Naval Research Laboratory
Washington, DC 20375-5320

NRL/6306/MR—2022/2

Bioinspired Surface Treatments for Improved Decontamination: “Dual-Layer” Polyurethane-PDMS Topcoat

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November 8, 2022

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* 08-11-2022	**2. REPORT TYPE** NRL Memorandum Report	**3. DATES COVERED** *(From - To)*

4. TITLE AND SUBTITLE Bioinspired Surface Treatments for Improved Decontamination: “Dual-Layer” Polyurethane-PDMS Topcoat	**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--2022/2
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 a surface treatment prepared by combining a polyurethane pre-polymer, isocyanate compound, and amine-terminated PDMS on paint surfaces. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphonate, 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:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Anthony Malanoski
a. REPORT U	**b. ABSTRACT** U	**c. THIS PAGE** U	U	28	**19b. TELEPHONE NUMBER** *(include area code)* (202) 404-5432

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

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EXECUTIVE SUMMARY

The Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) initiated a program in January 2015 for evaluation of bioinspired treatments suitable for use as a top coat on painted surfaces with the intention of achieving improved aqueous decontamination of these materials. Funding was provided by the Defense Threat Reduction Agency (DTRA, CB10125). This report details results for evaluation of a surface treatment prepared by combining a polyurethane pre-polymer, isocyanate compound, and amine-terminated PDMS. The materials were deposited on polyurethane paint coated aluminum coupons. 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.

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BIOINSPIRED SURFACE TREATMENTS FOR IMPROVED DECONTAMINATION: "DUAL-LAYER" POLYURETHANE-PDMS TOPCOAT

INTRODUCTION

The DoD Chemical and Biological Defense Program (CBDP) seeks to provide technologies for protection of forces in a contaminated environment, including those for 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 and develop top-coat type treatments suitable for application to painted surfaces that would reduce retention of chemical threat agents following standard decontamination approaches. The effort sought to survey relevant and related areas of research and evaluate identified technologies under appropriate methods to determine efficacy, scalability, and durability. The current document summarizes results for tests of topcoats prepared by combining a polyurethane pre-polymer, isocyanate compound, and amine-terminated PDMS. The work was inspired by a trend in literature reports of polyurethane-based coatings with "slippery" properties from PDMS functionality.

For the original work reported in the literature, researchers were interested in developing omniphobic surfaces that did not have some of the disadvantages of previously developed materials.[1,2] Previous coatings initially focused on mimicking methods nature had developed that depend on micro roughness such as seen for lotus leaves. These types of surfaces fail at high pressure and are often fragile as well as not possessing optical clarity. Slippery liquid-infused porous surface (SLIPS) coatings inspired by pitcher plant characteristics avoids some of the issues with initial coatings but presented other issues such as retention of the infused liquid. Urethanes and epoxies loaded with omniphobic polymers have previously been tested but optical clarity is rarely achieved due to phase separation of components. The researchers developed a synthesis method to generate optically clear urethane coatings using PDMS. These coatings exhibited the desired omniphobic surface coating properties as well as maintaining optical clarity. The use of urethanes should result in a coating with good mechanical properties and durability. The potential for these coating to exhibit useful reduction of chemical threat agents was investigated.

For the complete system, a series of 4 variants were prepared using the synthesis outlined in the methods (Figure 1). Images of the previously tested paint only coating are also presented. Following deposition of the coating materials evaluation was performed using standard approaches including measurement of sessile, sliding, and shedding contact angles and quantification of retention for the simulant compounds. Addition of the coating had little impact on the visible characteristics of the coupons.

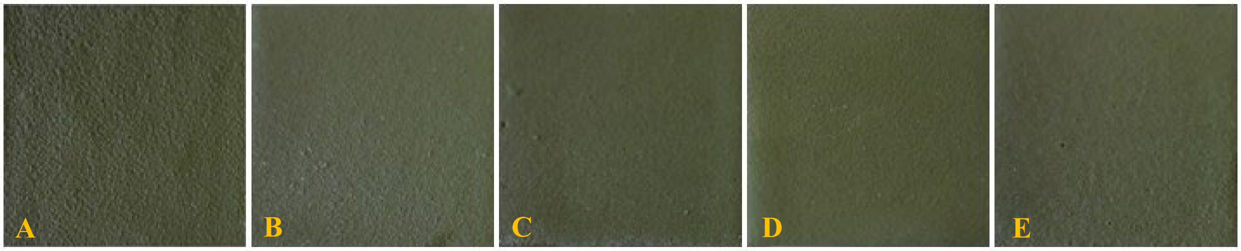

Fig. 1 — Images of painted coupons from initial series with (A) Paint only; (B) Mn~850-900; (C) Mn~3,000; (D) Mn~5,600; (E) Mn~27,000.

Manuscript approved October 27, 2022.

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 "Dual-Layer" Polyurethane-PDMS Topcoats was adapted from published articles. [1,2] The following reagents were used in the synthesis: Polyurethane diol solution (PU) (average M_n ~ 320, 88 wt% in H_2O, Aldrich), isophorone diisocyanate (IPDI) (Aldrich), $NH_2PDMSNH_2$ reagents include poly(dimethylsiloxane), bis(3-aminopropyl) terminated (M_n ~ 27,000, Aldrich) and aminopropyl terminated polydimethylsiloxane (DMS-A11 M_n ~ 850-900, DMS-A15 M_n ~ 3000, DMS-A21 M_n ~ 5000, from Gelest), Acetone, hexanes. In a 20 mL vial, 0.25 g PU diol (~ 0.7 mmol) was dispersed in 10 mL acetone with sonication. 0.39 g IPDI was added (1.8 mmol) and the mixture was sonicated for 1 h. While PU/IPDI/acetone was being sonicated, 8 painted Al coupons were rinsed with 2-propnaol and dried in an oven at ~ 60 °C. In a 120 mL PFA jar, 0.25 g of a selected $NH_2PDMSNH_2$ was dissolved in 50 mL hexanes (5 mg/mL). Dried painted substrates were allowed to cool to RT. They were coated with PU/IPDI/acetone mixture using a transfer pipet (enough to wet surface, solvent quickly evaporated). Substrates were heated in oven at 100 °C for 20 min. After allowing to cool to RT, substrates were immersed in $NH_2PDMSNH_2$/hexanes for 10 s. Substrates were heated in oven at 100 °C for 6 h.

RESULTS

Analysis of the support surface in the absence of additional coatings provides a point of comparison for evaluating the benefits of the surface treatments. Each table includes data on the relevant support material, a painted aluminum coupon and for a Fomblin Y lubricated painted aluminum coupon. Results for a new 3M ceramic based coating were considered. Application of the coatings considered here reduced the surface energy of the painted surface (Table 1 and Figure 2); The four variants of "Dual-Layer" Polyurethane-PDMS all had surface free eneigies lower than both the painted and the Fomblin Y lubricated coupons. The Mn~850-900 coating has the lowest surface energy of any coating in the comparison. All of the surfaces were fully wetted by heptane. No sliding on the surfaces was noted below an incline of 60°. No shedding behavior was noted for these surfaces.

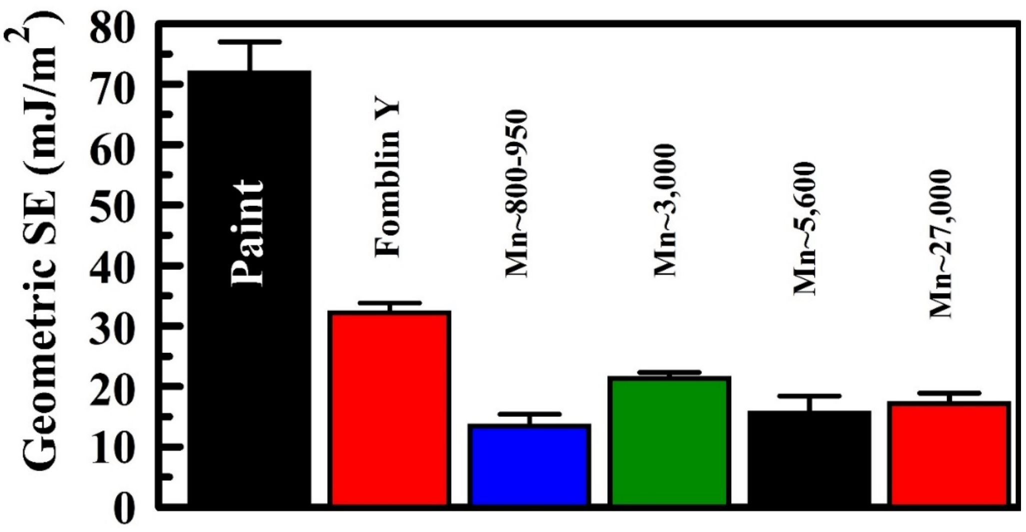

Fig. 2 — Geometric surface energy (mJ/m^2) for the evaluated coatings. Paint and Fomblin Y results provided for comparison.

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

Coupon	Liquid	Sessile Angle	Sliding Angle	Shedding Angle	Geometric Surface Energy (mJ/m^2)
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	
Mn~850-900	water	109.7 ± 0.7	>60	>60	13.4 ± 2.0
	ethylene glycol	91.0 ± 2.1	>60	>60	
	n-heptane	--	--	--	
Mn ~3,000	water	98.8 ± 1.1	>60	>60	21.3 ± 1.0
	ethylene glycol	78.6 ± 0.76	>60	>60	
	n-heptane	--	--	--	
Mn ~5,600	water	98.3 ± 2.3	>60	>60	15.6 ± 2.8
	ethylene glycol	91.3 ± 3.1	>60	>60	
	n-heptane	--	--	--	
Mn ~27,000	water	98.4 ± 1.9	>60	>60	17.1 ± 1.8
	ethylene glycol	80.0 ± 2.1	>60	>60	
	n-heptane	--	--	--	

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 at 10 and 2 min, respectively. DMMP does not spread during the course of the 30 min incubation. The coatings considered here produced differing results. DMMP spread was negligible for all the ceramic based coatings; application of Fomblin Y had a negative impact on this behavior. DFP spread was slower and possibly reduced for Mn~800-950 and for MN~27,000 while for the others the spread of the droplet was faster and larger; although spreading across the complete coupon as for the painted coupon did not occur. Possibly interaction with coating and DFP limited amount of DFP available to spread. MES spread was also negligible for all the coatings and was significantly reduced as compared to the paint only surface, and all of the surfaces provided reductions larger/equivalent to that noted for the Fomblin Y lubricated surface.

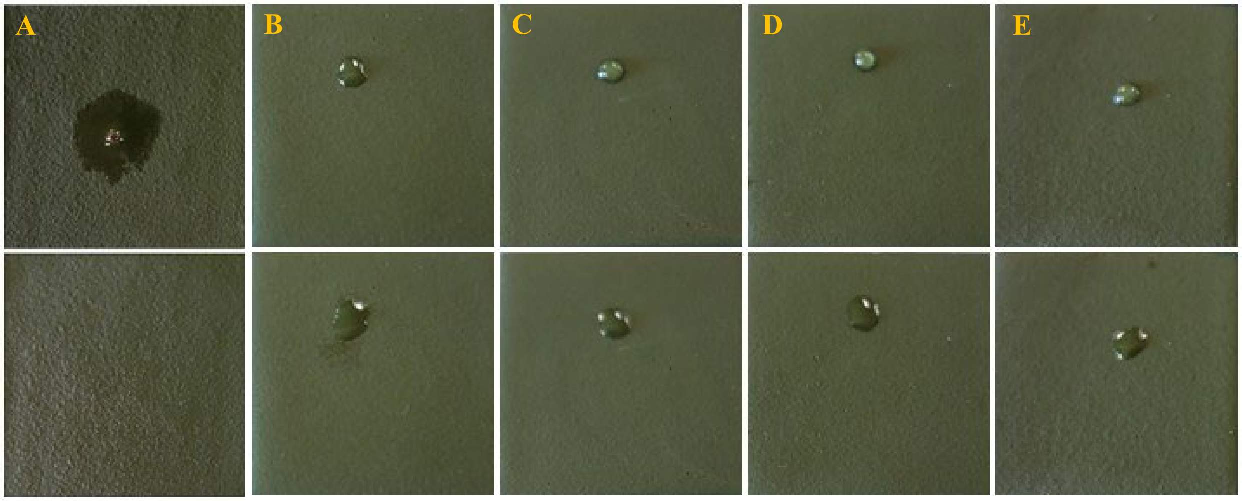

Fig. 3 — Images from initial series of coupons at 0 and 30 min following MES exposure: (A) Paint only; (B) Mn~850-900; (C) Mn~3,000; (D) Mn~5,600; (E) Mn~27,000.

The coupons were subjected to simulant exposure (10 g/m^2), aging, washing, and drying. These materials showed little change in the appearance or wetting characteristics over these processing steps. When the soapy water process was employed (Figure 5; Table 2), retention of all targets was less for the Fomblin Y lubricated paint than for the paint only surface. Here, the four variant coatings produced less retention of all targets from that seen for the Fomblin Y lubricated coupons. The Mn~850-900 coating appeared overall have the best reduction in retention across all targets except for paraoxon. It was among the worst performers for that target although there was still a significant reduction compared to painted or Fomblin Y lubricated coupons. In some cases the performed slightly worse but not by much. The only target where this was not the case was for CEES. For that agent, the retention of the commercially available coatings was worse by a larger factor.

For comparison, paint only coupons retained significant amounts of target at 5.48, 6.20, 4.28, and 0.52 g/m^2, no data for CEES. When no rinsing or decontamination steps were used, paint only coupons 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.

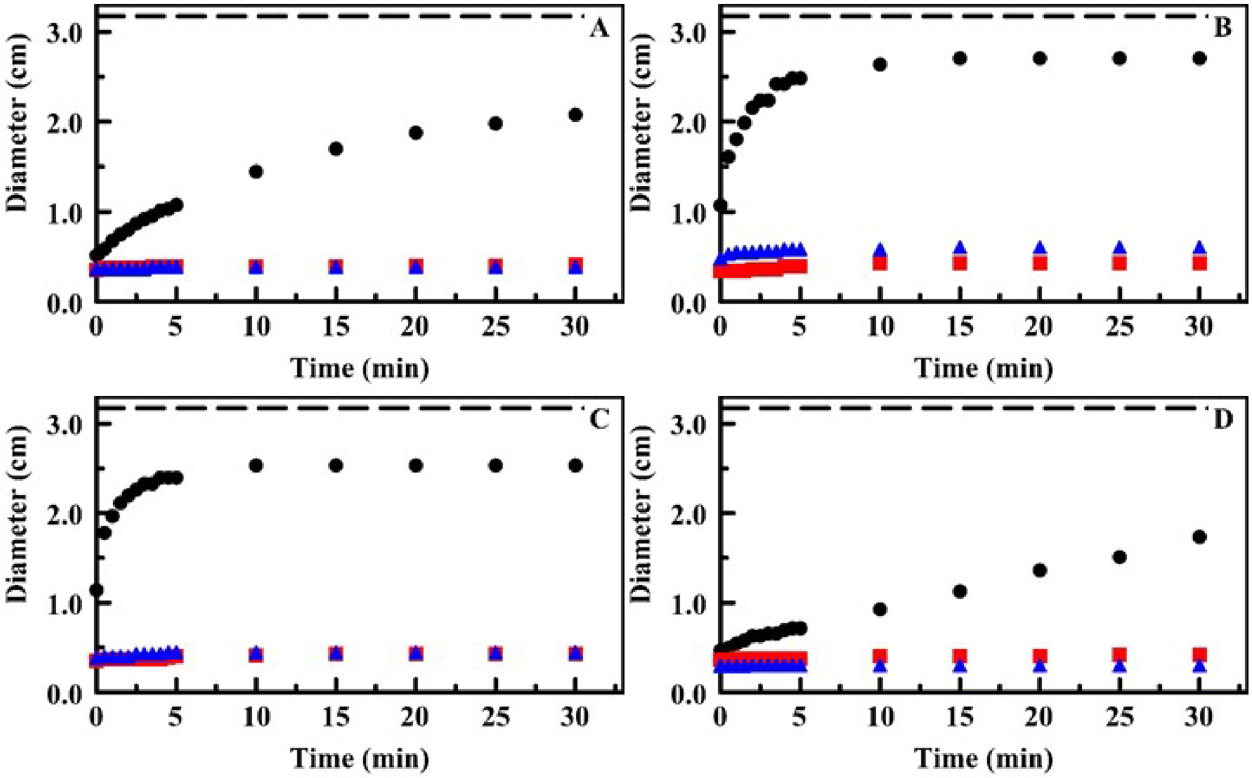

Fig. 4 — Droplet diameters over time following exposure to DFP (black), MES (red), and DMMP (blue) for painted coupons with (A) Mn~800-950; (B) Mn~3,000; (C) Mn~5,600; and (D) Mn~27,000.

Table 2 – 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
Mn~850-900	0.80	0.16	ND	0.15	0.38
Mn~3,000	0.33	0.83	0.01	0.25	0.54
Mn~5,600	0.56	0.55	ND	0.24	0.84
Mn~27,000	0.86	0.57	ND	0.12	0.42

ND = not detected

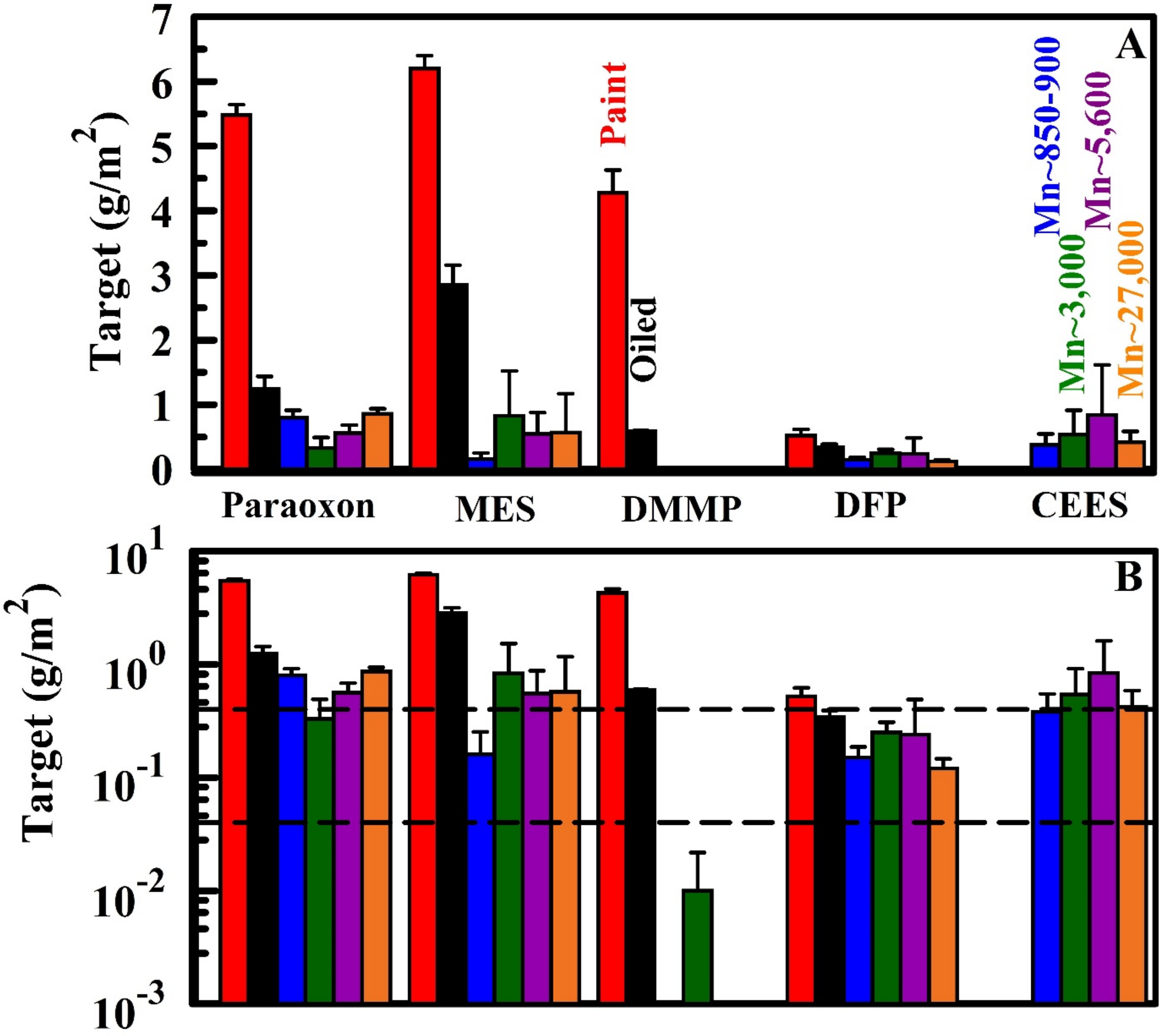

Fig. 5 — Target retention by coupons from initial series following treatment with an air stream and rinsing with soapy water shown on a linear scale (A) and (B) on a log scale 3M materials: (left to right) painted (red), Fomblin Y (black), Mn~850-900 (blue), Mn~3,000 (green), Mn~5,600 (purple), Mn~27,000 (orange).

CONCLUSIONS

The "Dual-Layer" polyurethane-PDMS topcoats inspired from synthesis protocols available in the literature coatings yielded interesting results. The wetting behaviors resulted in larger contact angles for all materials. All materials exhibited low surface energies. The droplet spreading behavior was negligible for MES and DMMP targets on all the materials. For the DFP, spread may have been reduced and for some of the coatings the rate of spread was much slower. Different coatings provided increased resistance to all targets which in some cases reached the higher reduction target or were close to reaching that target. In the case of DMMP the reduction was excellent with significant reductions in retention seen for all coatings. These materials had little to no impact on coupon visual appearance and none showed any visible damage from target application. Spectrophotometric analysis is necessary to determine the overall impact on color and reflectivity. The reduction in retention is not as large as has been found for other coatings tested but was significant. At this time, further testing such as the impact of outdoor aging on these materials is not warranted but further variations of these coatings should be tested to see if the performance can be further improved.

ACKNOWLEDGEMENTS

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

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1. Khan, F.; Khan, A.; Tuhin, M.O.; Rabnawaz, M.; Li, Z.; Naveed, M. A novel dual-layer approach towards omniphobic polyurethane coatings. *RSC Adv* **2019**, *9*, 26703-26711, doi:10.1039/c9ra04923a.
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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.

Appendix A
PU/IPDI/NH2PDMSNH2 850-900 COUPON IMAGES

Fig. A1 — DFP on PU/IPDI/NH2PDMSNH2 850-900. 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.

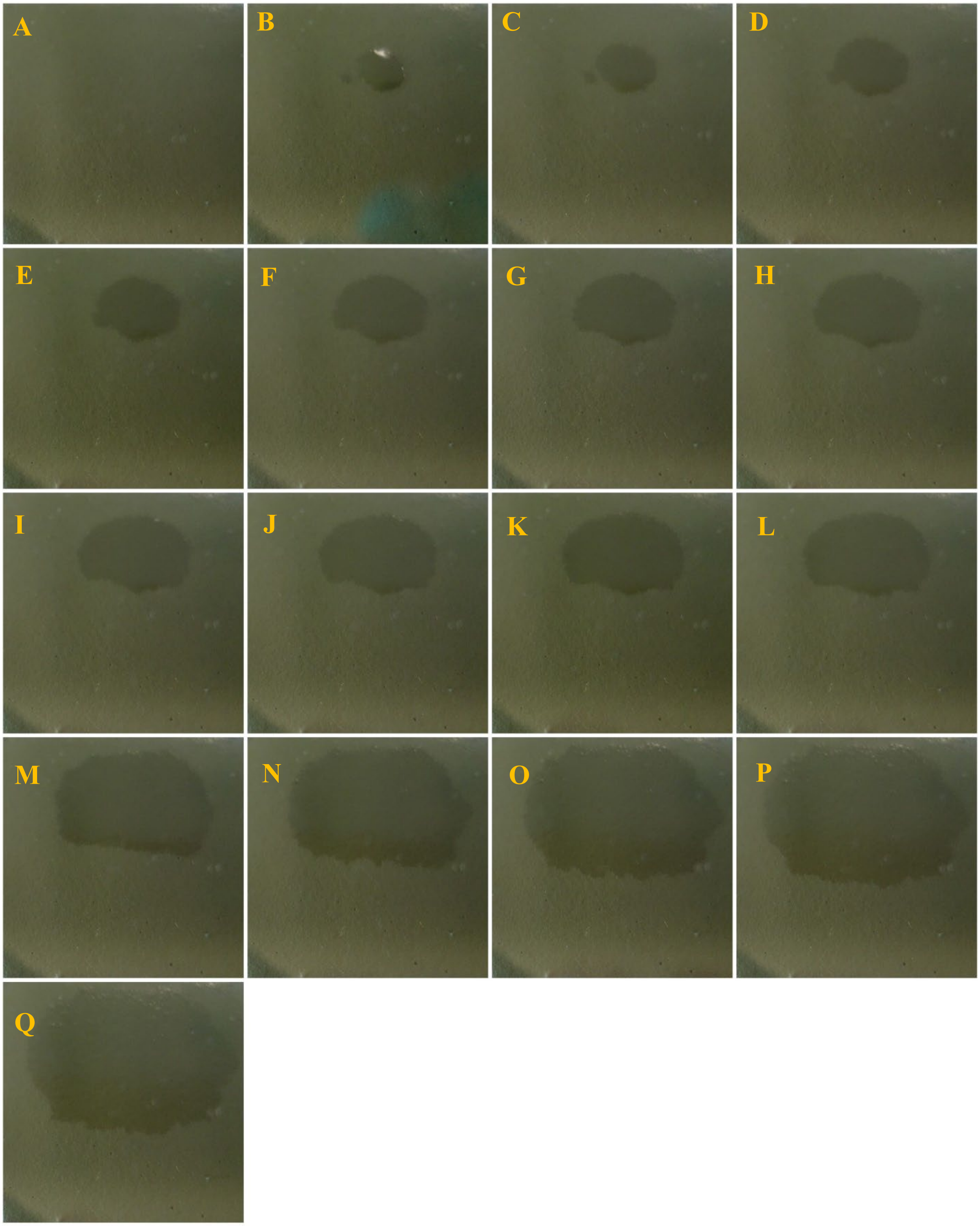


Fig. A2 — MES on PU/IPDI/NH2PDMSNH2 850-900. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

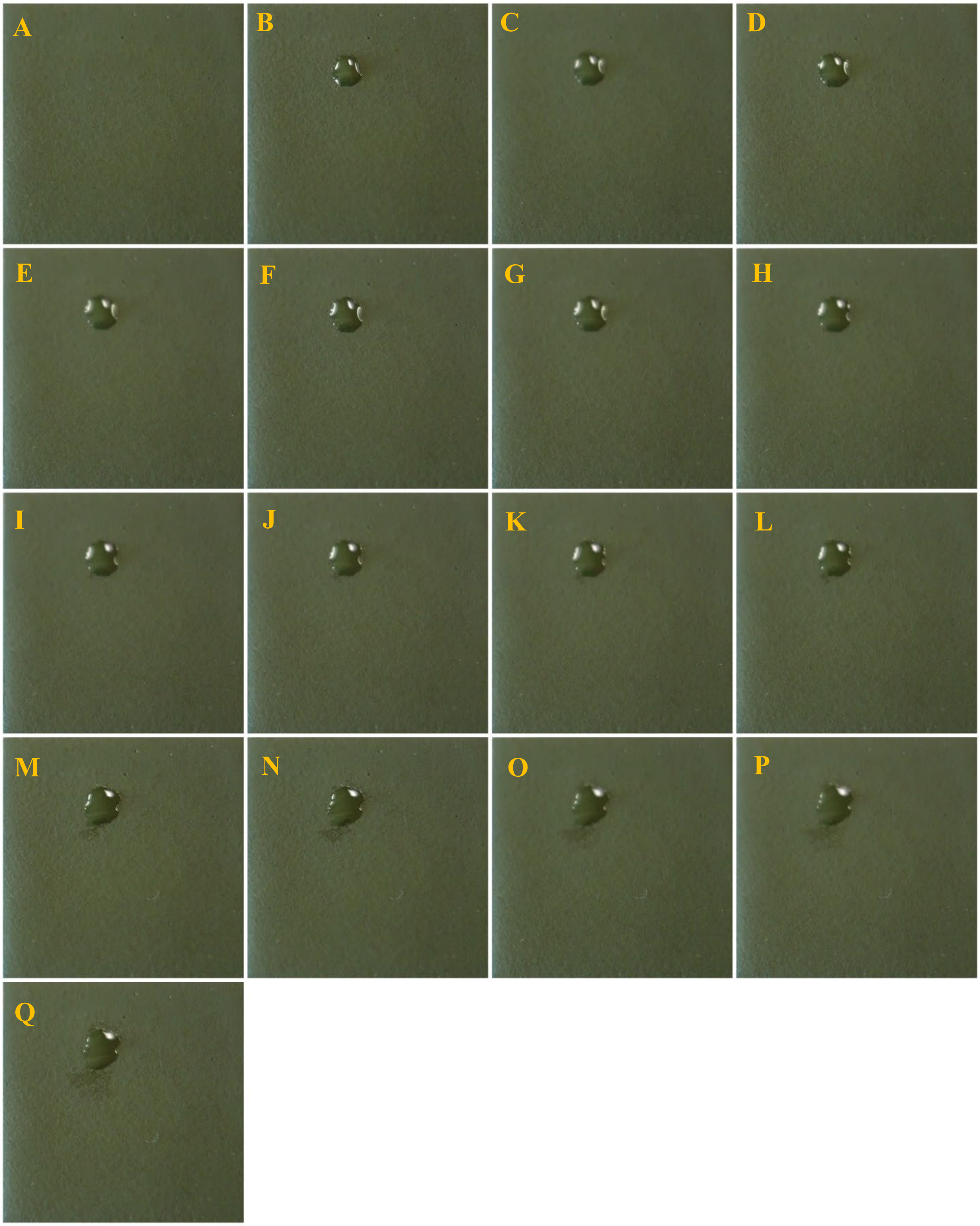
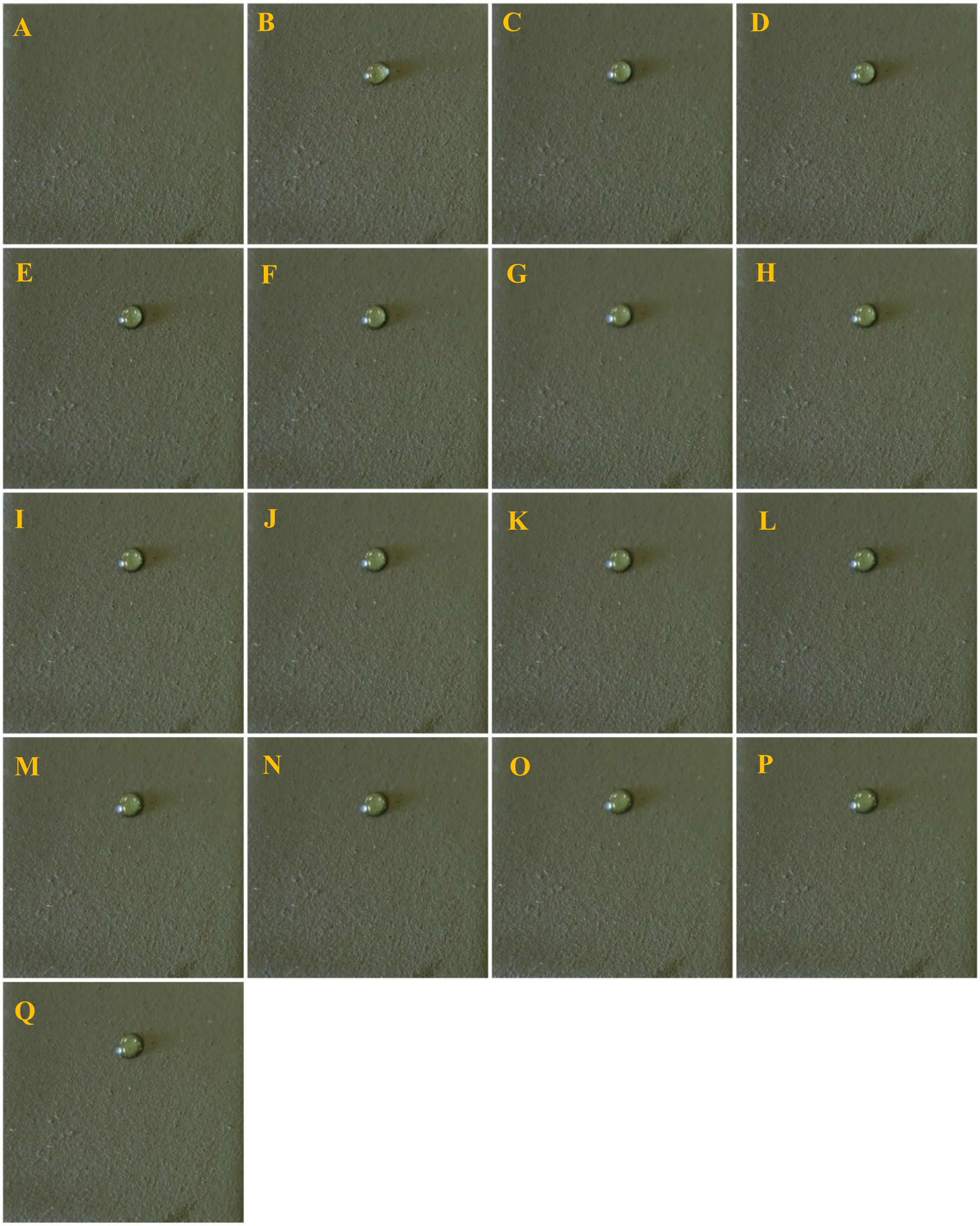


Fig. A3 — DMMP on PU/IPDI/NH2PDMSNH2 850-900. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix B

PU/IPDI/NH2PDMSNH2 3000 COUPON IMAGES

Fig. B1 — DFP on PU/IPDI/NH2PDMSNH2 3000. 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.

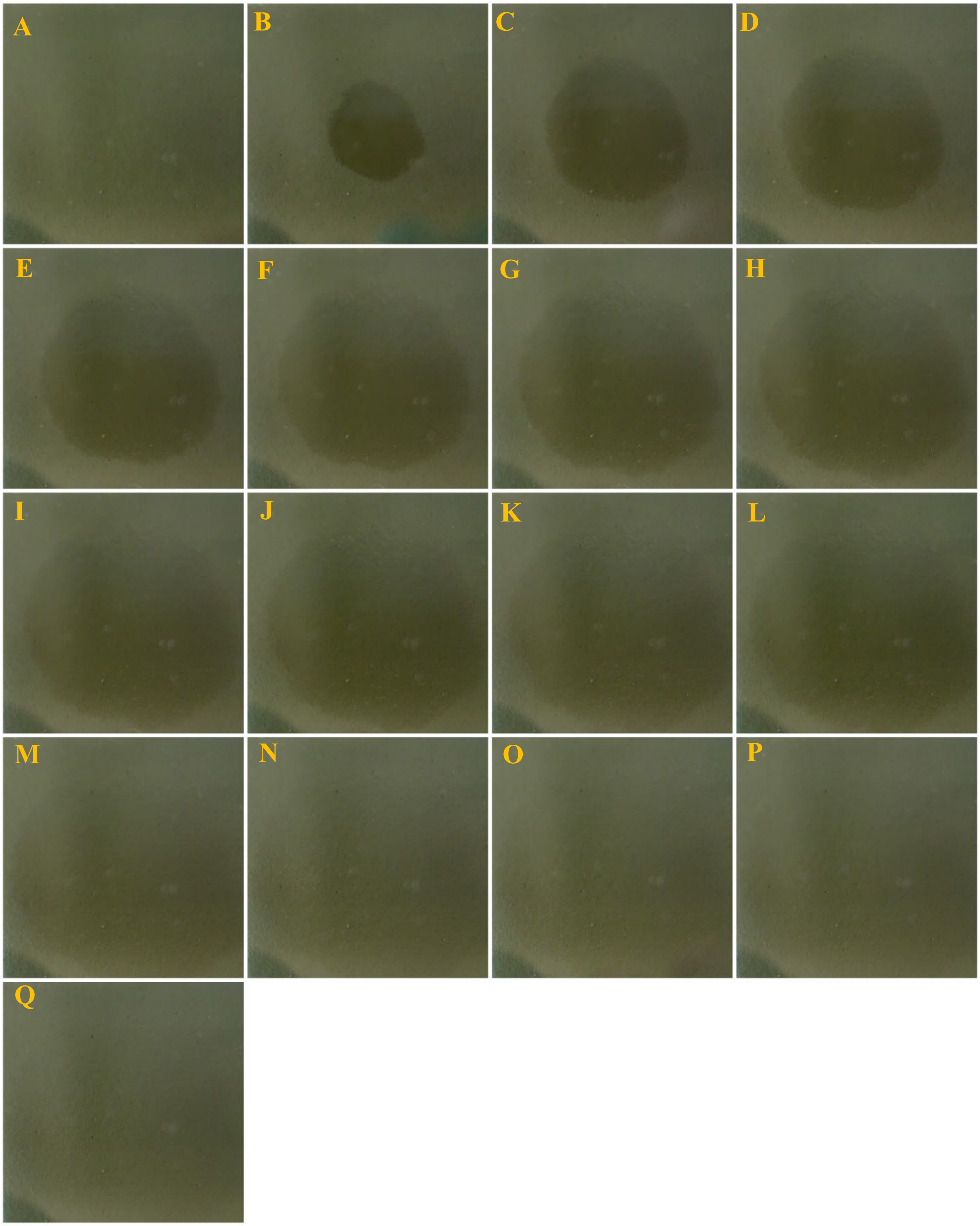


Fig. B2 — MES on PU/IPDI/NH2PDMSNH2 3000. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

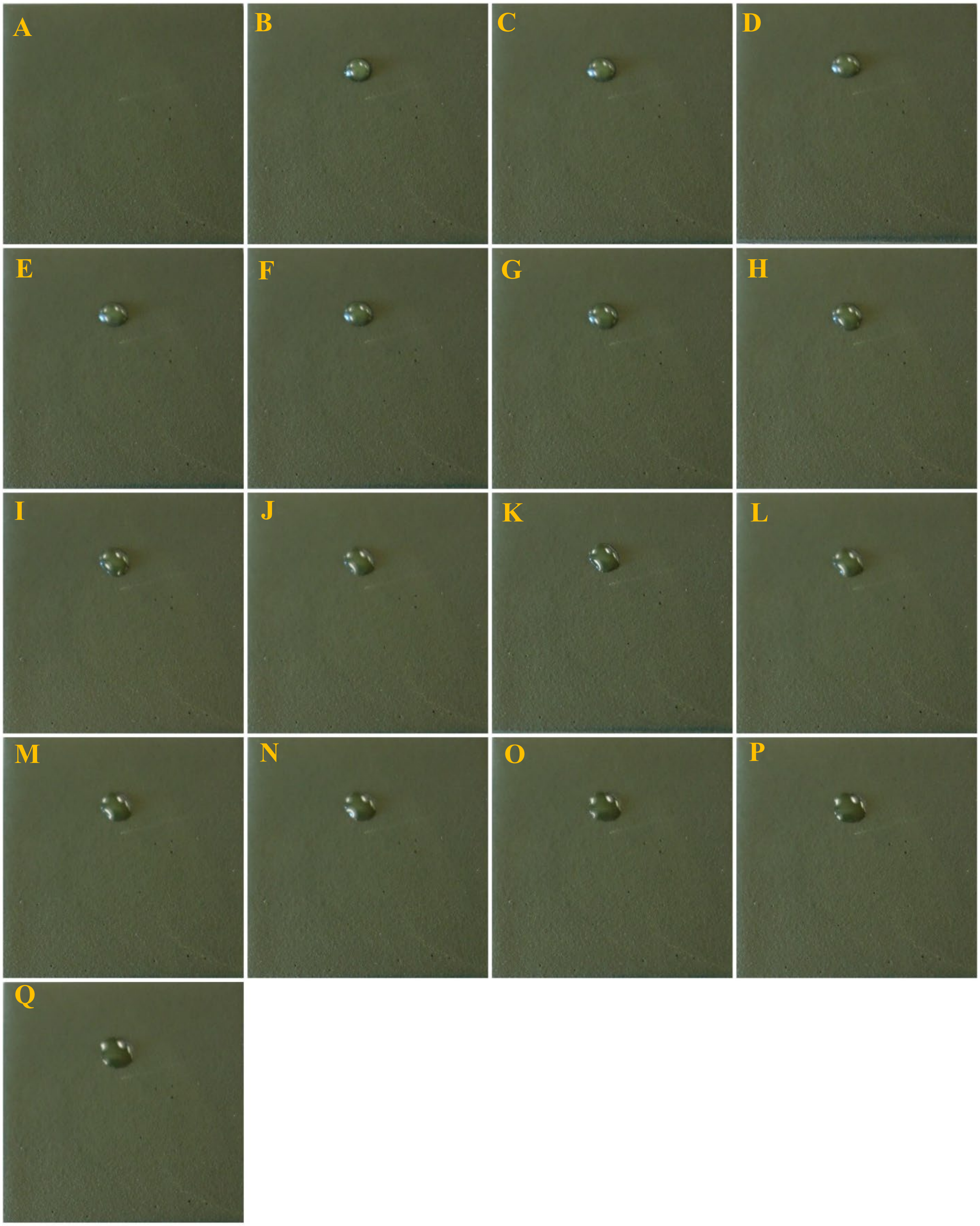
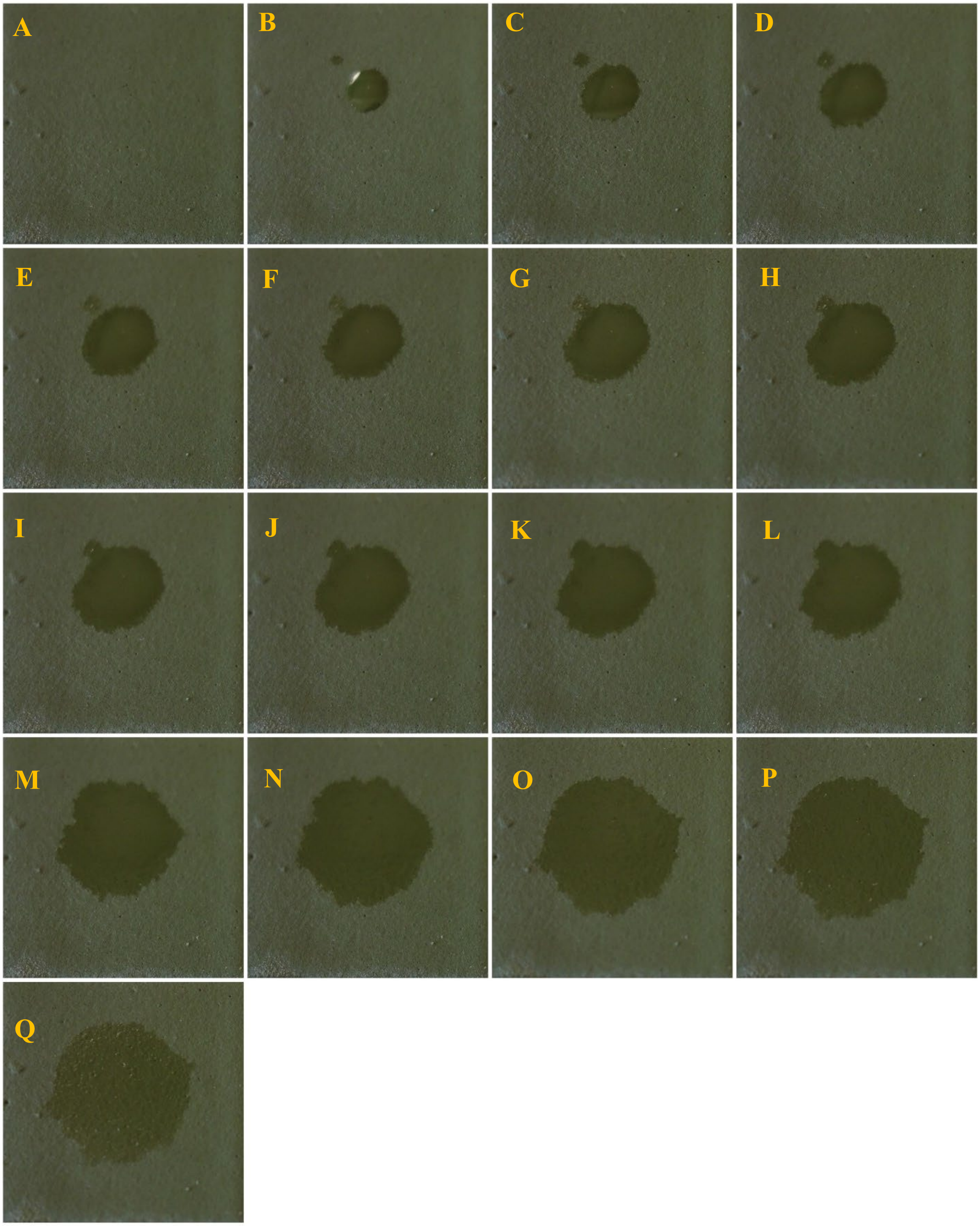


Fig. B3 — DMMP on PU/IPDI/NH2PDMSNH2 3000. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix C

PU/IPDI/NH2PDMSNH2 5600 COUPON IMAGES

Fig. C1 — DFP on PU/IPDI/NH2PDMSNH2 5600. 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.

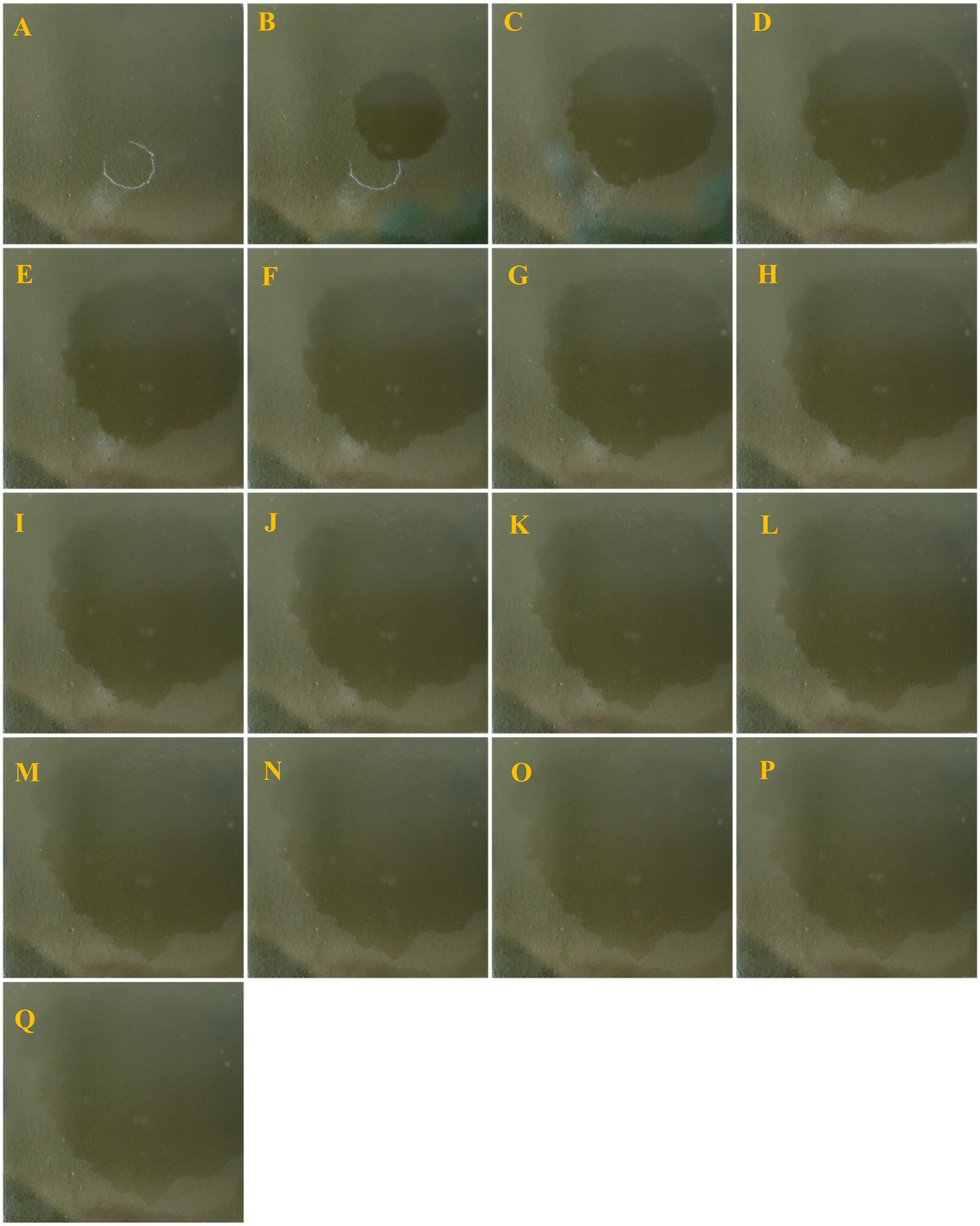


Fig. C2 — MES on PU/IPDI/NH2PDMSNH2 5600. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

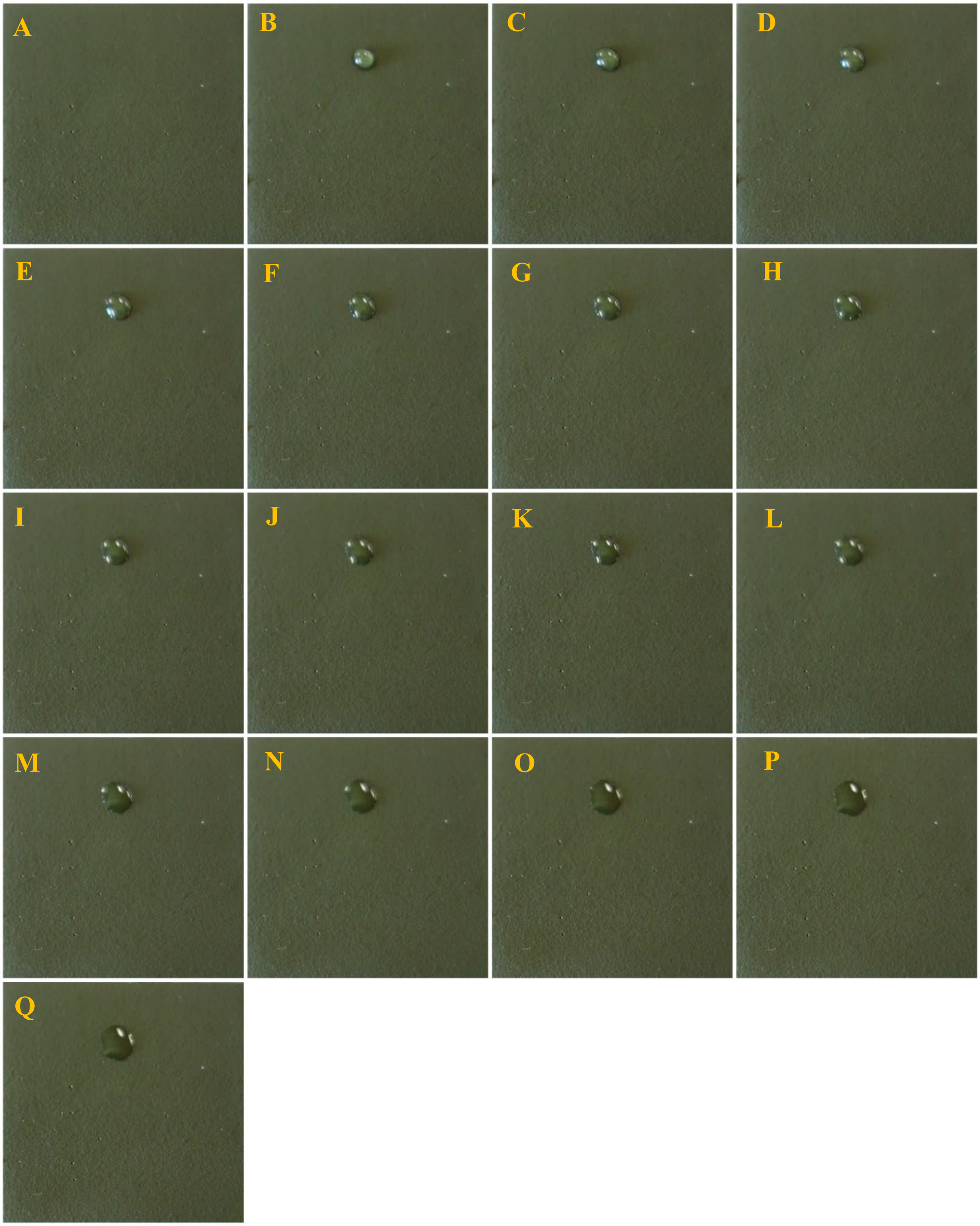
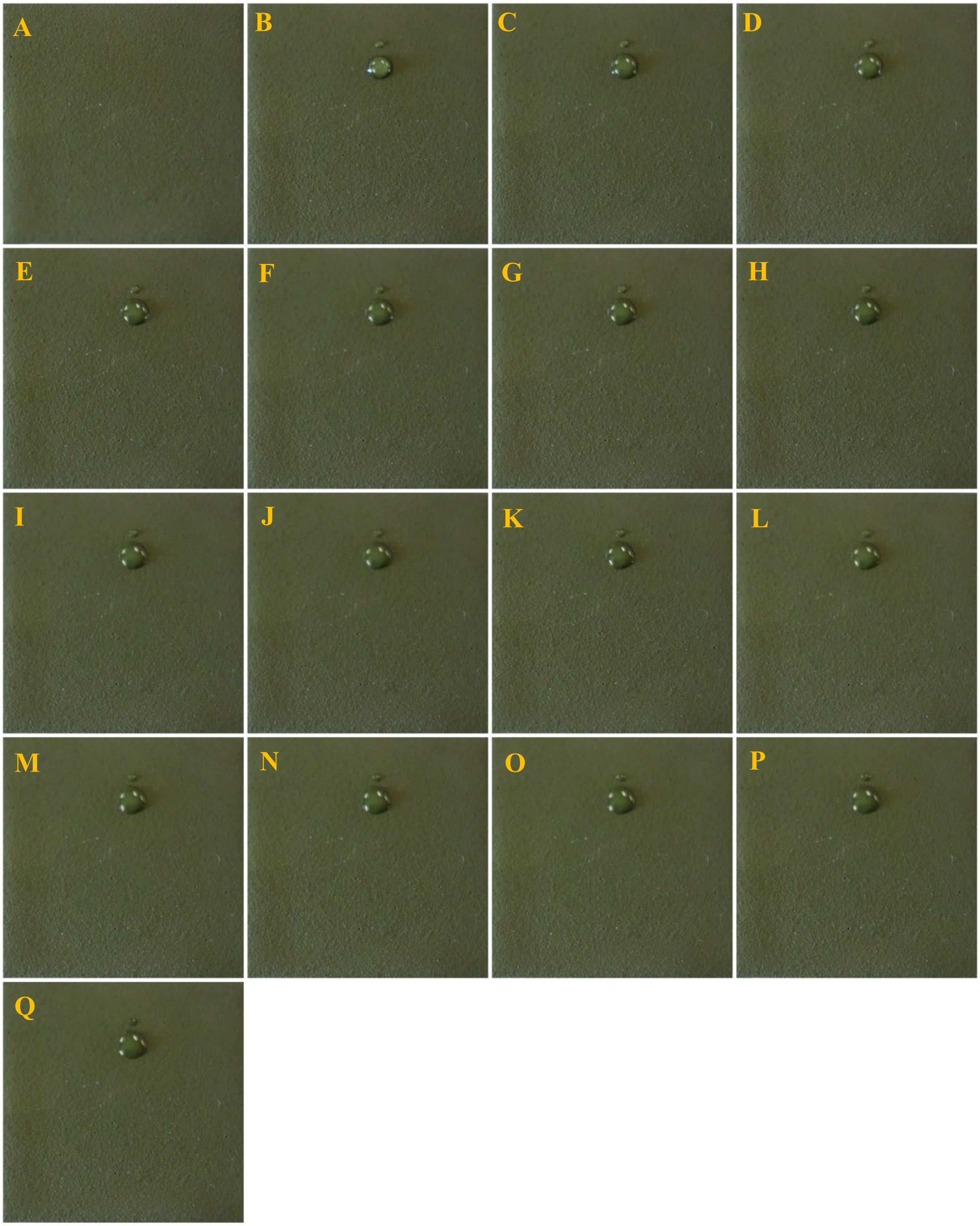


Fig. C3 — DMMP on PU/IPDI/NH2PDMSNH2 5600. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix D

PU/IPDI/NH2PDMSNH2 27000 COUPON IMAGES

Fig. D1 — DFP on PU/IPDI/NH2PDMSNH2 27000. 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.

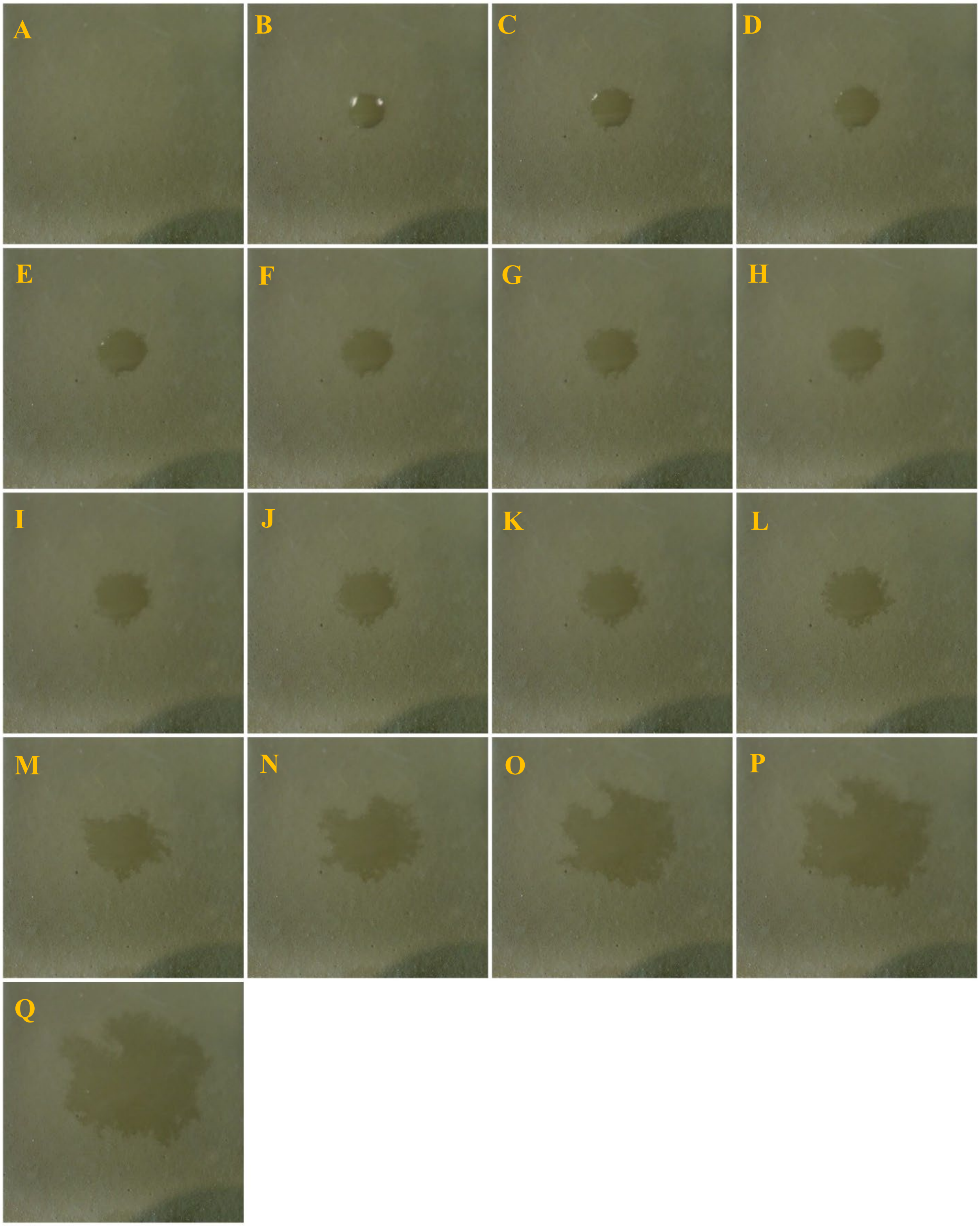


Fig. D2 — MES on PU/IPDI/NH2PDMSNH2 27000. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target

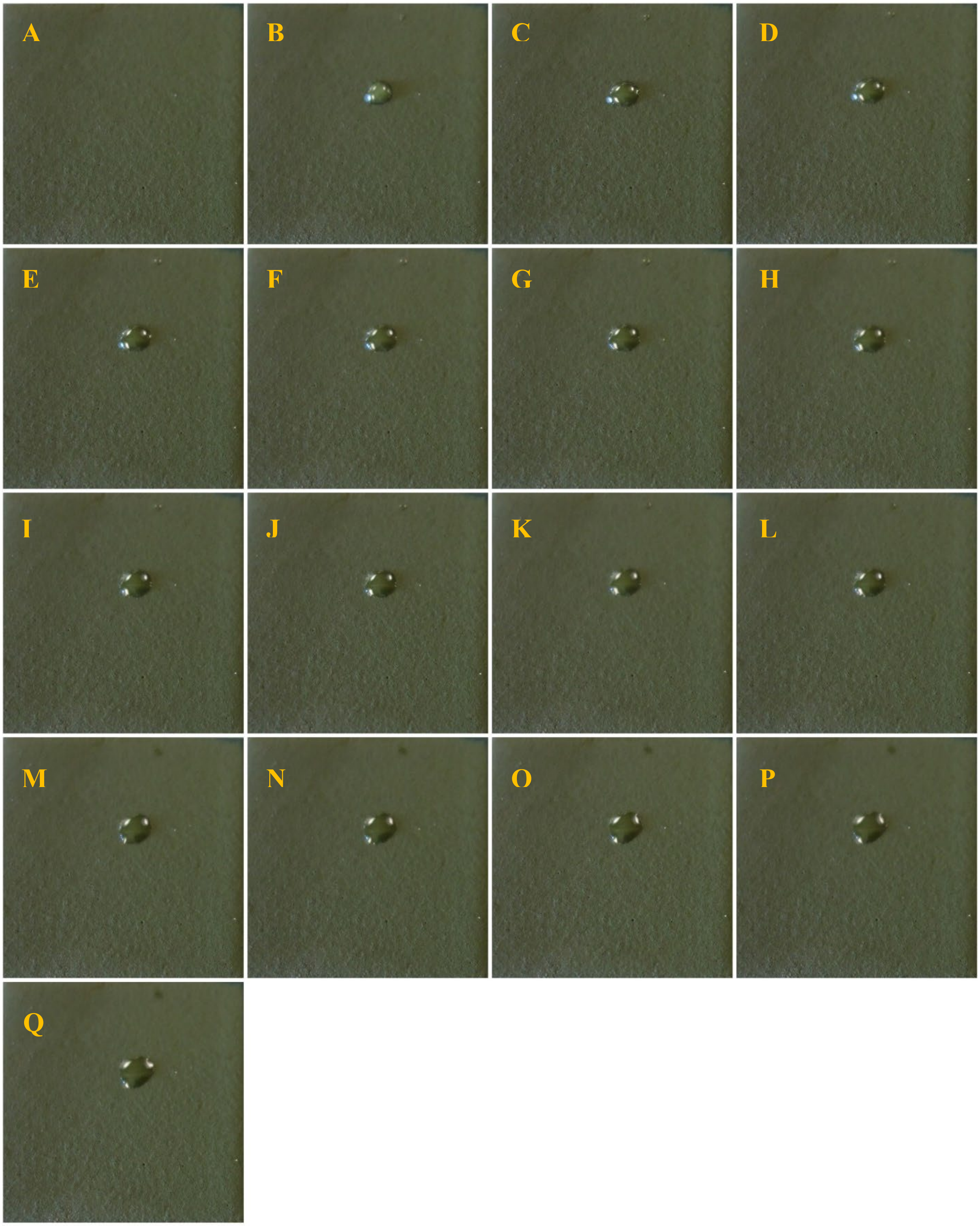


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Fig. D3 — DMMP on PU/IPDI/NH2PDMSNH2 27000. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.