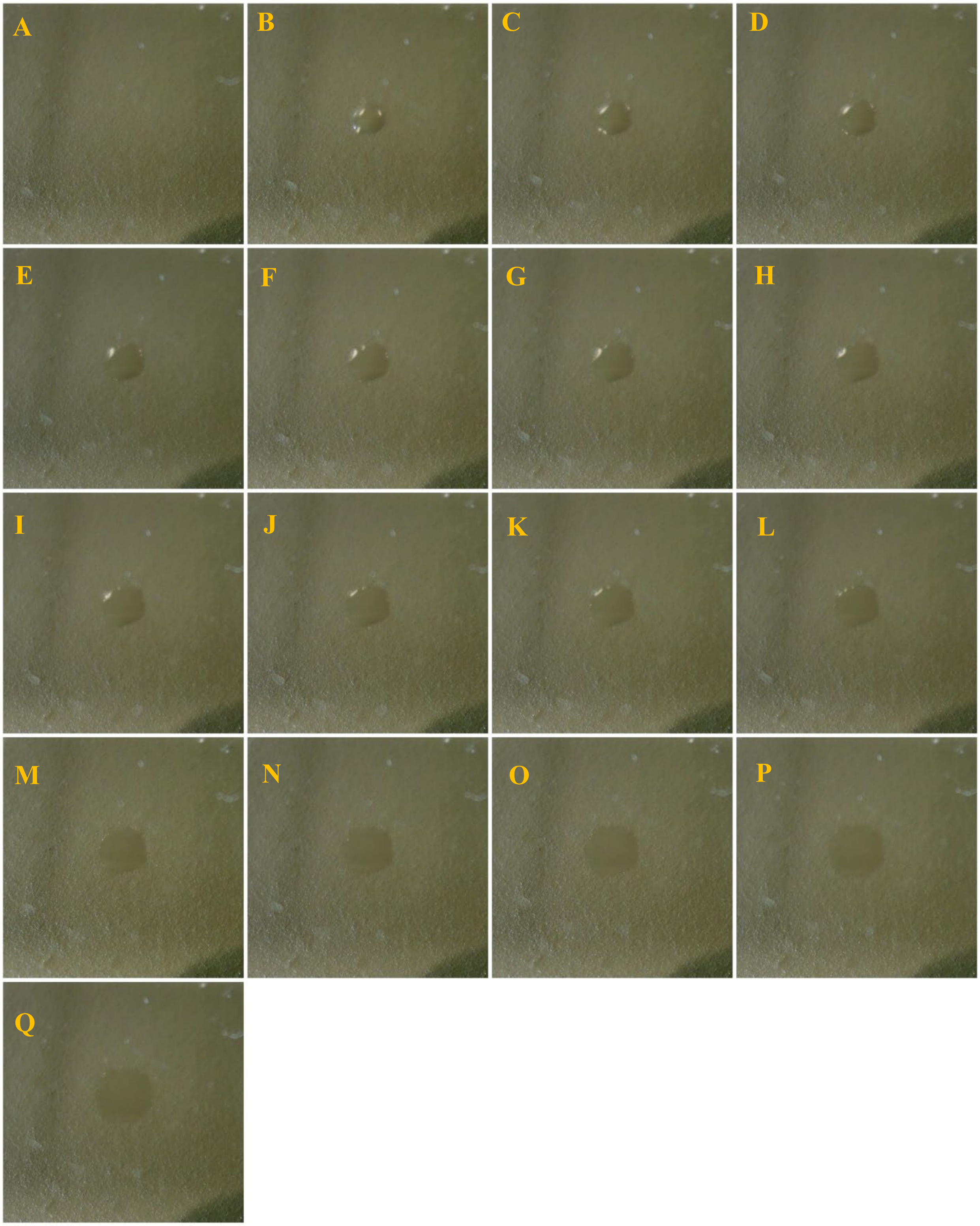


Fig. G2 — MES on PFTS low ECA dip coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

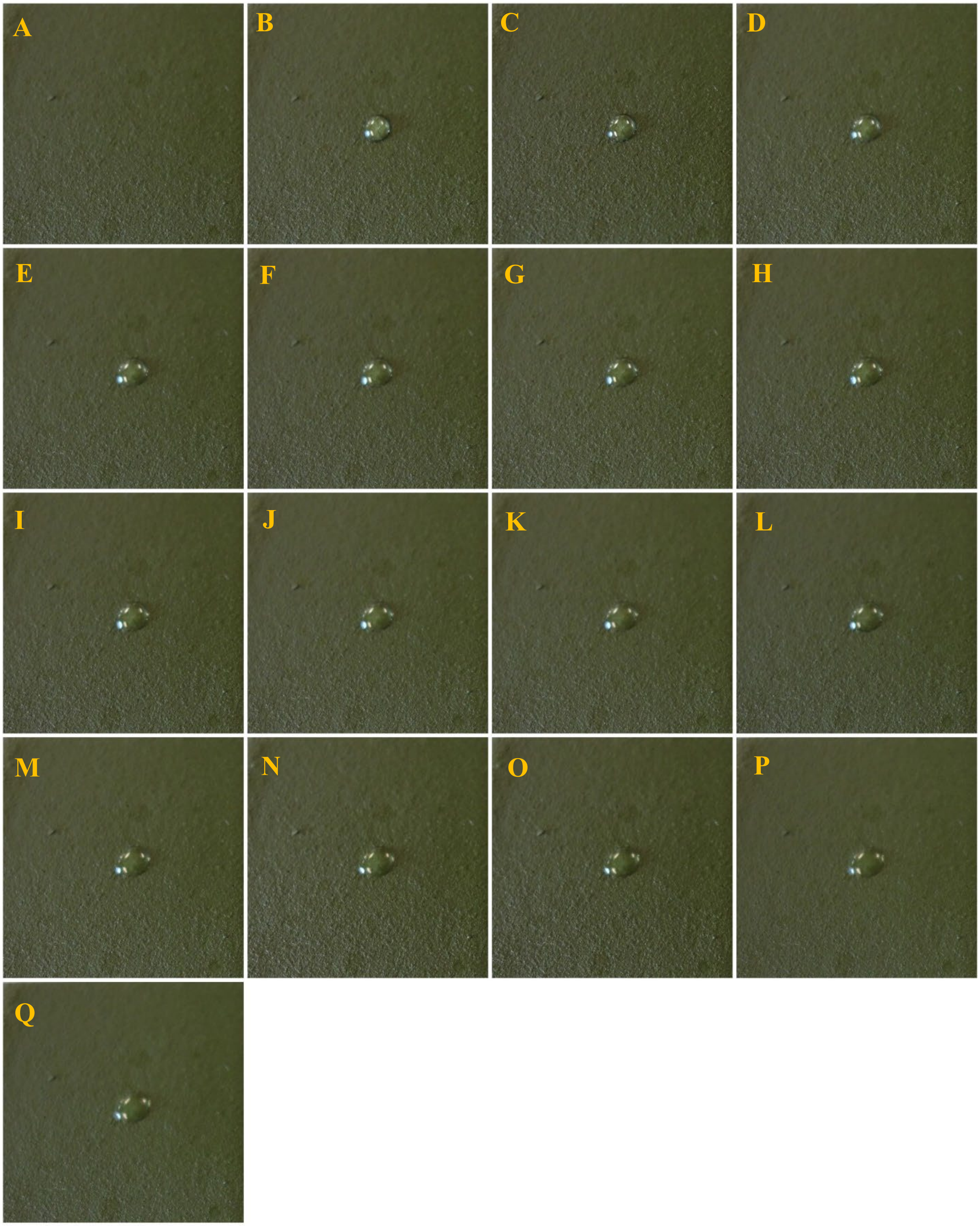
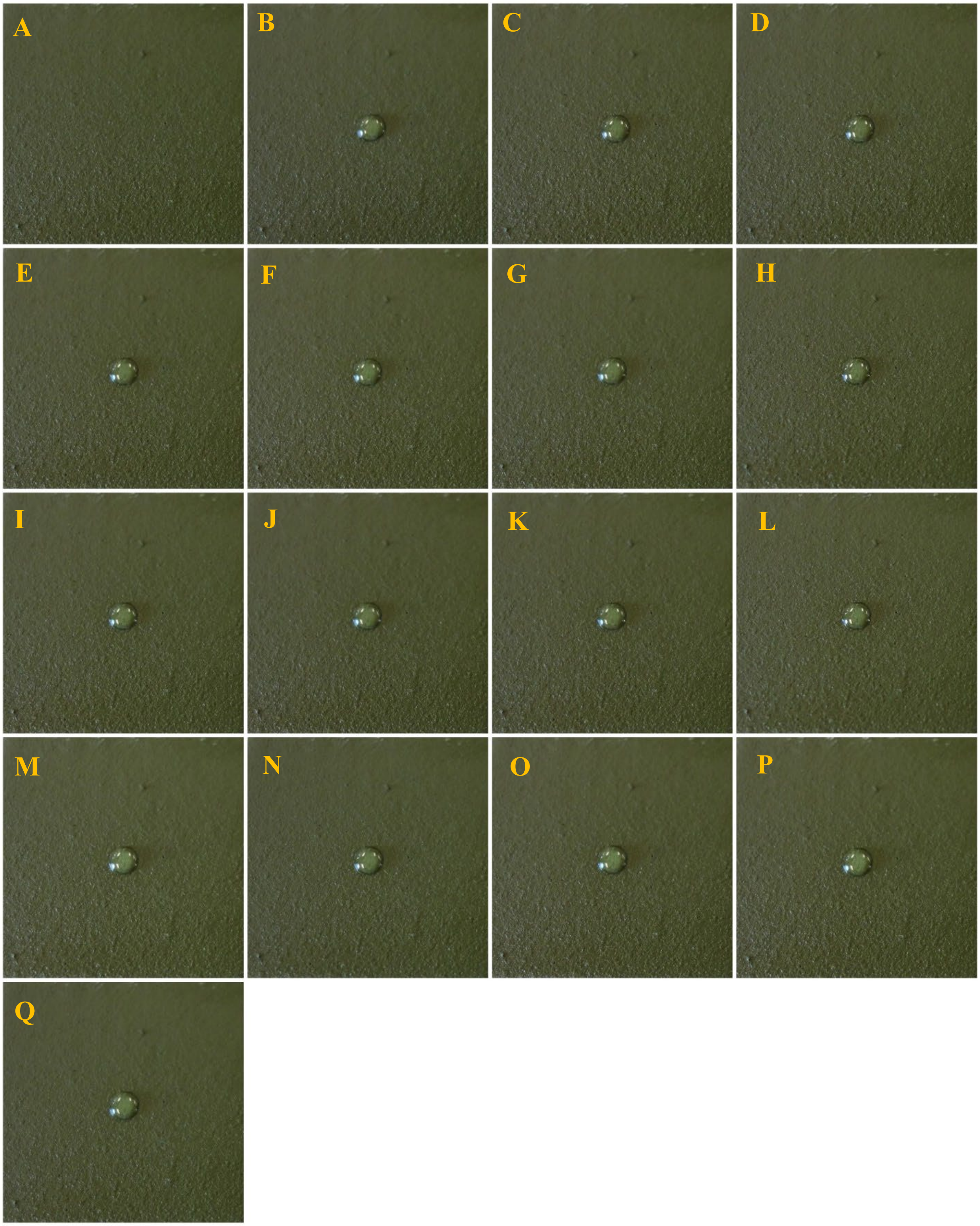


Fig. G3 — DMMP on PFTS low ECA dip coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix H

PFTS low ECA spray coated COUPON IMAGES

Fig. H1 — DFP on PFTS low ECA spray coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

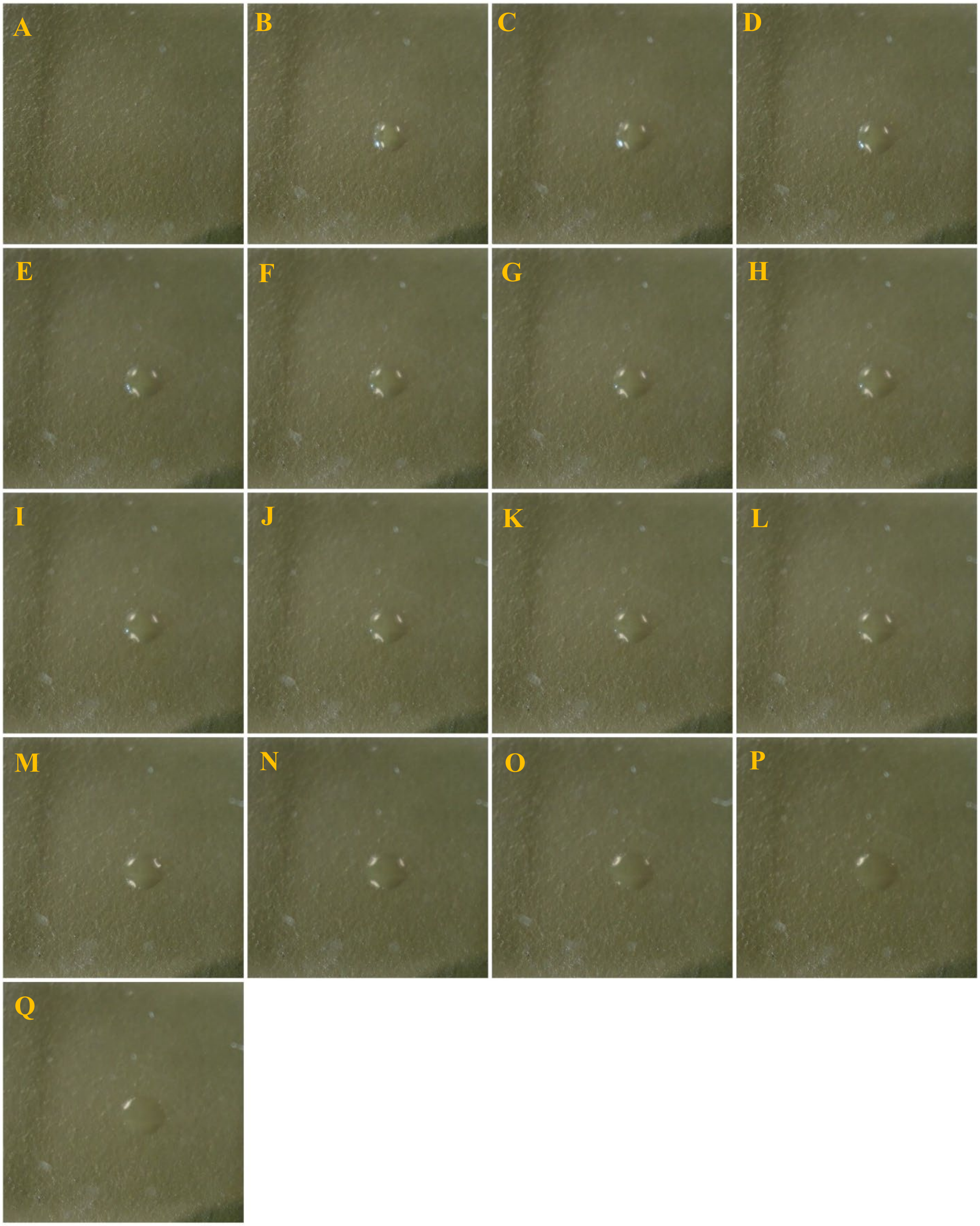


Fig. H2 — MES on PFTS low ECA spray coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

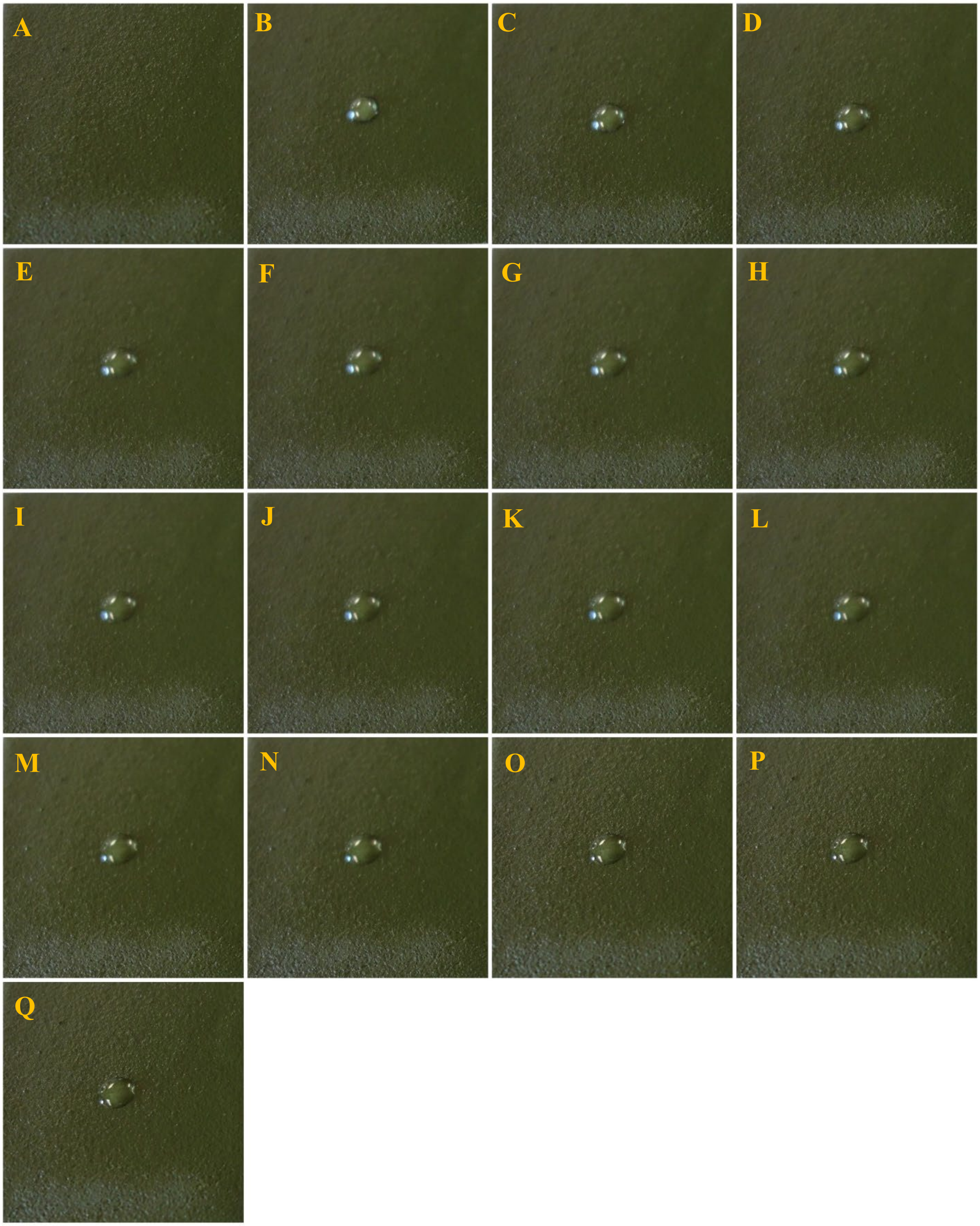
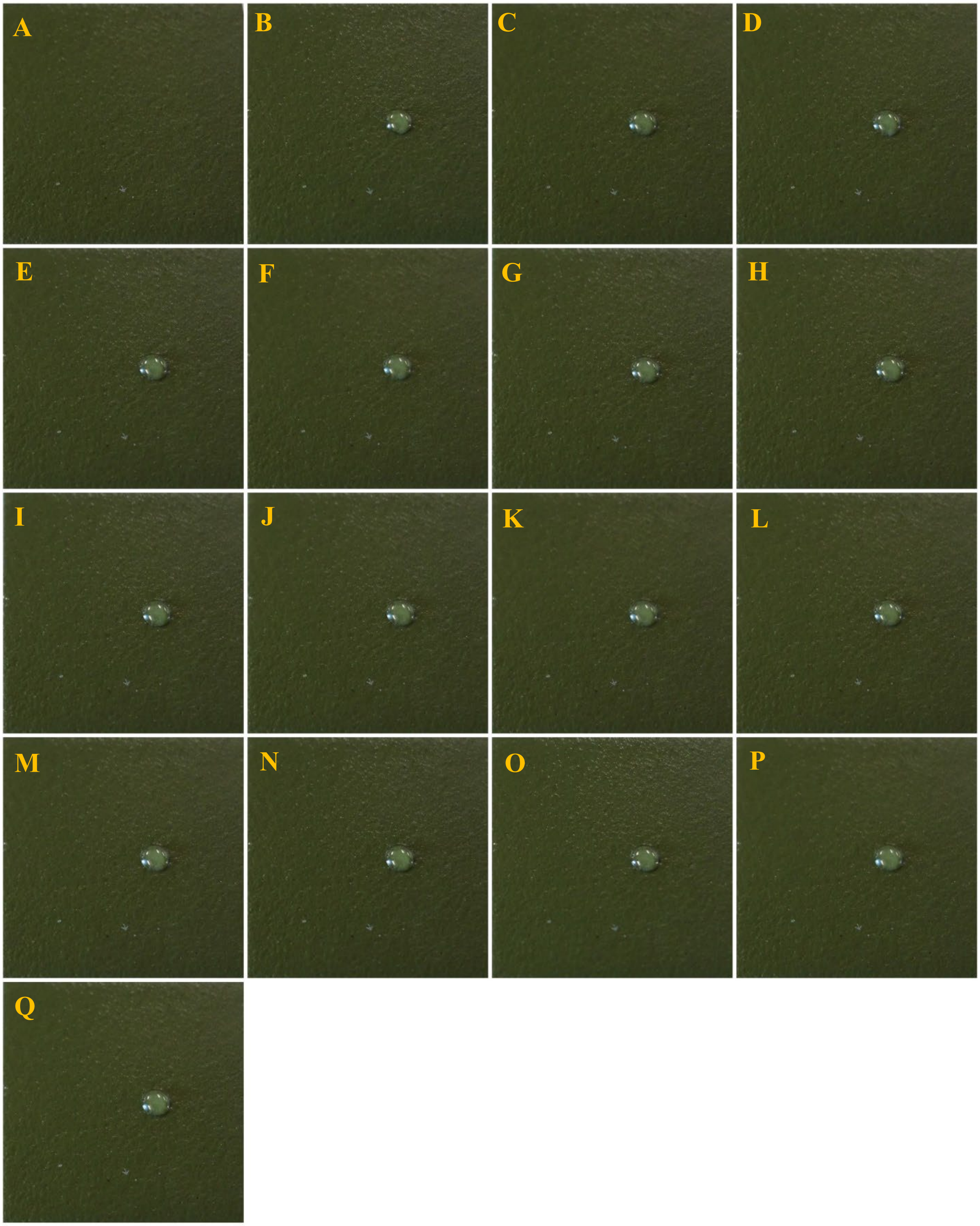


Fig. H3 — DMMP on PFTS low ECA spray coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix I

PFTS medium ECA dip coated COUPON IMAGES

Fig. I1 — DFP on PFTS medium ECA dip coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

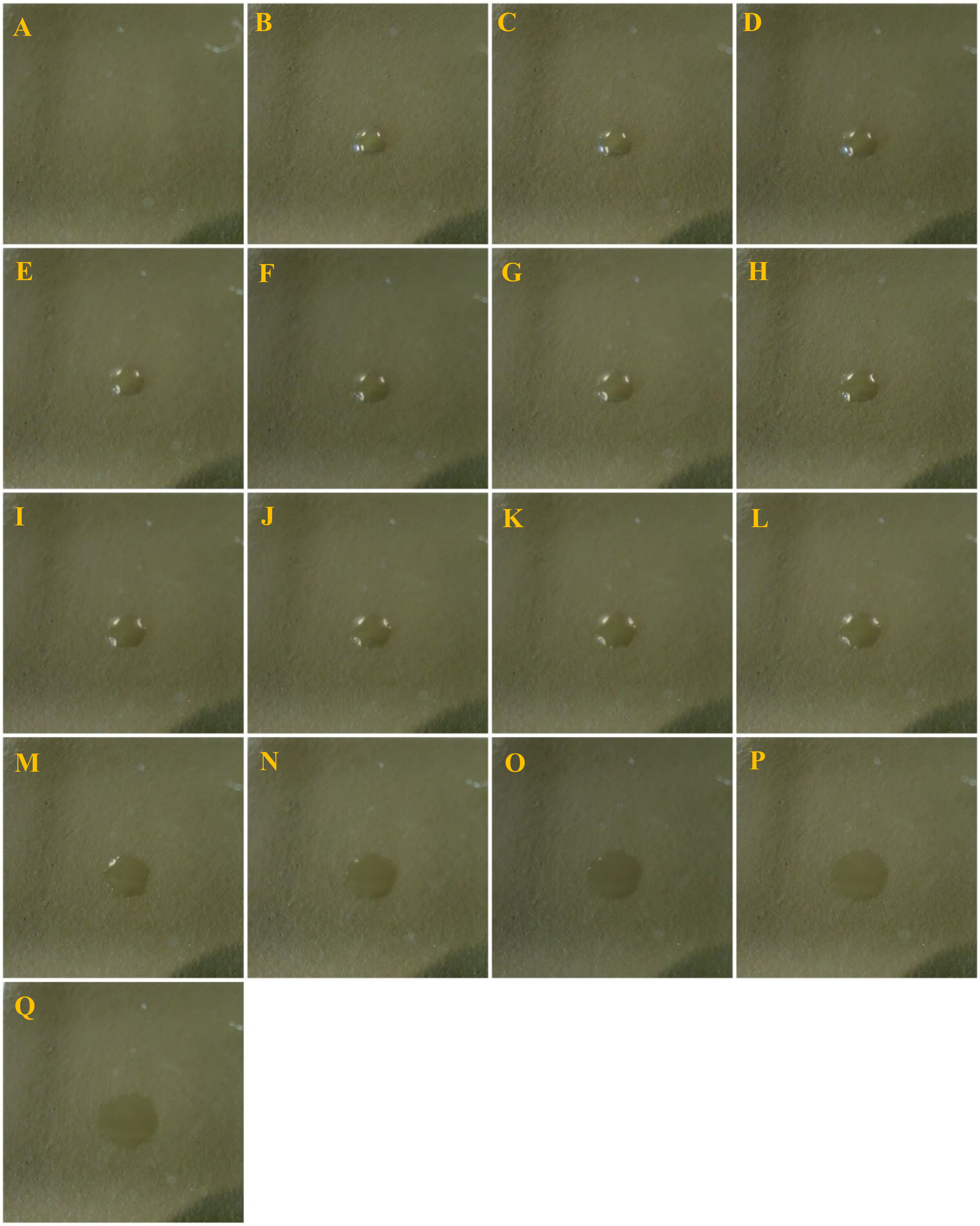


Fig. I2 — MES on PFTS medium ECA dip coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

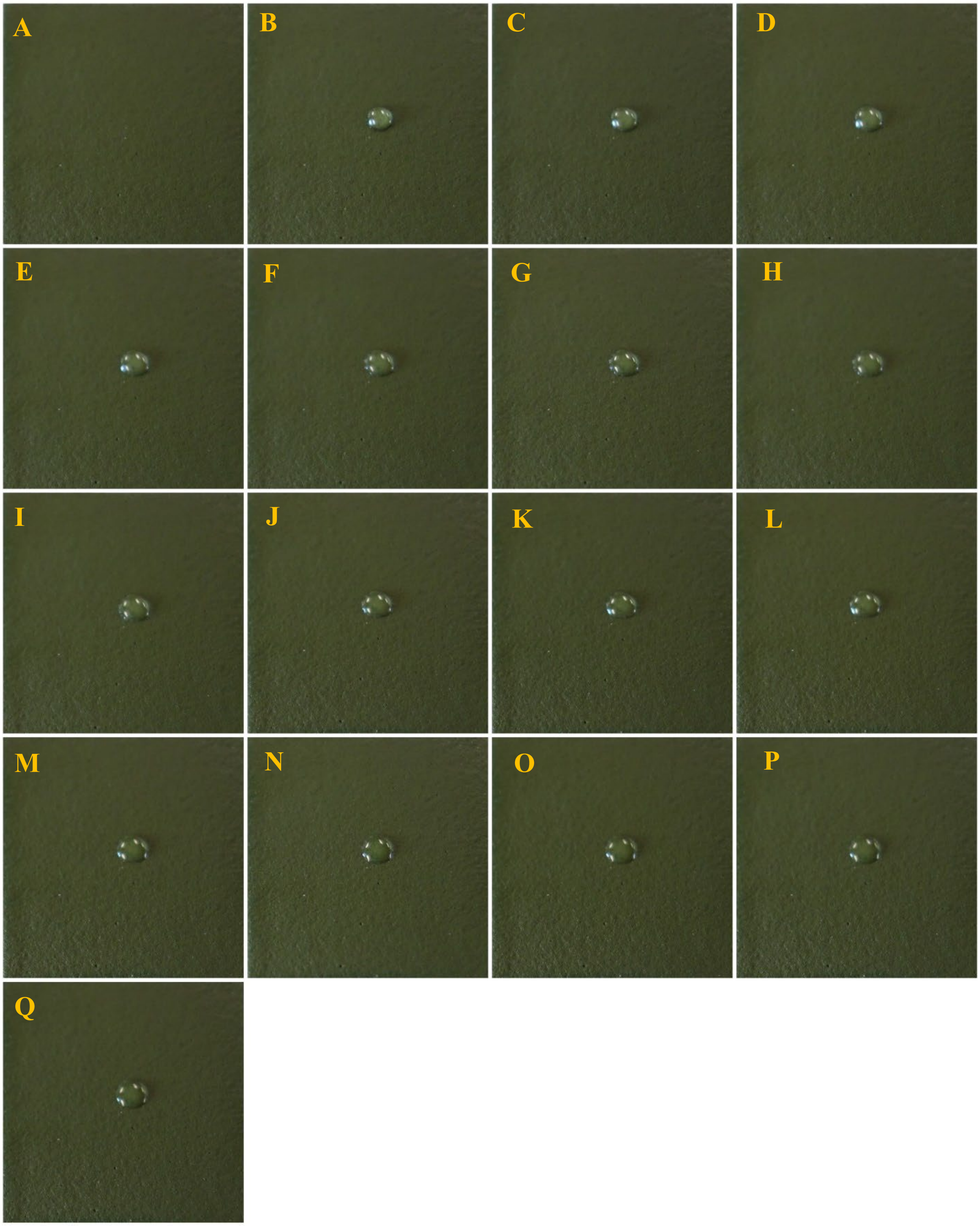
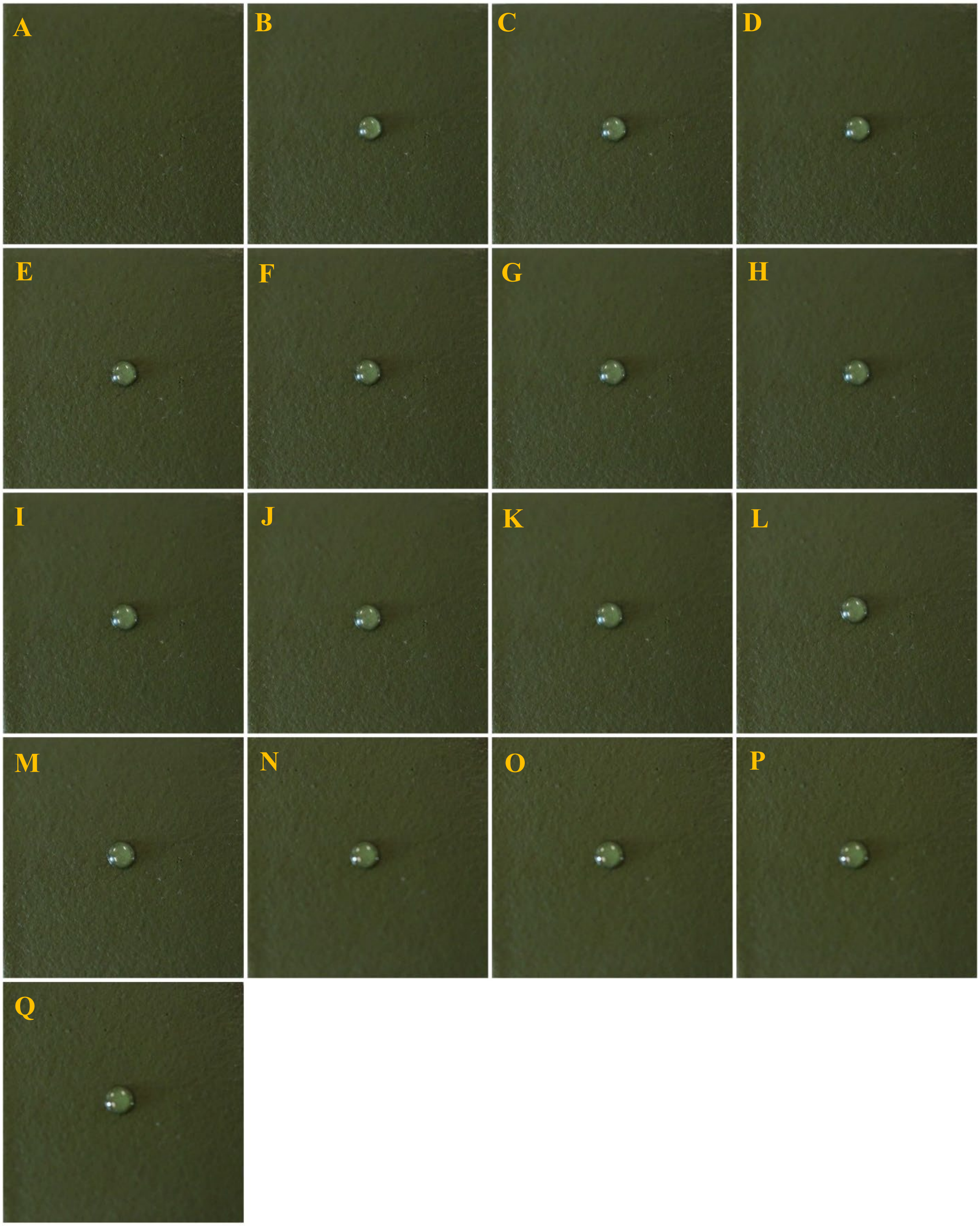


Fig. I3 — DMMP on PFTS medium ECA dip coated. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix J

PFTS medium ECA spray coated COUPON IMAGES

Fig. J1 — DFP on PFTS medium ECA spray coated . Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

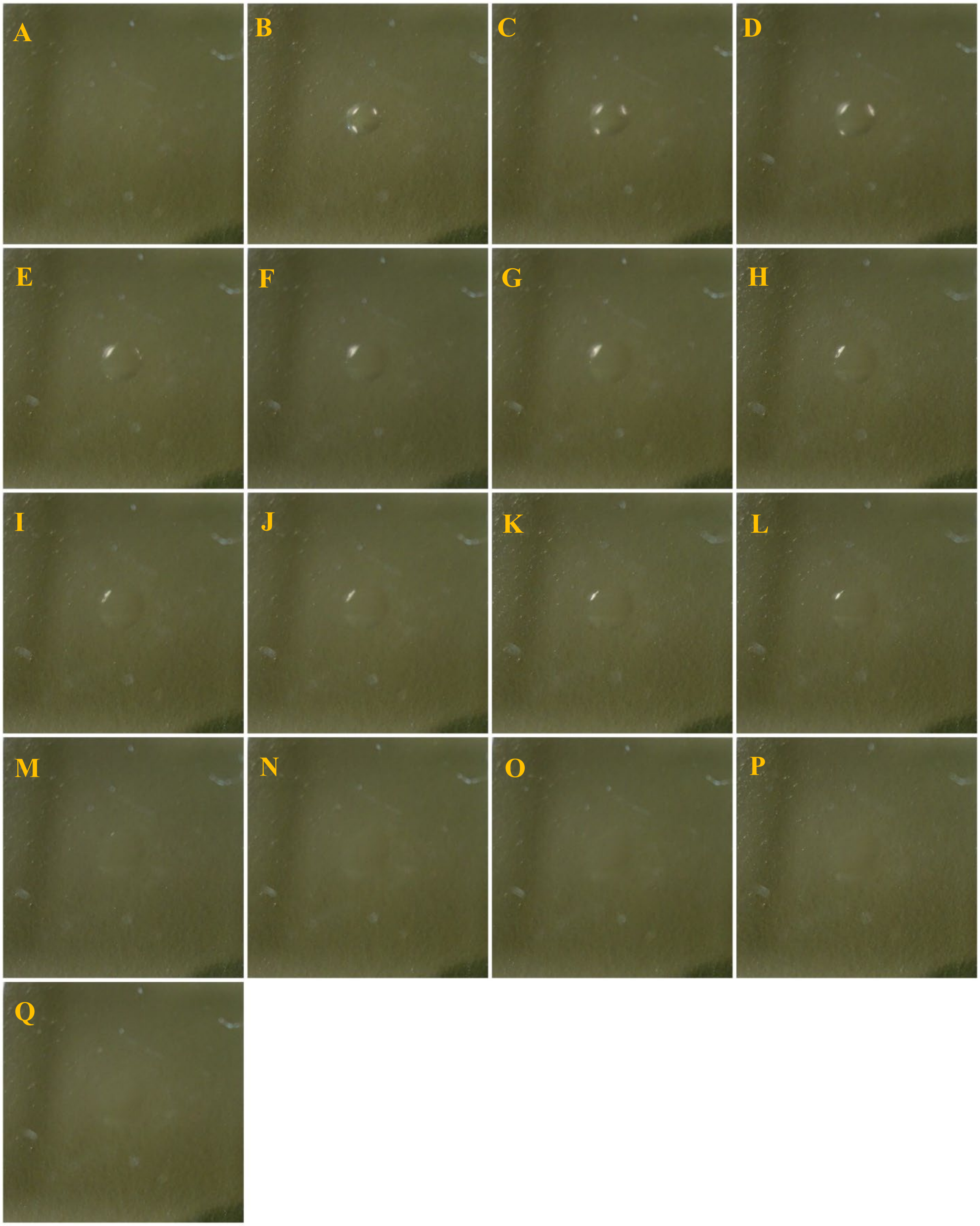


Fig. J2 — MES on PFTS medium ECA spray coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

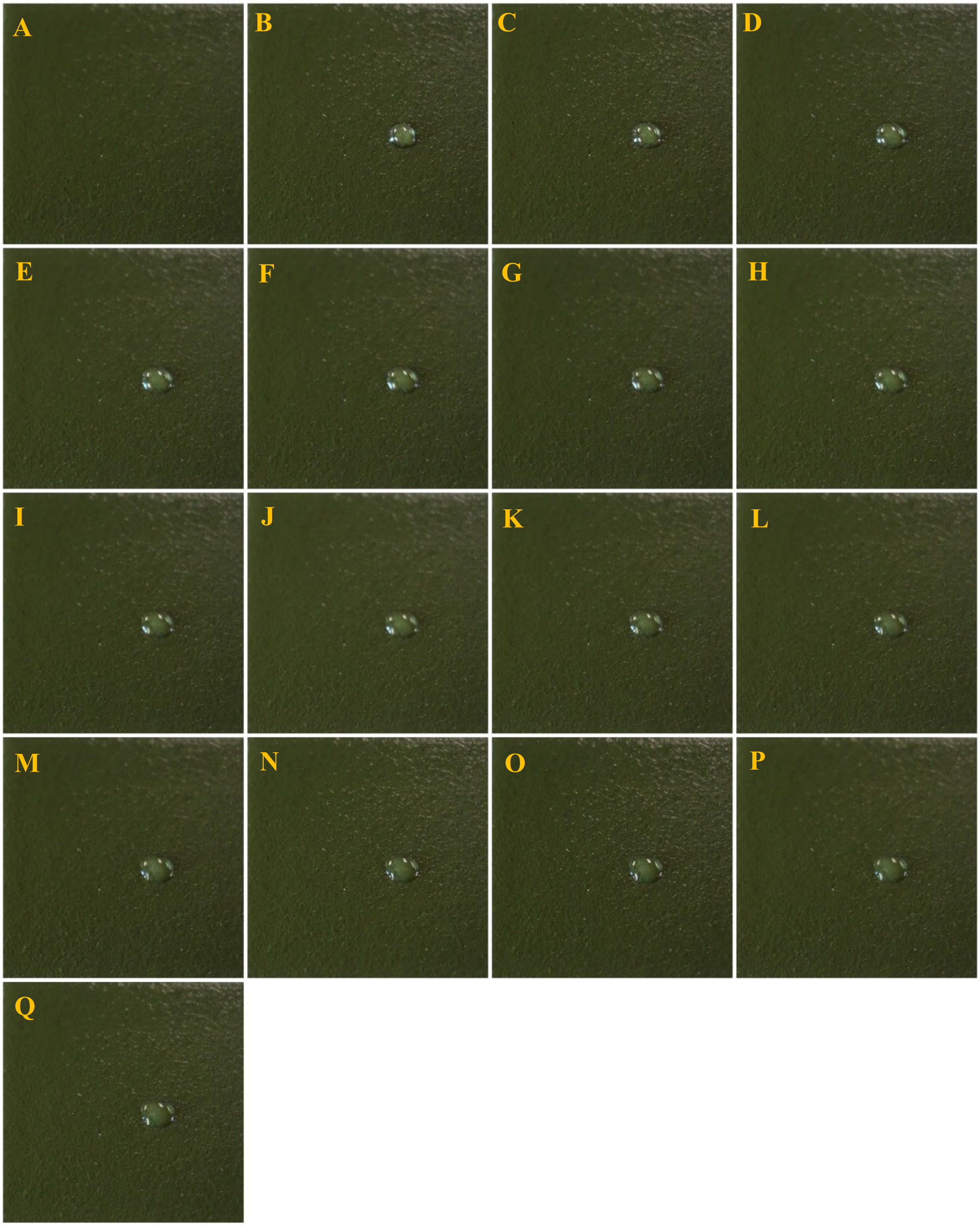
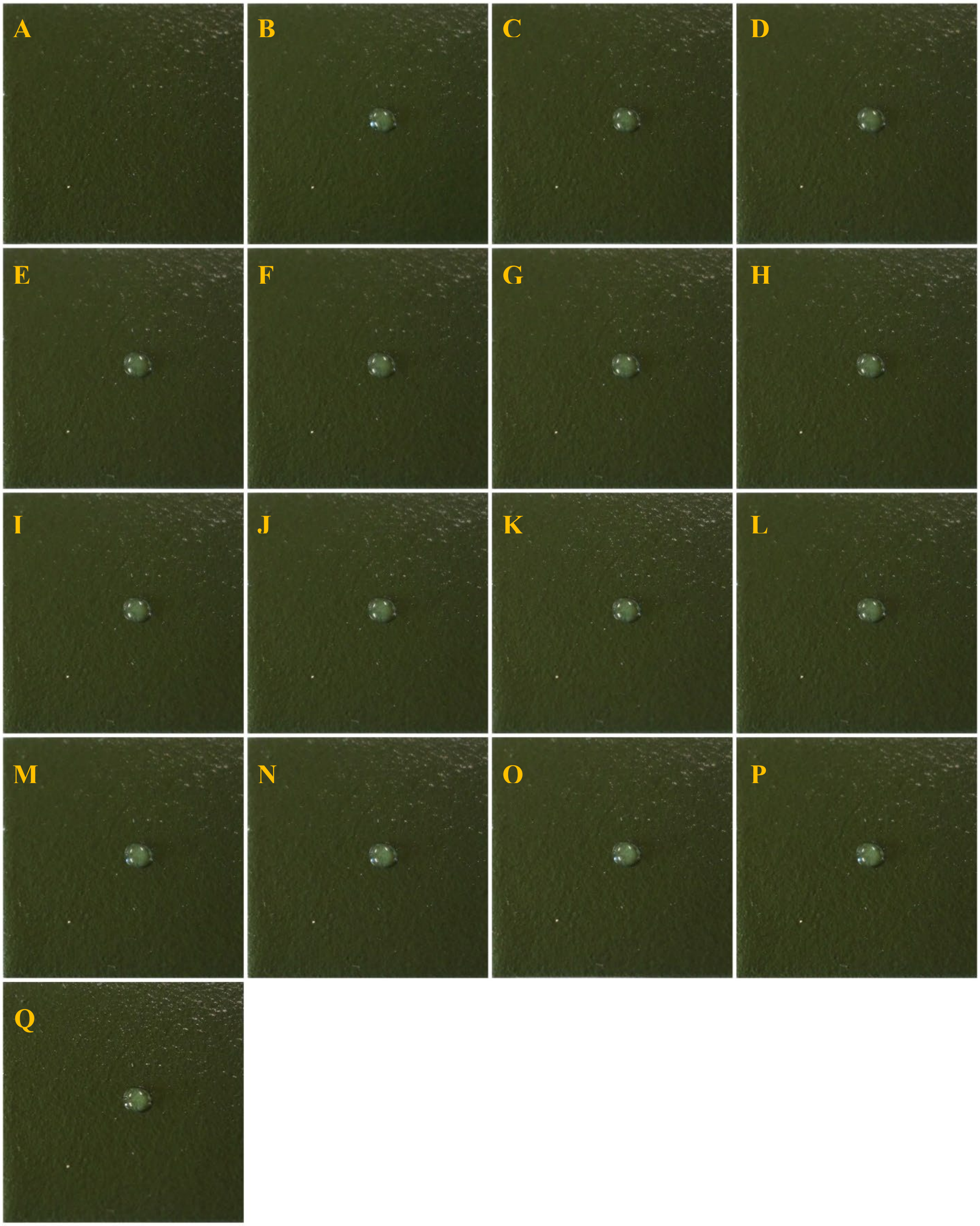


Fig. J3 — DMMP on PFTS medium ECA spray coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix K

PFTS high ECA dip coated COUPON IMAGES

Fig. K1 — DFP on PFTS high ECA dip coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

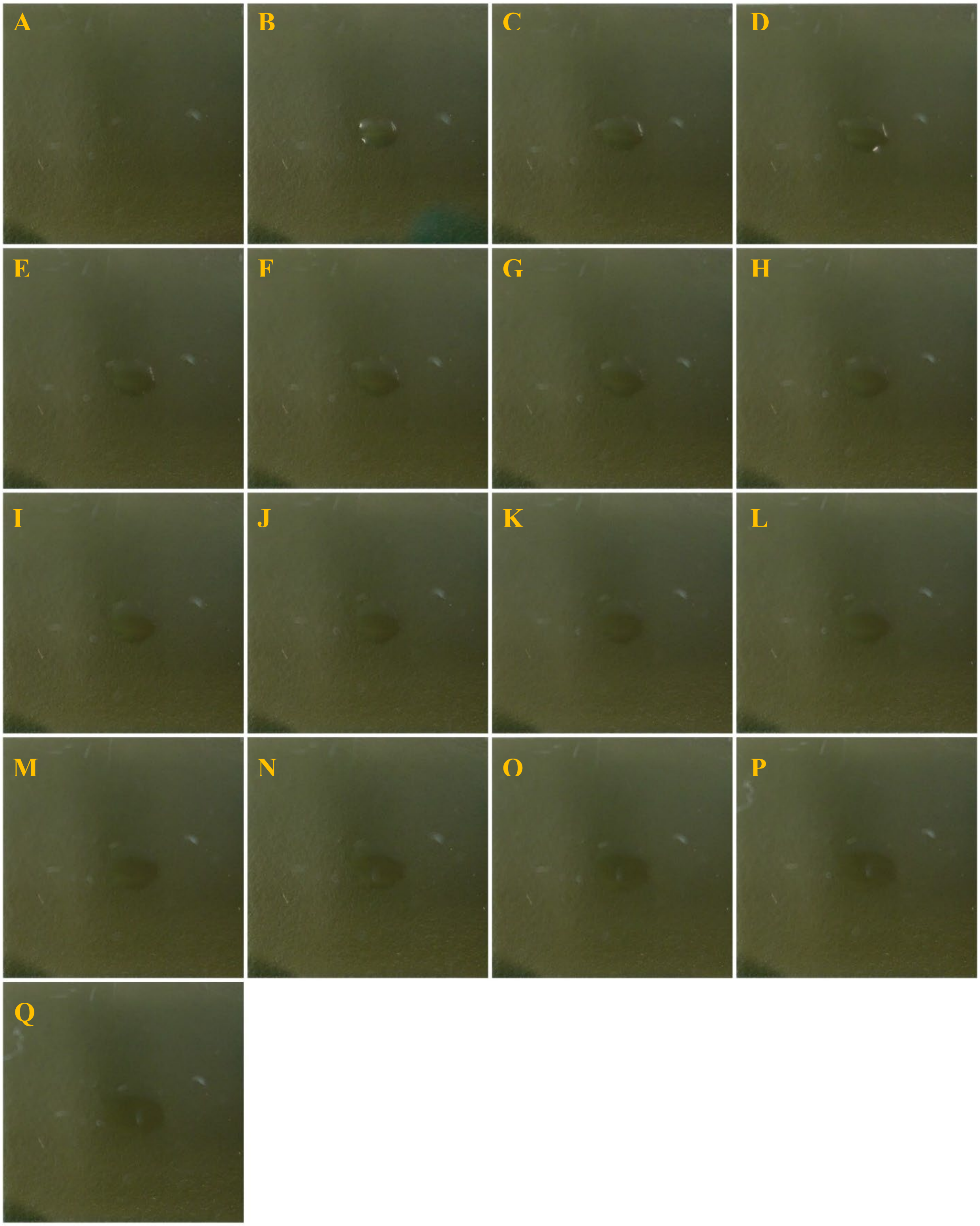


Fig. K2 — MES on PFTS high ECA dip coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

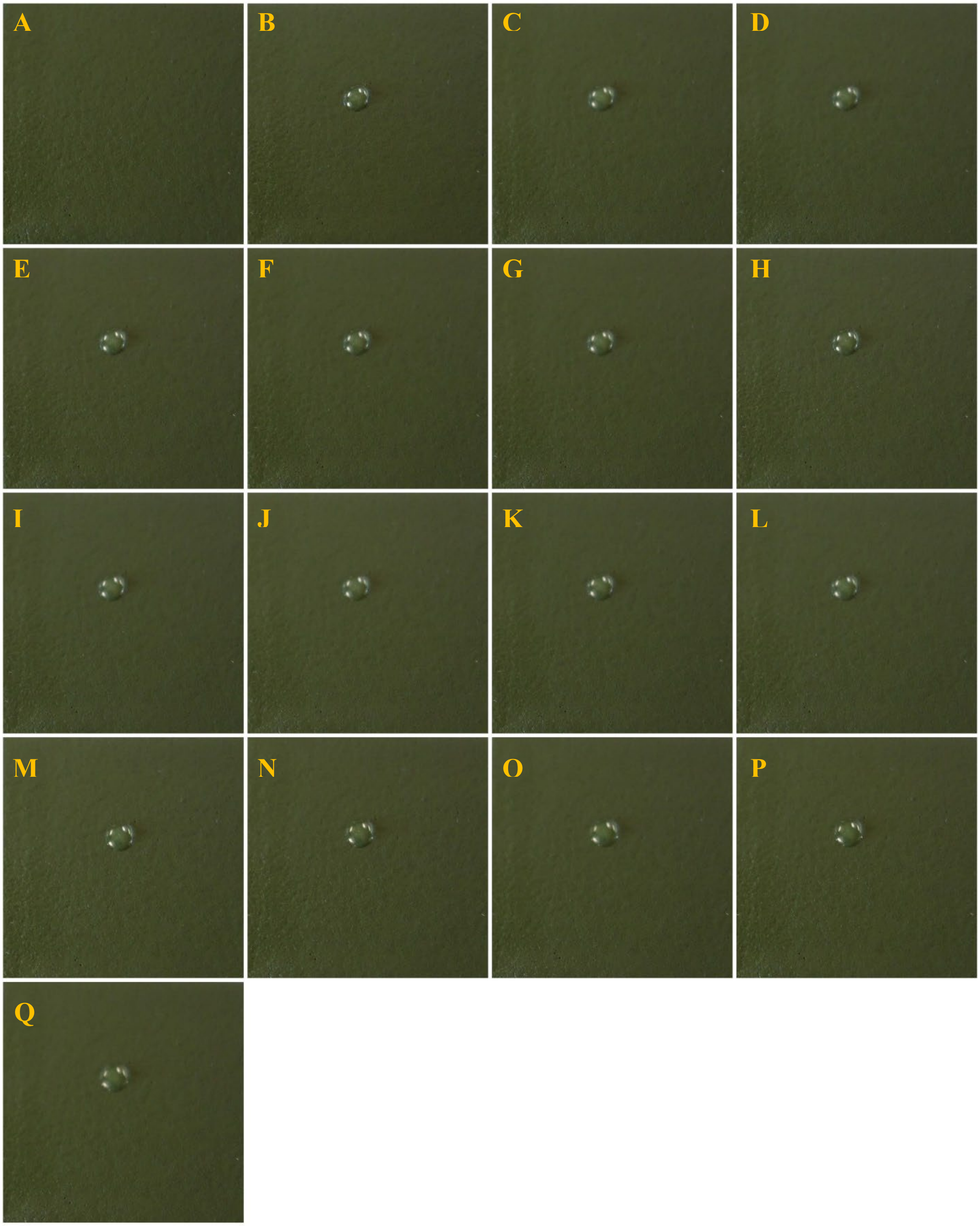
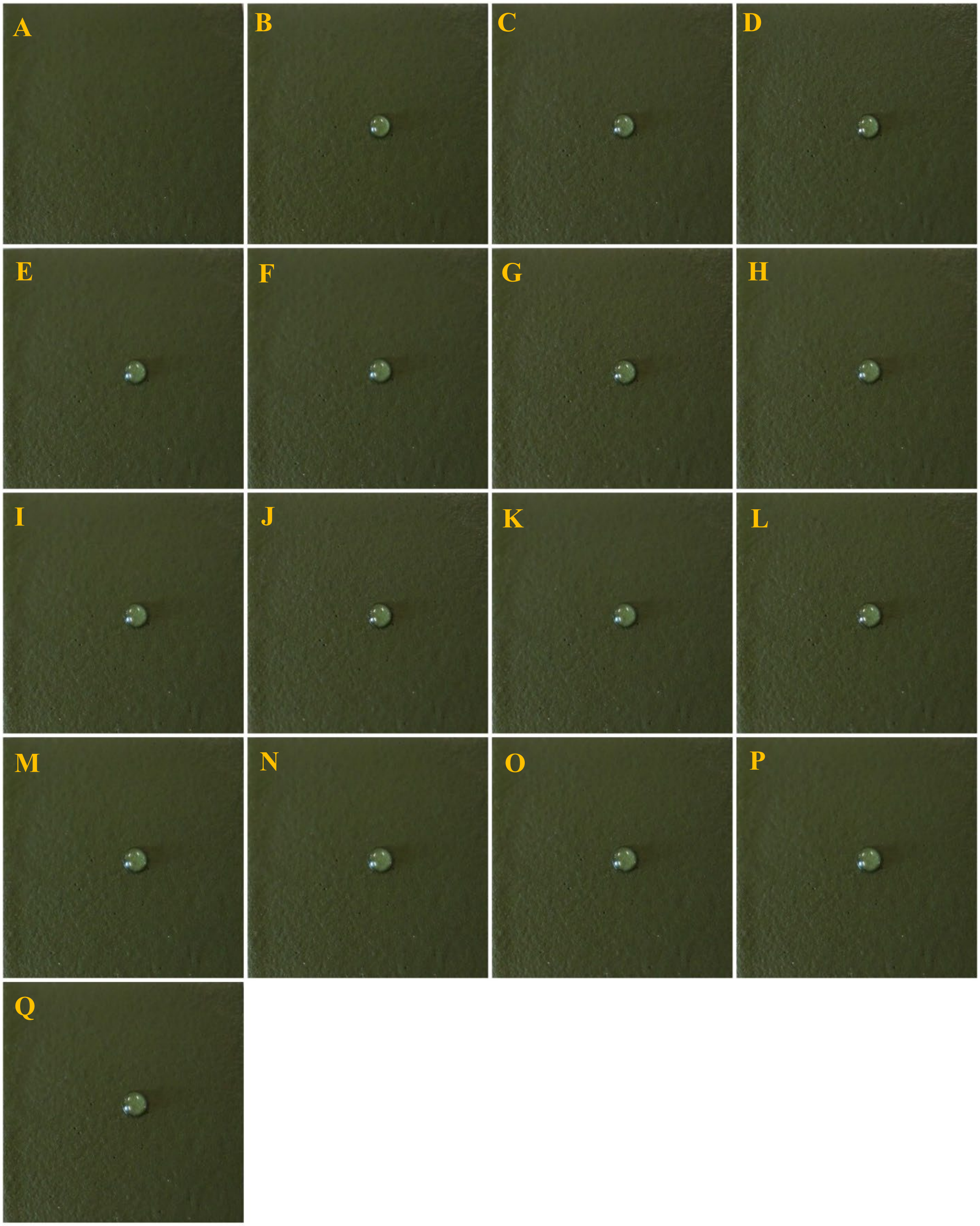


Fig. K3 — DMMP on PFTS high ECA dip coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix L

PFTS high ECA spray coated COUPON IMAGES

Fig. L1 — DFP on PFTS high ECA spray coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

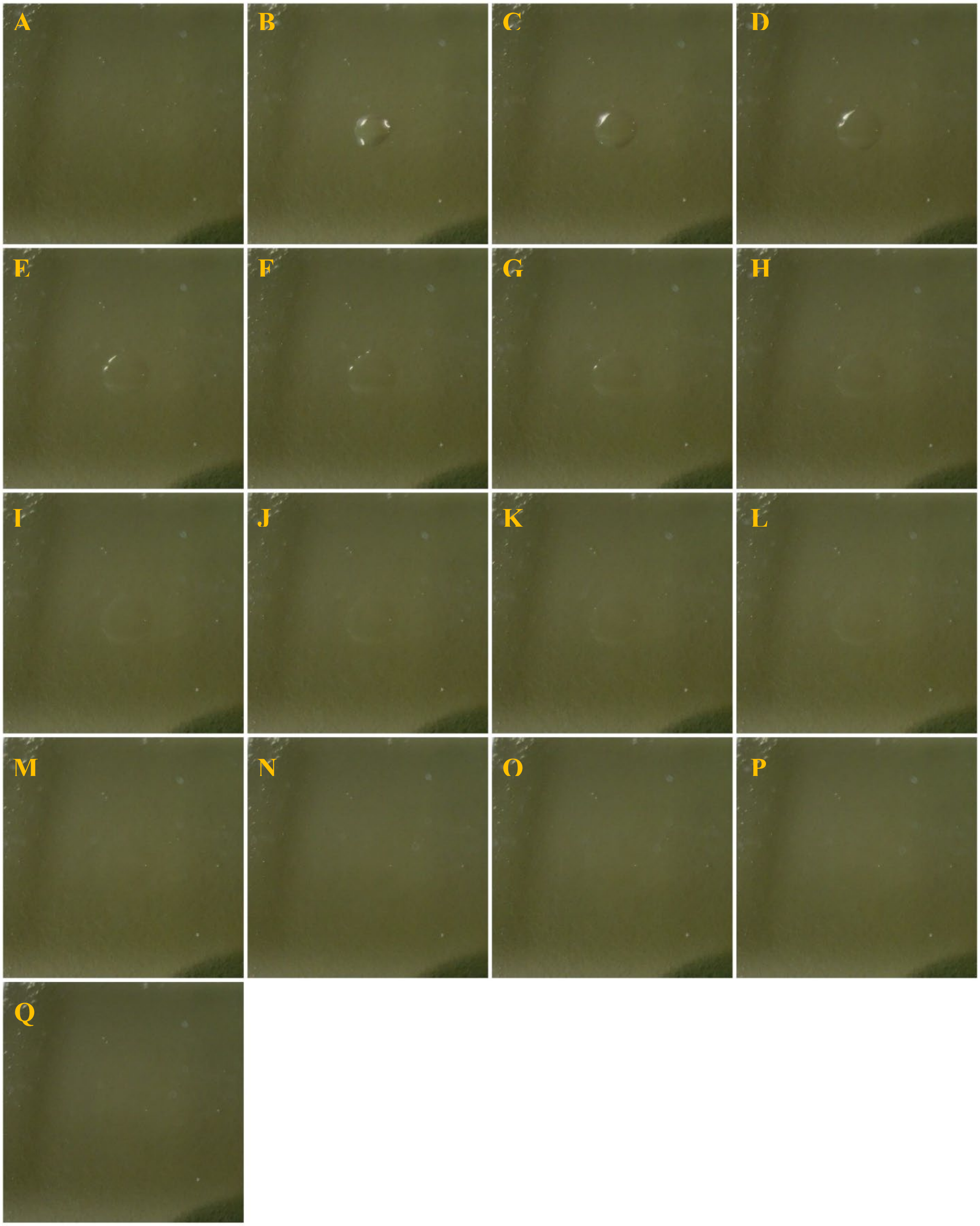


Fig. L2 — MES on PFTS high ECA spray coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

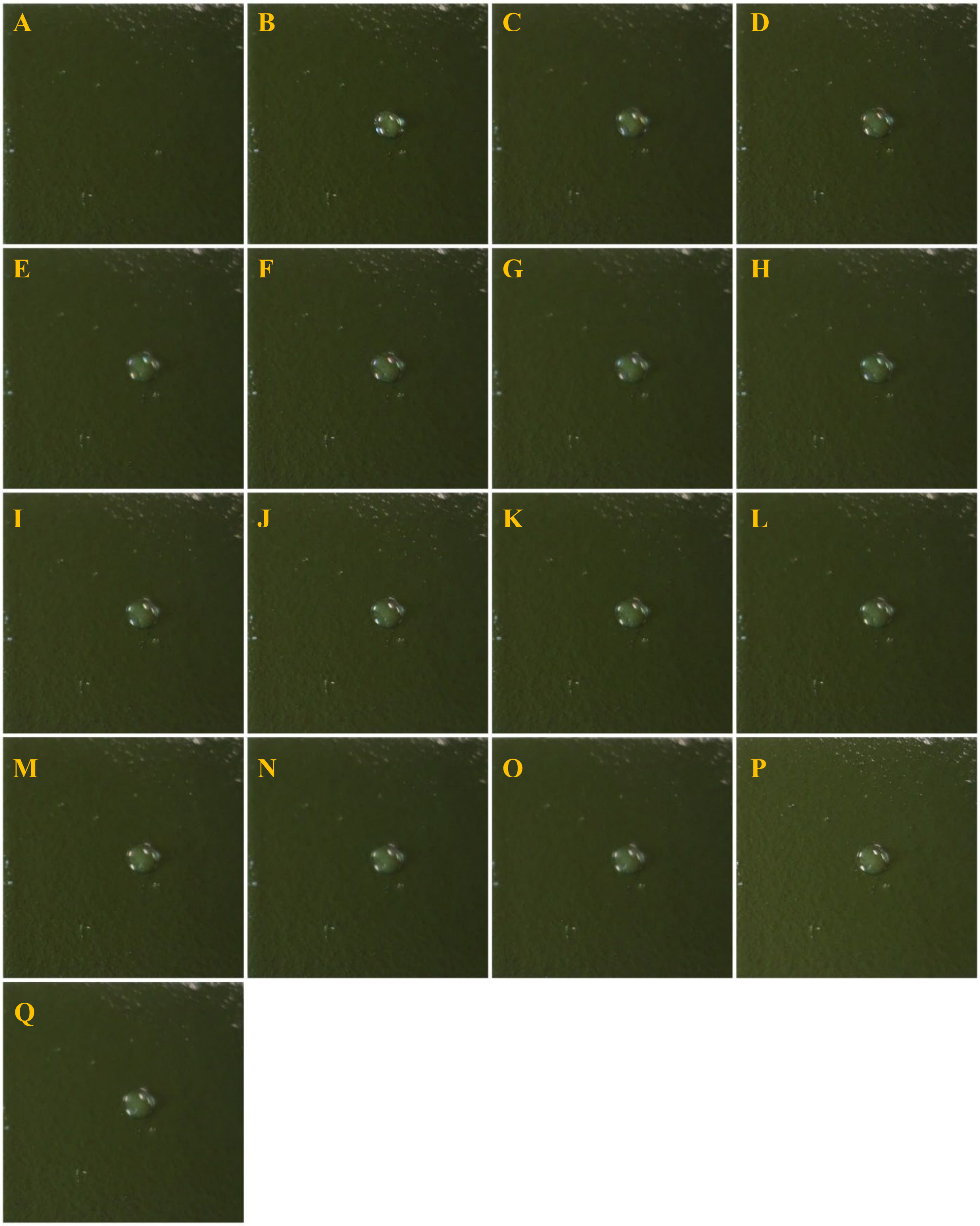
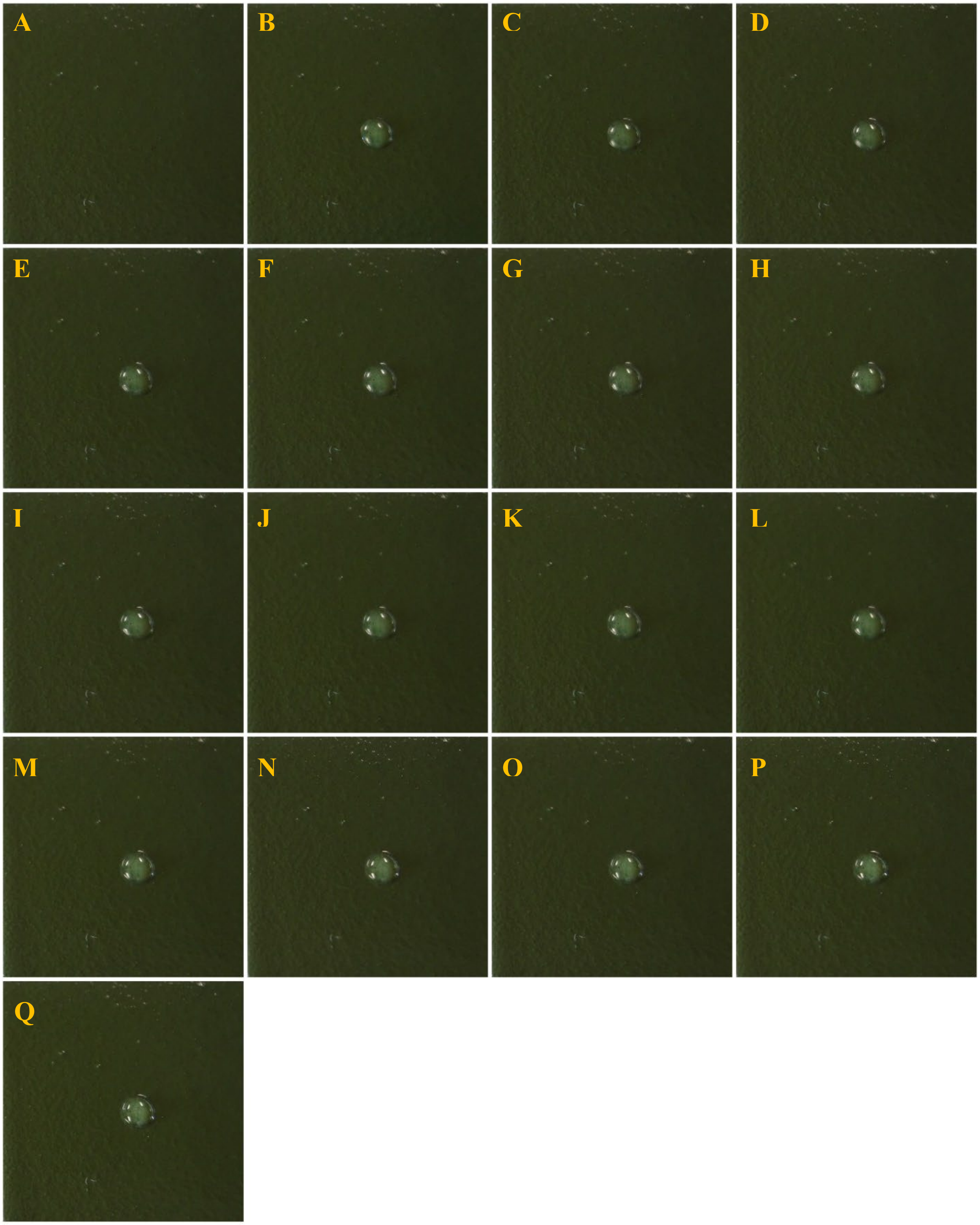


Fig. L3 — DMMP on PFTS high ECA spray coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix M

PFTS extra high ECA dip coated COUPON IMAGES

Fig. M1 — DFP on PFTS extra high ECA dip coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

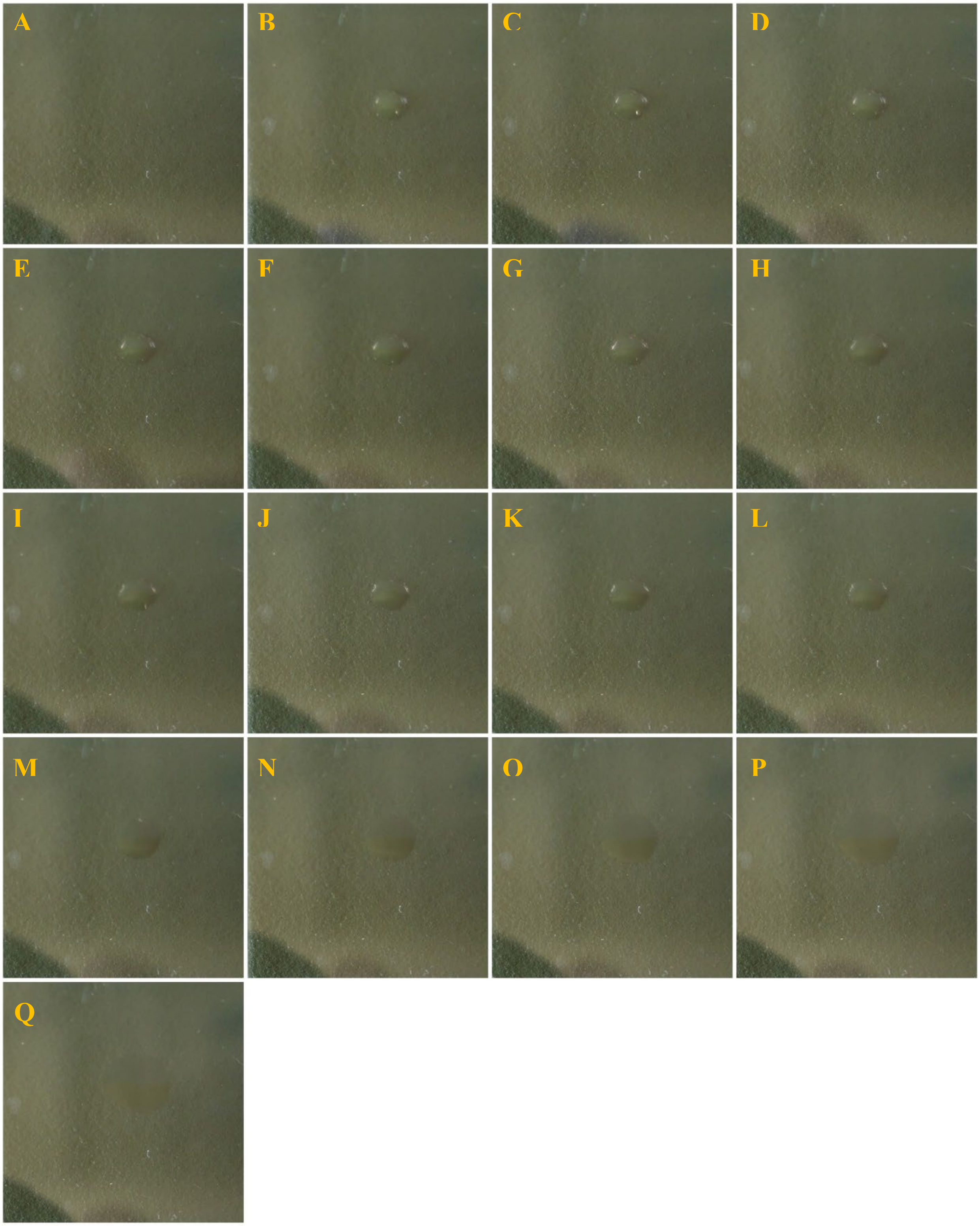


Fig. M2 — MES on PFTS extra high ECA dip coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

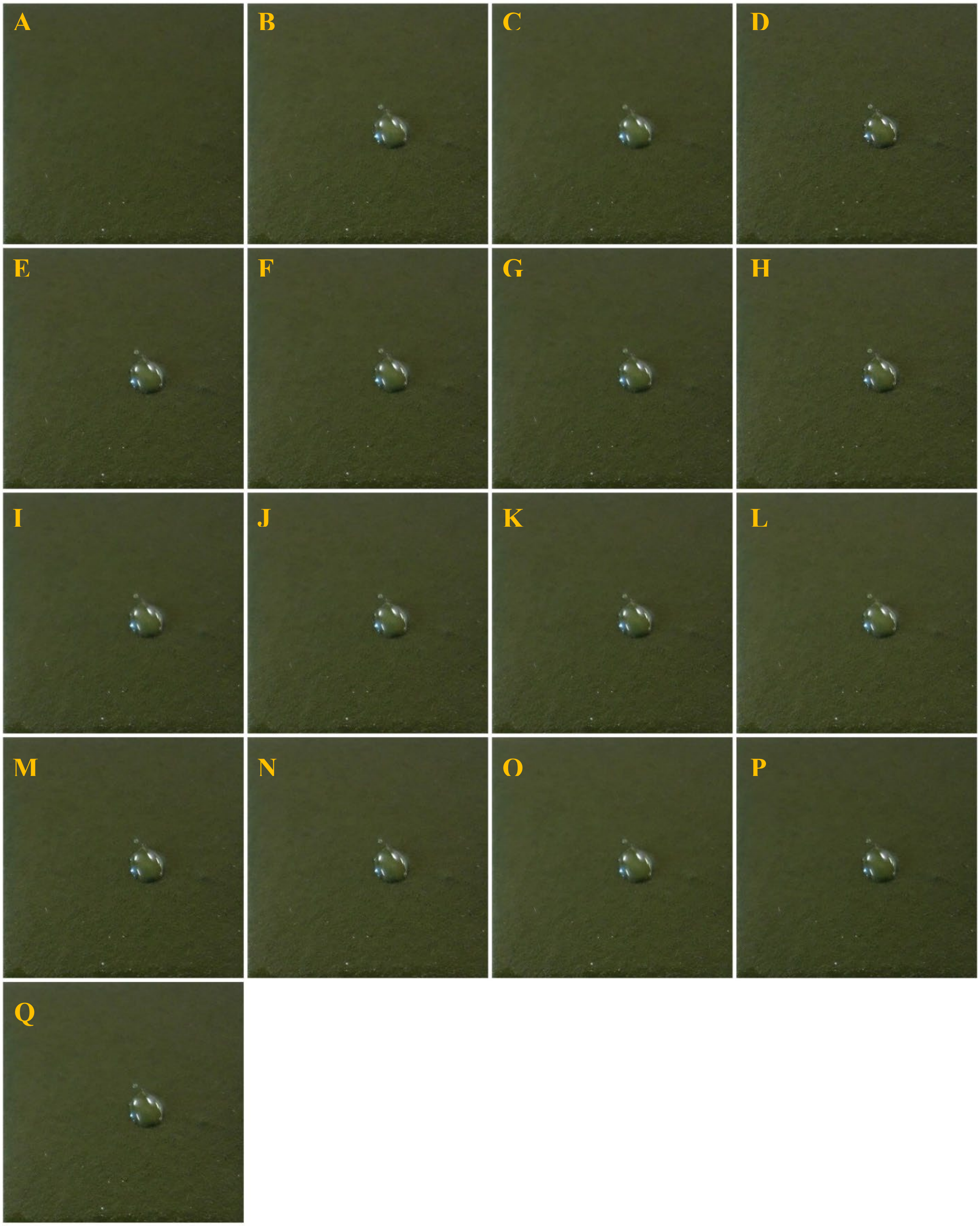
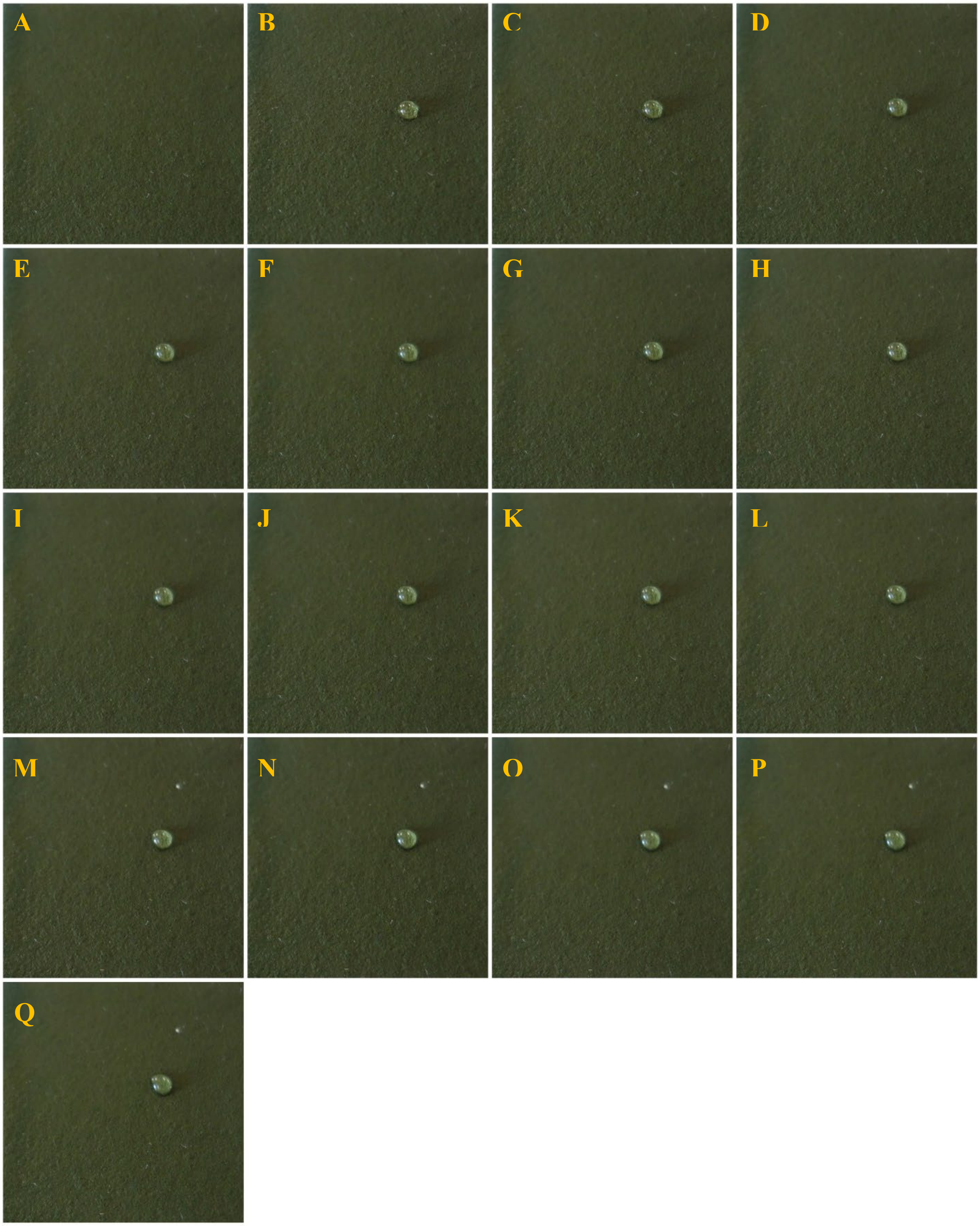


Fig. M3 — DMMP on PFTS extra high ECA dip coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix N

PFTS extra high ECA spray coated COUPON IMAGES

Fig. N1 — DFP on PFTS extra high ECA spray coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

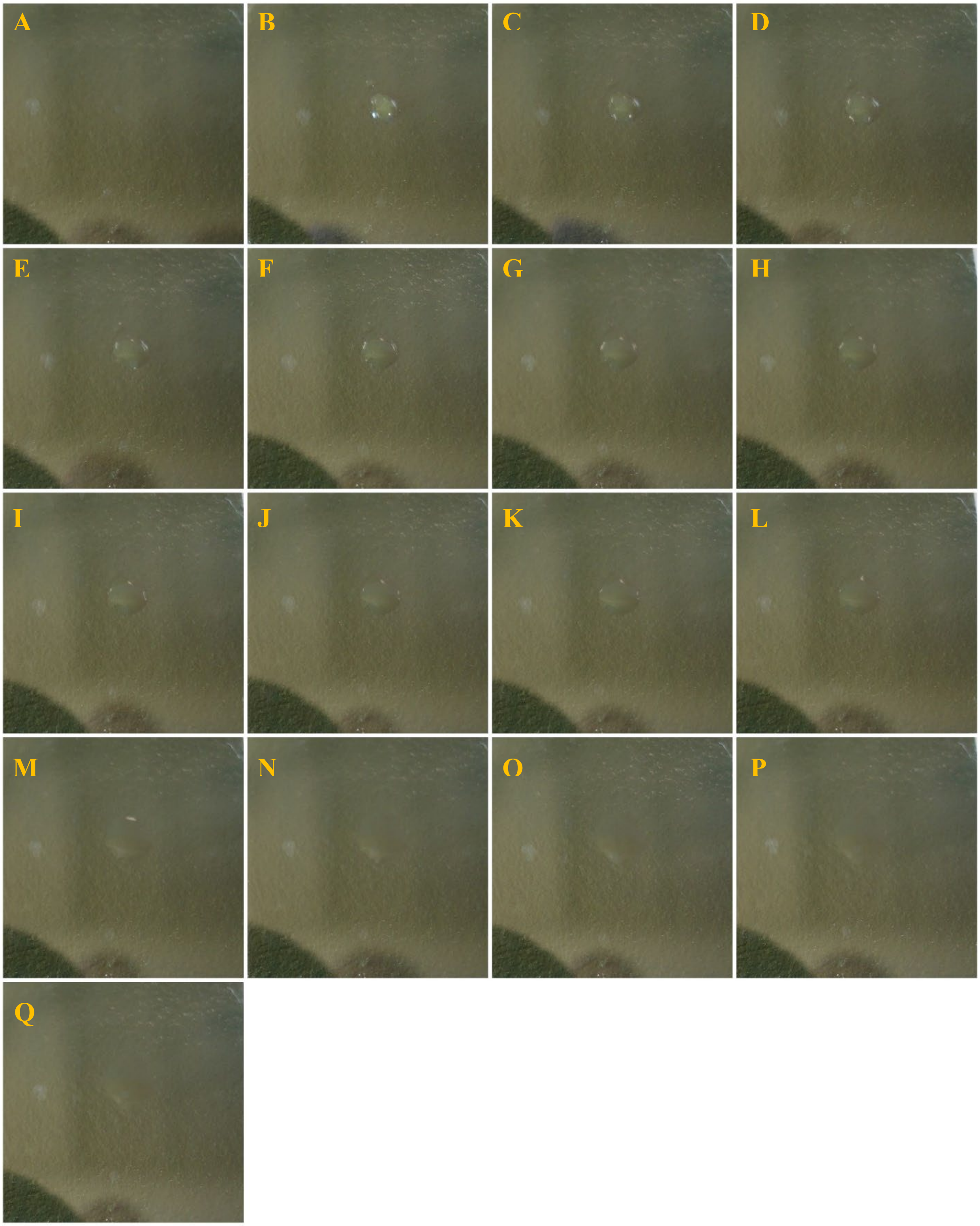


Fig. N2 — MES on PFTS extra high ECA spray coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

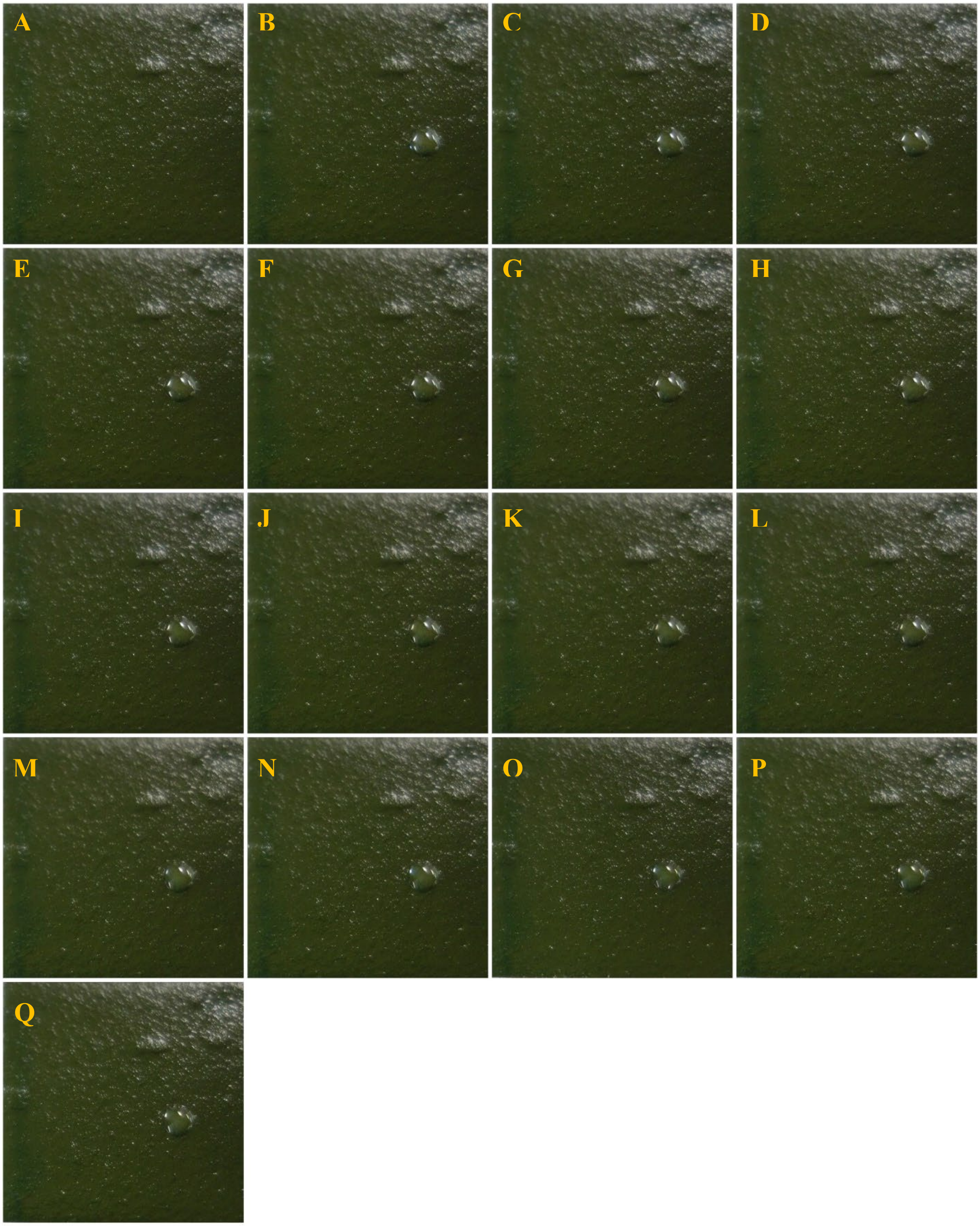


Fig. N3 — DMMP on PFTS extra high ECA spray coated. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.