Naval Research Laboratory
Washington, DC 20375-5320

NRL/6306/MR—2022/6

Bioinspired Surface Treatments for Improved Decontamination: "Liquid-like" Oil Repellent Coating

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

December 13, 2022

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
13-12-2022

2. REPORT TYPE
NRL Memorandum Report

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE

Bioinspired Surface Treatments for Improved Decontamination: “Liquid-like” Oil Repellent Coating

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--2022/6

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 treating with an IPDI-PDMS “liquid-like” oil repellent coating. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphonate, dimethyl fluorophosphates, 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	28	**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 a surface treatment prepared by treating with an IPDI-PDMS "liquid-like" oil repellent coating. The materials were deposited on polyurethane paint coated aluminum coupons. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphonate, dimethyl fluorophosphates, 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: "LIQUID-LIKE" OIL REPELLENT COATING

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 an IPDI-PDMS "liquid-like" oil repellent coating.

Slippery omniphobic covalently attached liquid (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. Two previous reports covered testing applications of SOCAL based coatings for reduction of target retention.[1,2] The current report focuses on evaluation of a new SOCAL material identified in the open literature.[3,4] The methods available in the open literature were modified to synthesize a coating at NRL.

For the complete system, aluminum coupons were coated with a polyurethane paint system and then four variations of the new SOCAL were prepared following the developed synthesis method presented in the methods (Figure 1). Images of the previously tested paint 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 in some cases an impact on the visible characteristics of the coupons.

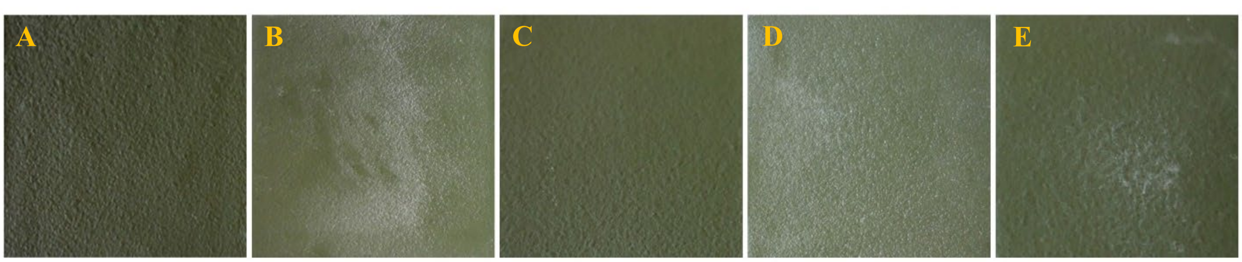


Fig. 1 — Images of painted coupons from initial series with (A) Paint only; (B) 1x Mn~27,000; (C) 2x Mn~2,500; (D) 2x Mn~3,000; (E) 2x Mn~5,000.

Manuscript approved December 1, 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).[5] 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 IPDI-PDMS coatings was adapted from a published report. Painted coupons were initially modified with a tetraethyl orthosilicate (TEOS) coating. [3,4] A sol was prepared from 184 mL 2-propanol, 6 mL tetraethyl orthosilicate (TEOS), and 10 mL NH_4OH (~ 30% in H_2O 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 °C 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 °C over-night for the final curing step. Note: TEOS sol became cloudy the 3rd immersion step; no precipitate or visible discoloration was observed on painted surfaces. After preparing the TEOS coated coupons, amine modification of the surface was carried out. TEOS/paint coupons were immersed in 1 % (v/v) 3-aminopropyltriethoxysilane (APTES) in toluene at 70 °C for 2 d. Typically, 100 mL of 1 % APTES/toluene was prepared per 240 mL PFA jar for modification of 4 TEOS/paint coupons. APTES grafted substrates were rinsed with toluene and ethanol. They were stored in Fluoroware and dried in an oven at 60 °C. After that preparation, the final copolymer coatings were applied. Solutions of isophorone diisocyanate (IPDI) in toluene (0.5 mg/mL) and aminopropyl-terminated polydimethylsiloxane (NH_2-PDMS-NH_2) in tetrahydrofuran (THF) (1 mg/mL) were used for grafting copolymers on substrates. NH_2-PDMS-NH_2 with Mn ~ 2,500 or 27,000 were obtained from Sigma-Aldrich (sold as Poly(dimethylsiloxane), bis(3-aminopropyl) terminated). PDMS with other molecular weights (e.g. 3,000 and 5,000) were obtained from Gelest (sold as Aminopropyl terminated polydimethylsiloxane). Typically, 100 mL of IPDI/toluene solution and 100 mL of NH_2-PDMS-NH_2/THF solution were prepared in 240 mL PFA jars.

Amine-grafted TEOS/paint substrates were immersed in IPDI/toluene solution at RT for 30 min. They were rinsed with toluene, then immersed in NH_2-PDMS-NH_2/THF solution at RT for 30 min. Substrates were rinsed with THF, then toluene. This procedure was either ended or repeated to attempt to build more IPDI/PDMS copolymer layers for a desired approximate molecular weight (typically labeled based on the molecular weight of NH_2-PDMS-NH_2 reagent used and the number of layers; e.g. 2 x MW 3000). Coated substrates were dried at 60 ℃ and stored in Fluoroware. The coating procedure was carried out in two separate batches with the 1x Mn~27,000 and the 2x Mn~3,000 being synthesized together and then a a later date the 2x Mn~2,500 and 2x Mn~5,000 being produced.

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. Application of the coatings considered here reduced the surface energy of the painted surface (Table 1 and Figure 3); The energy for the coatings from the first batch 1x Mn~27,000 and 2x Mn~3,000 did not result in as large a reduction in the surface energy. While those in the second set 2x Mn~2,500 and 2x Mn~5,000 both had energies well below a Fomblin Y coated surface. 2x Mn~2,500 produced the coating having 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. While it may be expected that a liquid-like coating might have low sliding and shedding angles, the tested liquids, water and ethylene glycol are not oils which is what the coating is targeted towards.

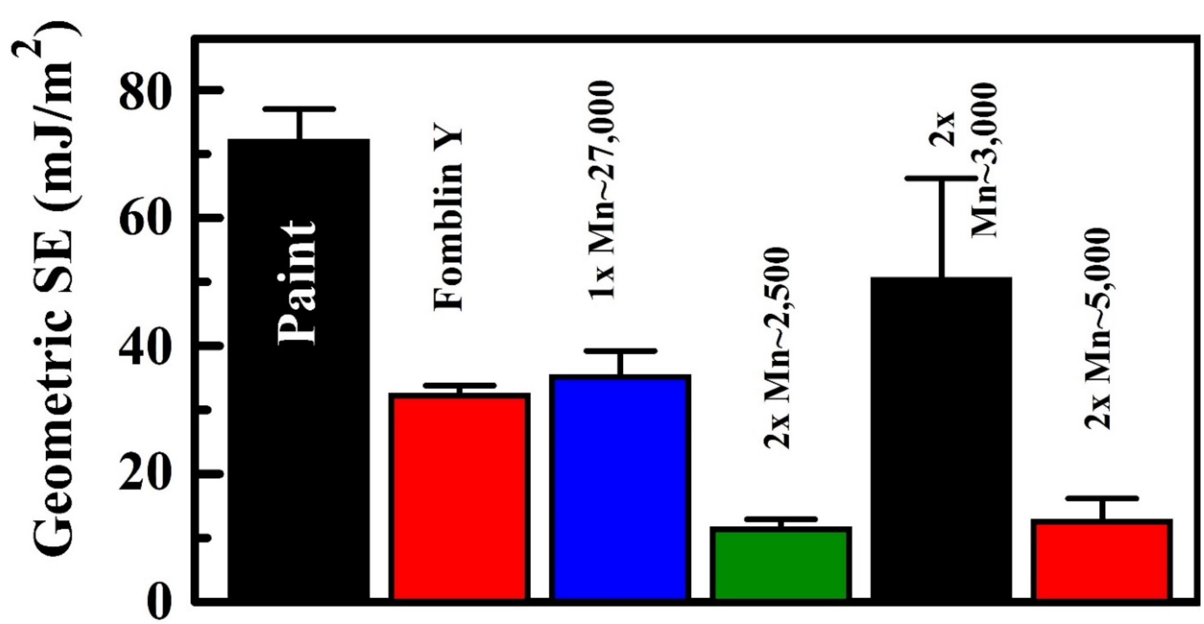


Fig. 2 — Geometric surface energy (mJ/m^2) for the evaluated coatings. Paint and Fomblin Y results provided for comparison.

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	
1x Mn~27,000	water	109.5 ± 1.0	>60	>60	35.13 ± 4.08
	ethylene glycol	99.4 ± 1.7	>60	>60	
	n-heptane	--	--	--	
2x Mn ~2,500	water	106.3 ± 1.6	>60	>60	11.3 ± 1.58
	ethylene glycol	95.8 ± 1.8	>60	>60	
	n-heptane	--	--	--	
2x Mn ~3,000	water	101.7 ± 4.3	>60	>60	50.3 ± 15.9
	ethylene glycol	92.7 ± 3.2	>60	>60	
	n-heptane	--	--	--	
2x Mn ~5,000	water	107.0 ± 3.4	>60	>60	12.5 ± 3.66
	ethylene glycol	97.2 ± 2.9	>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 coatings; application of Fomblin Y had a negative impact on this behavior. DFP spread was unchanged from what is observed for the paint only surface. MES spread was significantly reduced to negligible amounts for all but the 2x Mn~2,500 coating although significant was reduced compared to the paint only surface, and all of the surfaces provided reductions larger/equivalent to that noted for the Fomblin Y lubricated surface.

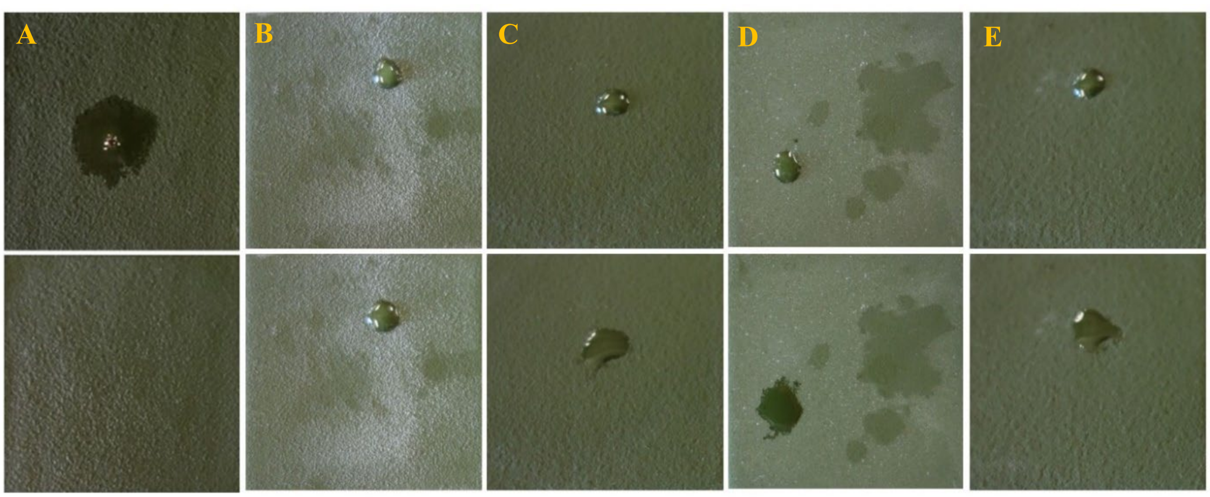


Fig. 3 — Images from initial series of coupons at 0 and 30 min following MES exposure: (A) Paint only; (B) 1x Mn~27,000; (C) 2x Mn~2,500; (D) 2x Mn~3,000; and (E) 2x Mn~5,000.

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, all the coatings except the 2x Mn~3,000 coating for Paraoxon and MES agents exhibited retentions below what was observed for either paint only or Fomblin Y coated surfaces. The 2x Mn~3,000 coating had retention performance better than paint only and similar to a Fomblin Y coated surface. The retention of DMMP was significantly reduced for all coating.in the same range as the previously tested coatings. For DFP, all coatings demonstrated a small reduction in retention of target compared to the paint only of Fomblin Y coated coupons.

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.

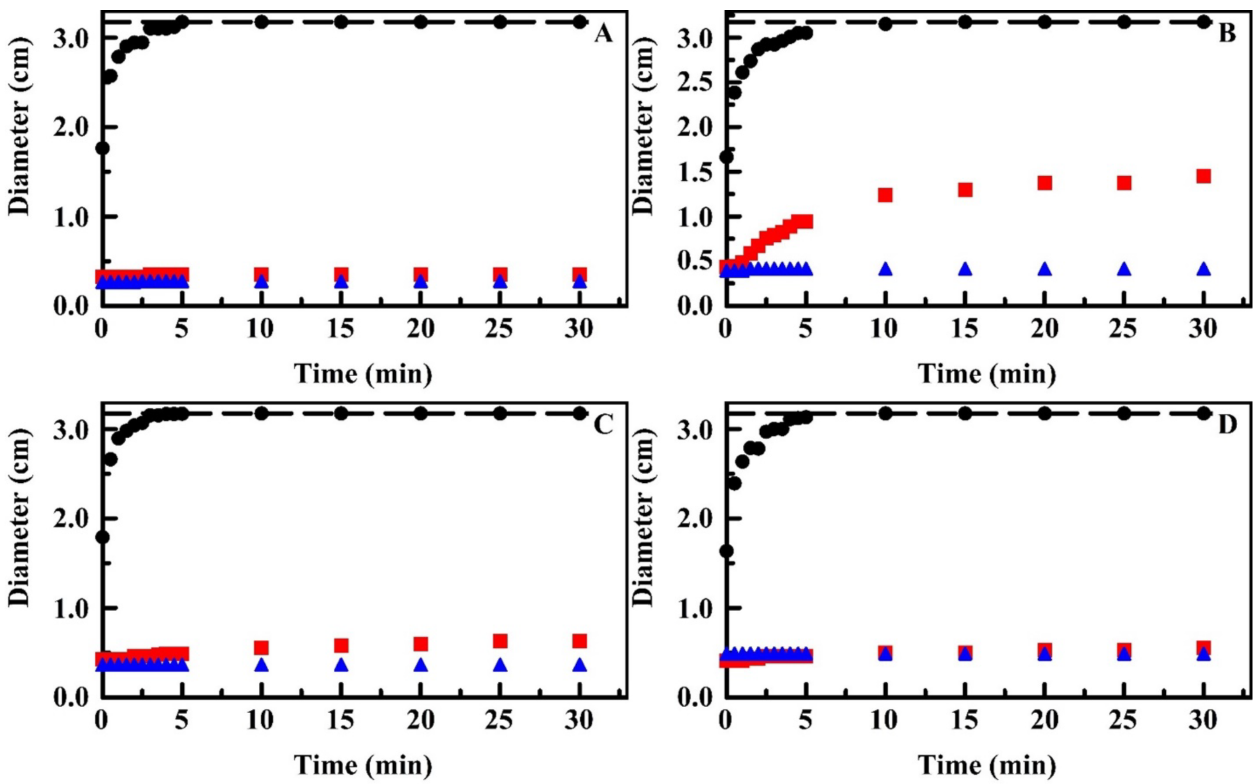


Fig. 4 — Droplet diameters over time following exposure to DFP (black), MES (red), and DMMP (blue) for painted coupons with (A) 1x Mn~27,000; (B) 2x Mn~2,500; (C) 2x Mn~3,000; and (D) 2x Mn~5,000.

.

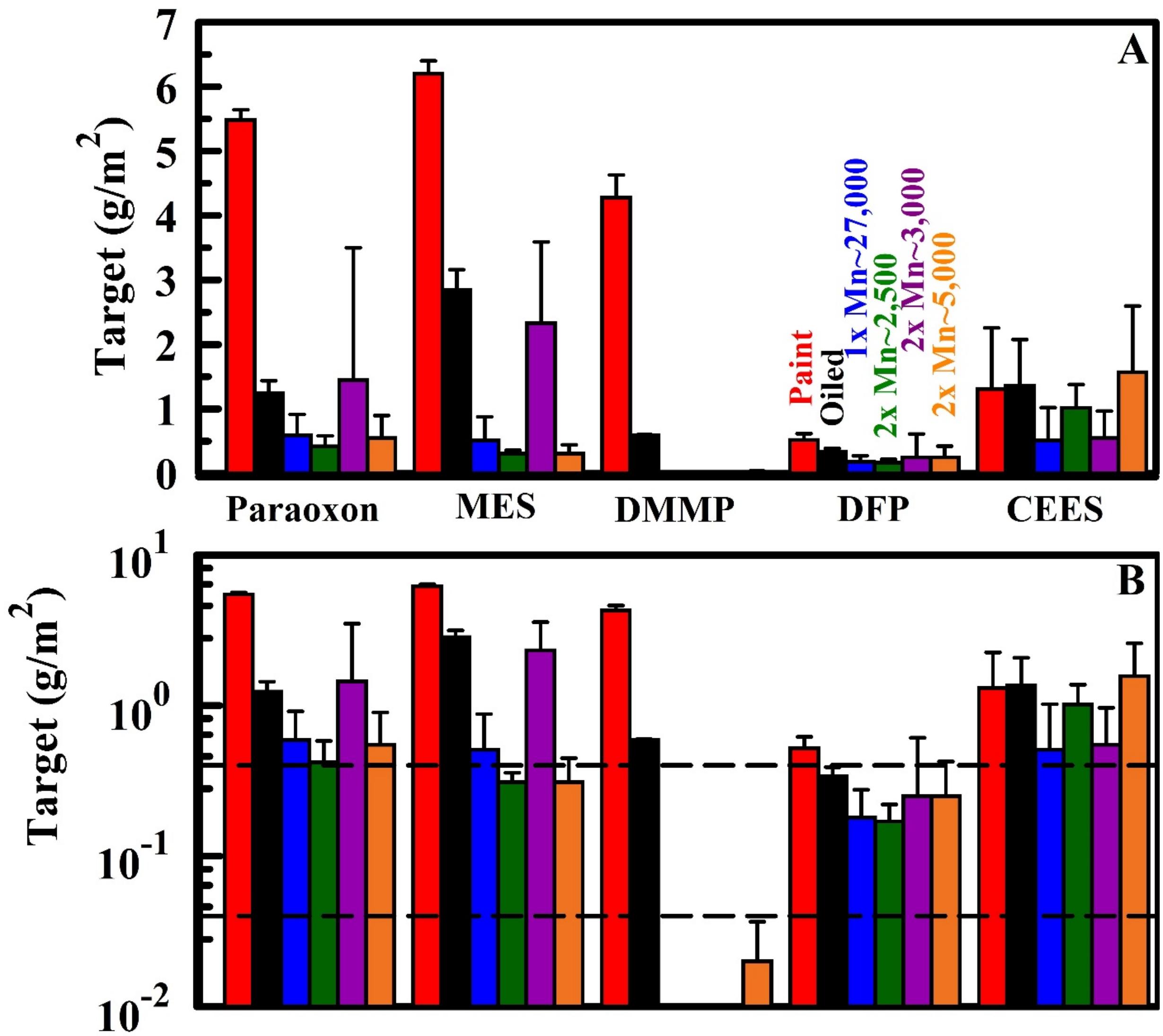


Fig. 5 — Target retention by coupons from initial series following treatment with an air stream and rinsing with soapy water shown on a linear scale (A) and (B) on a log scale 3M materials: (left to right) painted (red), Fomblin Y (black), 1x Mn~27,000 (blue), 2x Mn~2,500 (green), 2x Mn~3,000 (purple), 2x Mn~5,000 (orange).

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
1x Mn~27,000	0.59	0.51	ND	0.18	0.51
2x Mn~2,500	0.42	0.31	ND	0.17	1.02
2x Mn~3,000	1.45	2.33	ND	0.25	0.55
2x Mn~5,000	0.55	0.31	0.02	0.25	1.57

ND = not detected

CONCLUSIONS

A new variation of SOCAL coatings, IPDI-PDMS “liquid-like” oil coating was tested and yielded interesting results with wetting behaviors that were highly water repellent. All materials exhibited a mix of slightly lower surface energies relative to the paint only and in the range of the Fomblin Y coated coupons or in some cases coating with surface energies lower than that. The droplet spreading behavior for DFP was unaffected by this coating and behavior similar to the paint only coupon was observed. MES droplet spread was significantly reduced on these coating. Overall retention of all targets except DMMP was reduced by a moderate amount compared to the paint only or Fomblin Y coated coupons. For DMMP, the retention was significantly reduced. These materials had small 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. No further testing of current coating is warranted but new variations of the coating might be worth evaluating against these initial characterization tests.

ACKNOWLEDGEMENTS

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

REFERENCES

1. White, B.; Melde, B.; Malanoski, A.; Moore, M. *Bioinspired Surface Treatments for Improved Decontamination: Slippery Omniphobic Covalently Attached Liquid (SOCAL)*; NRL/MR/6930-17,9761; US Naval Research Laboratory, Washington, DC, 2017.
2. White, B.; Malanoski, A.; Moore, M.; Melde, B. *Bioinspired Surface Treatments for Improved Decontamination: Variations on Slippery Omniphobic Covalently Attached Liquid (SOCAL) Coatings*; NRL/MR/6930-19,9847; US Naval Research Laboratory, Washington, DC, 2019.
3. Liu, P.; He, W.Q.; Lu, G.; Zhang, H.D.; Wang, Z.Y.; Yao, X. Condensation-assisted micro-patterning of low-surface-tension liquids on reactive oil-repellent surfaces. *Journal of Materials Chemistry A* **2017**, *5*, 16344-16351, doi:10.1039/c7ta02031g.
4. Liu, P.; Zhang, H.; He, W.; Li, H.; Jiang, J.; Liu, M.; Sun, H.; He, M.; Cui, J.; Jiang, L.; et al. Development of "Liquid-like" Copolymer Nanocoatings for Reactive Oil-Repellent Surface. *ACS Nano* **2017**, *11*, 2248-2256, doi:10.1021/acsnano.7b00046.
5. 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

IPDI-NH2PDMSNH2 1x Mn~27,000 on TEOS COUPON IMAGES

Fig. A1 — DFP on IPDI-NH2PDMSNH2 1x Mn~27,000 on TEOS. 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.

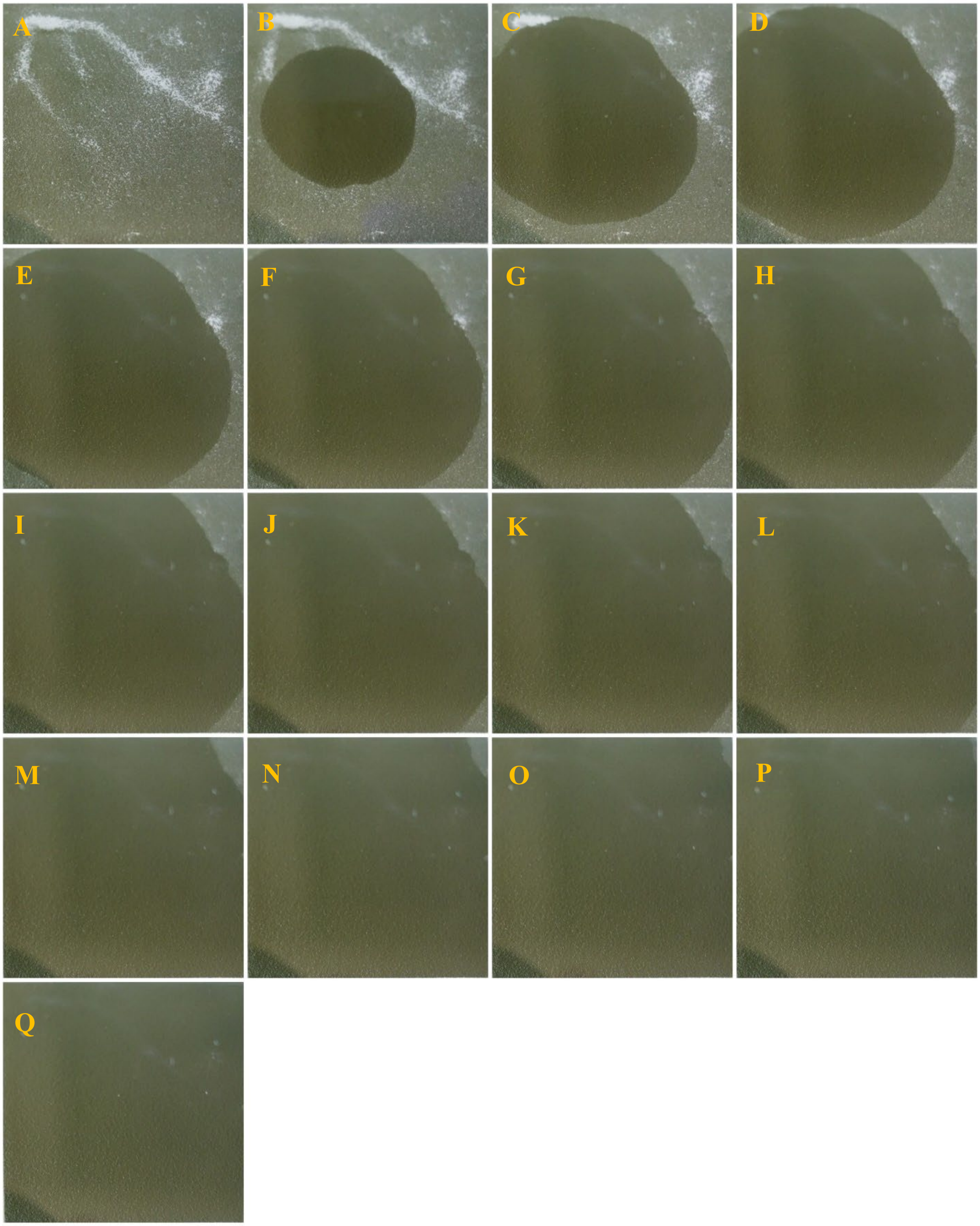


Fig. A2 — MES on IPDI-NH2PDMSNH2 1x Mn~27,000 on TEOS. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

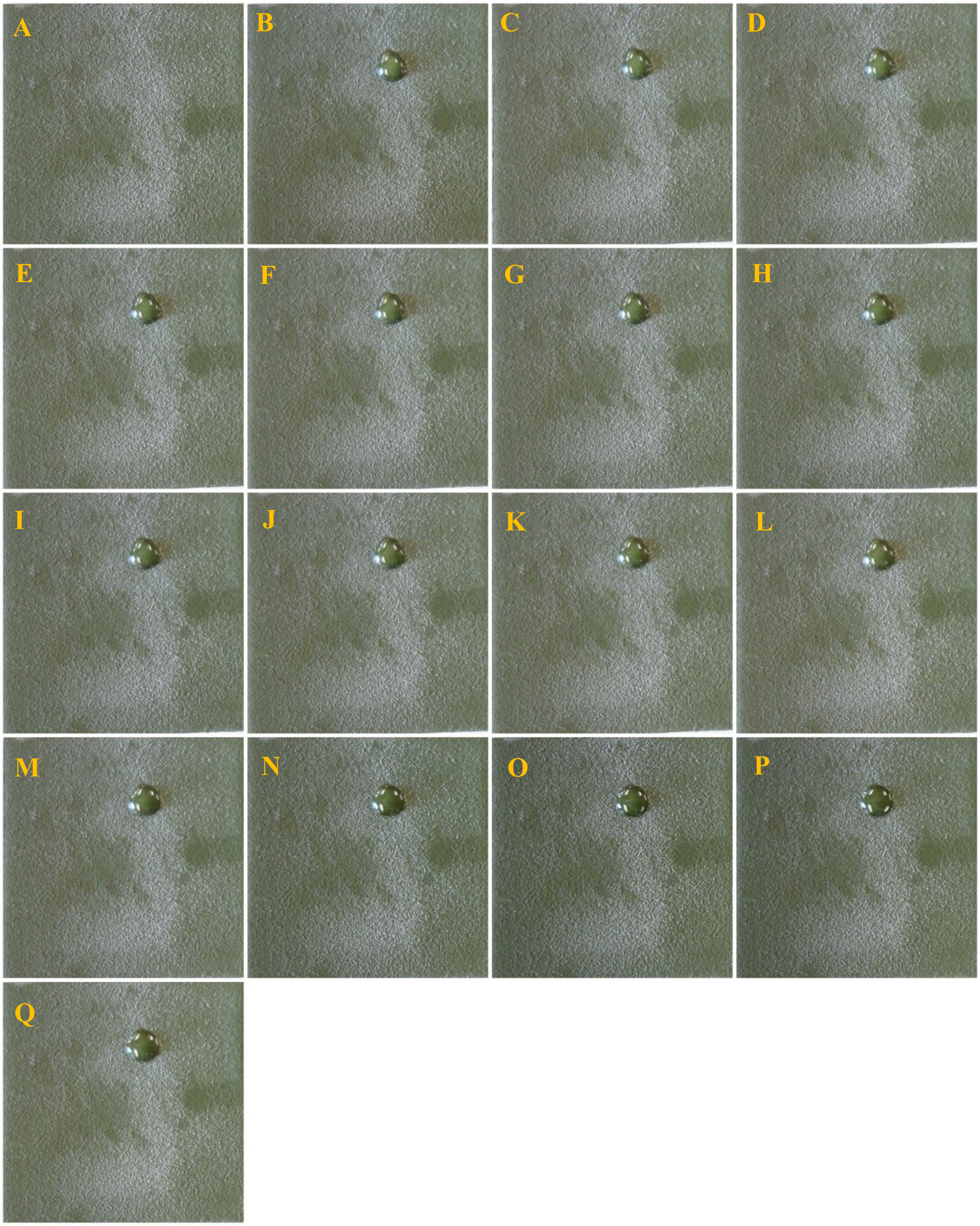
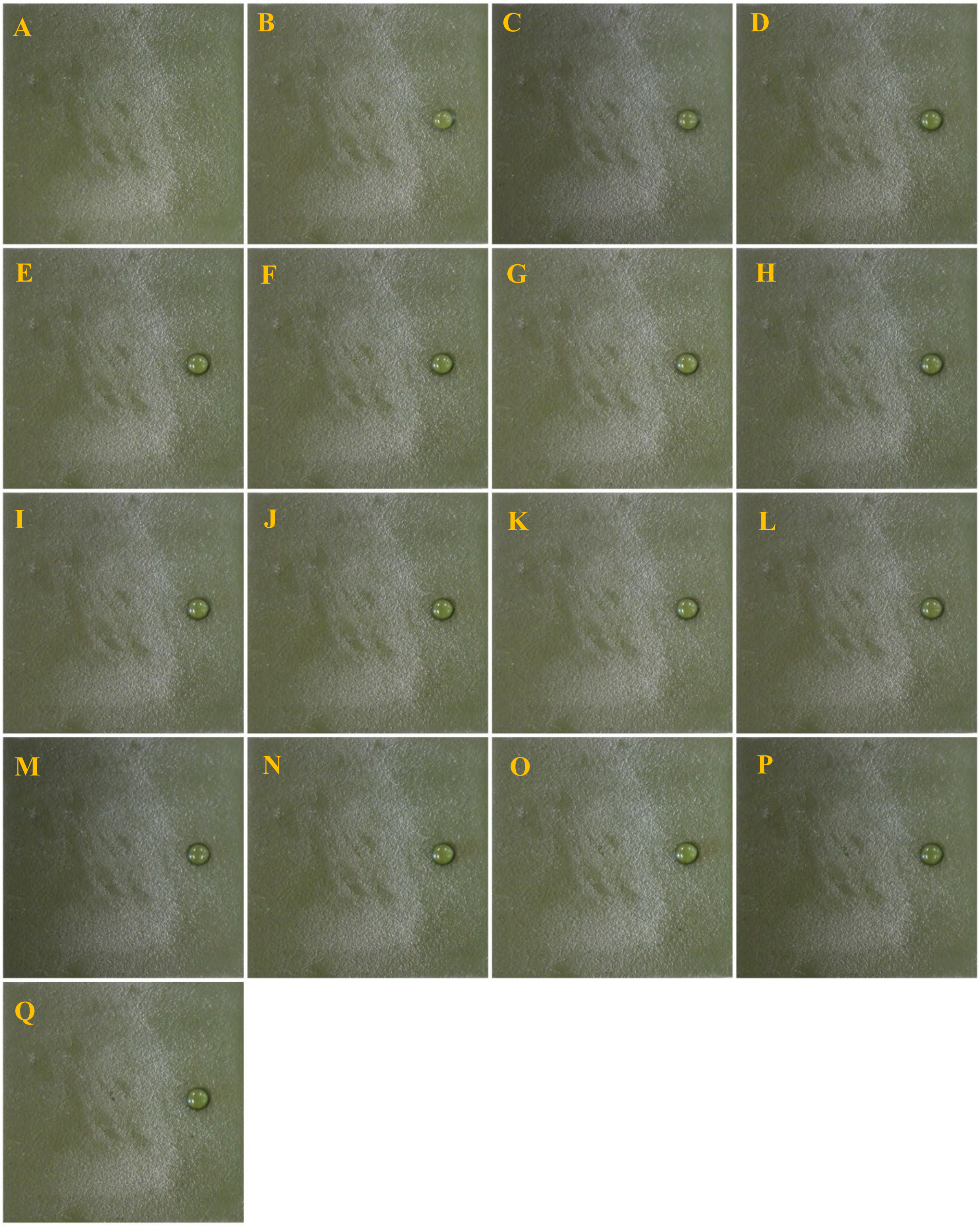


Fig. A3 — DMMP on IPDI-NH2PDMSNH2 1x Mn~27,000 on TEOS. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix B

IPDI-NH2PDMSNH2 2xMn ~2,500 on TEOS COUPON IMAGES

Fig. B1 — DFP on IPDI-NH2PDMSNH2 2xMn ~2,500 on TEOS. 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.

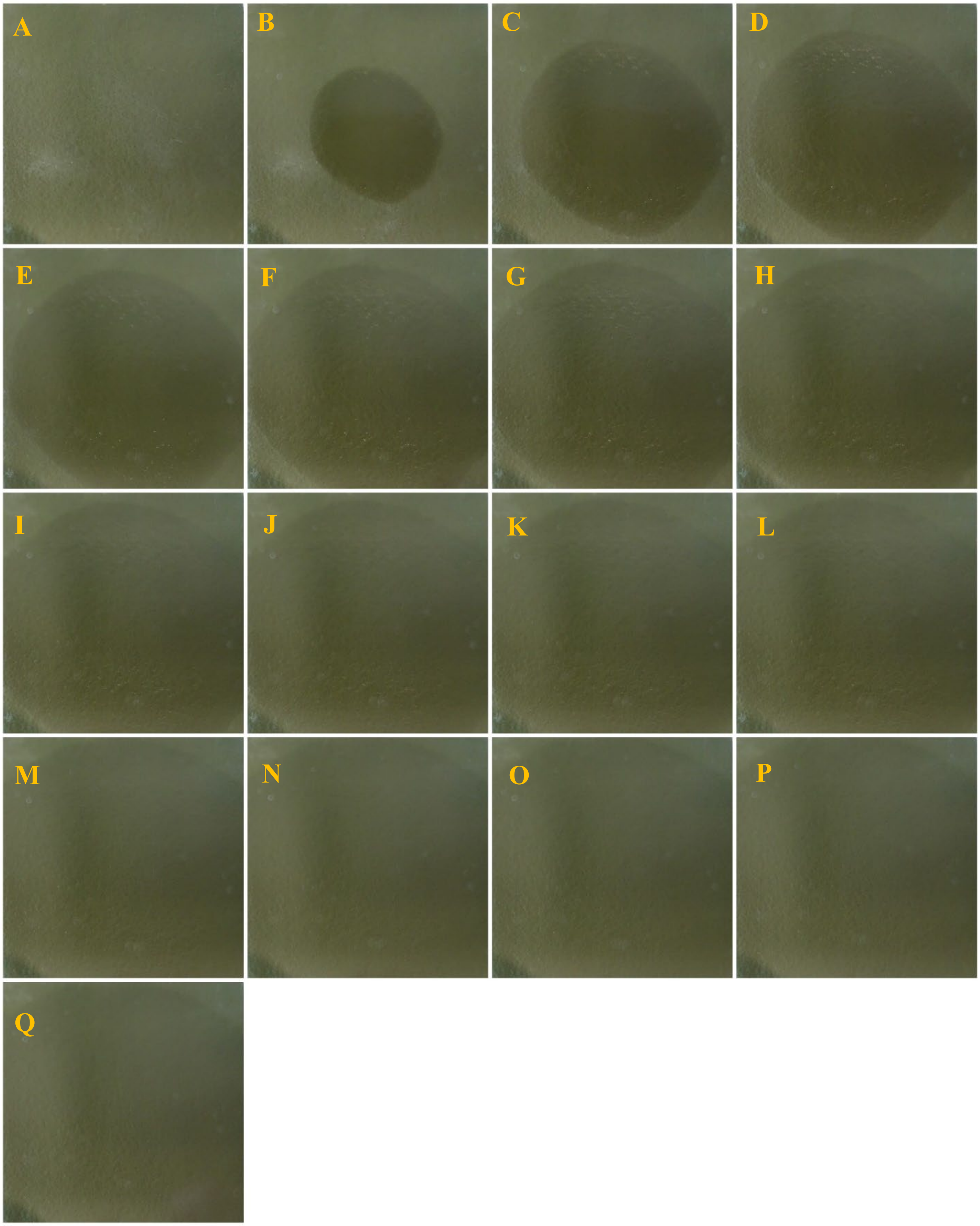


Fig. B2 — MES on IPDI-NH2PDMSNH2 2xMn ~2,500 on TEOS. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

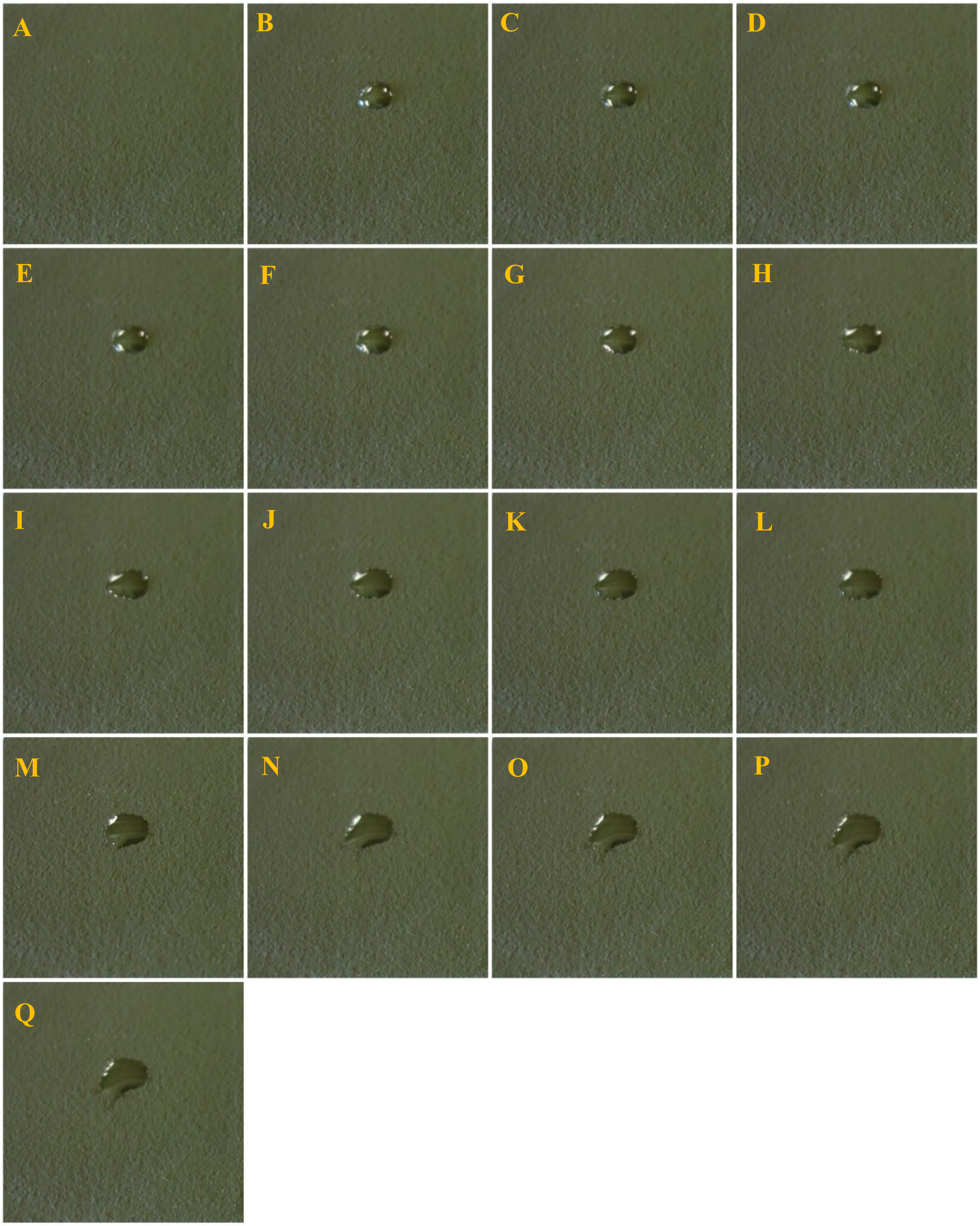
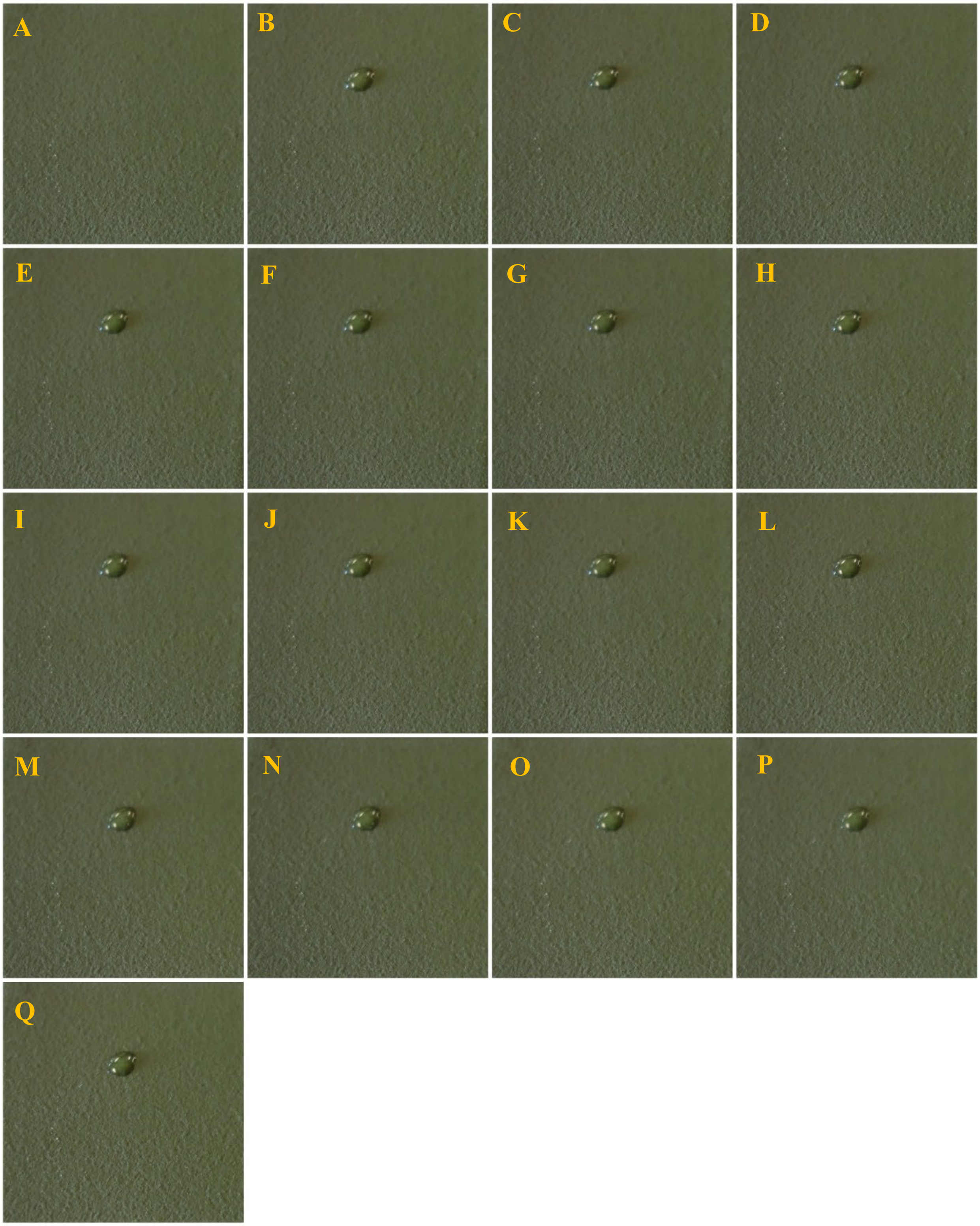


Fig. B3 — DMMP on IPDI-NH2PDMSNH2 2xMn ~2,500 on TEOS. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix C

IPDI-NH2PDMSNH2 2x Mn~3,000 on TEOS COUPON IMAGES

Fig. C1 — DFP on IPDI-NH2PDMSNH2 2x Mn~3,000 on TEOS. 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.

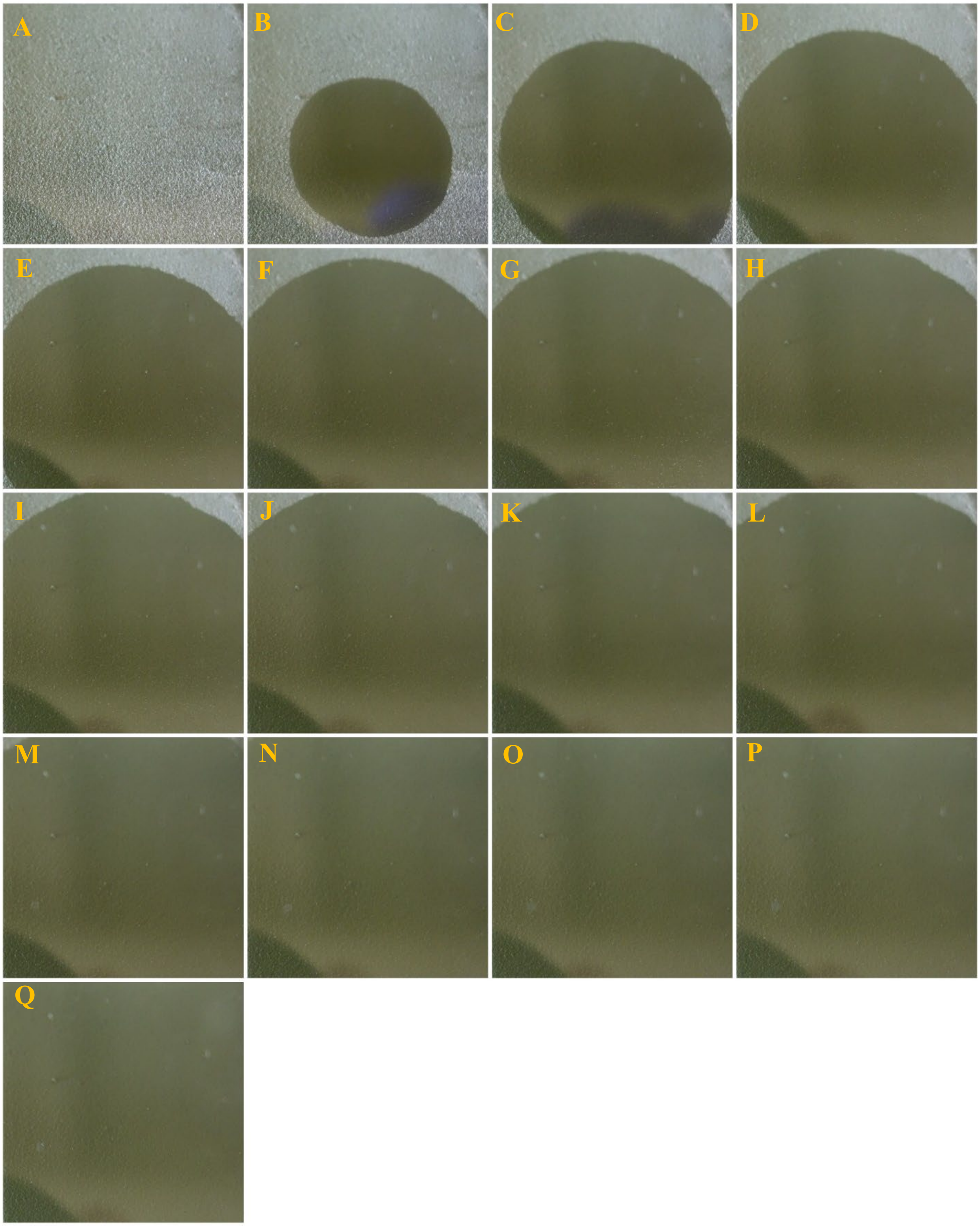


Fig. C2 — MES on IPDI-NH2PDMSNH2 2x Mn~3,000 on TEOS. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

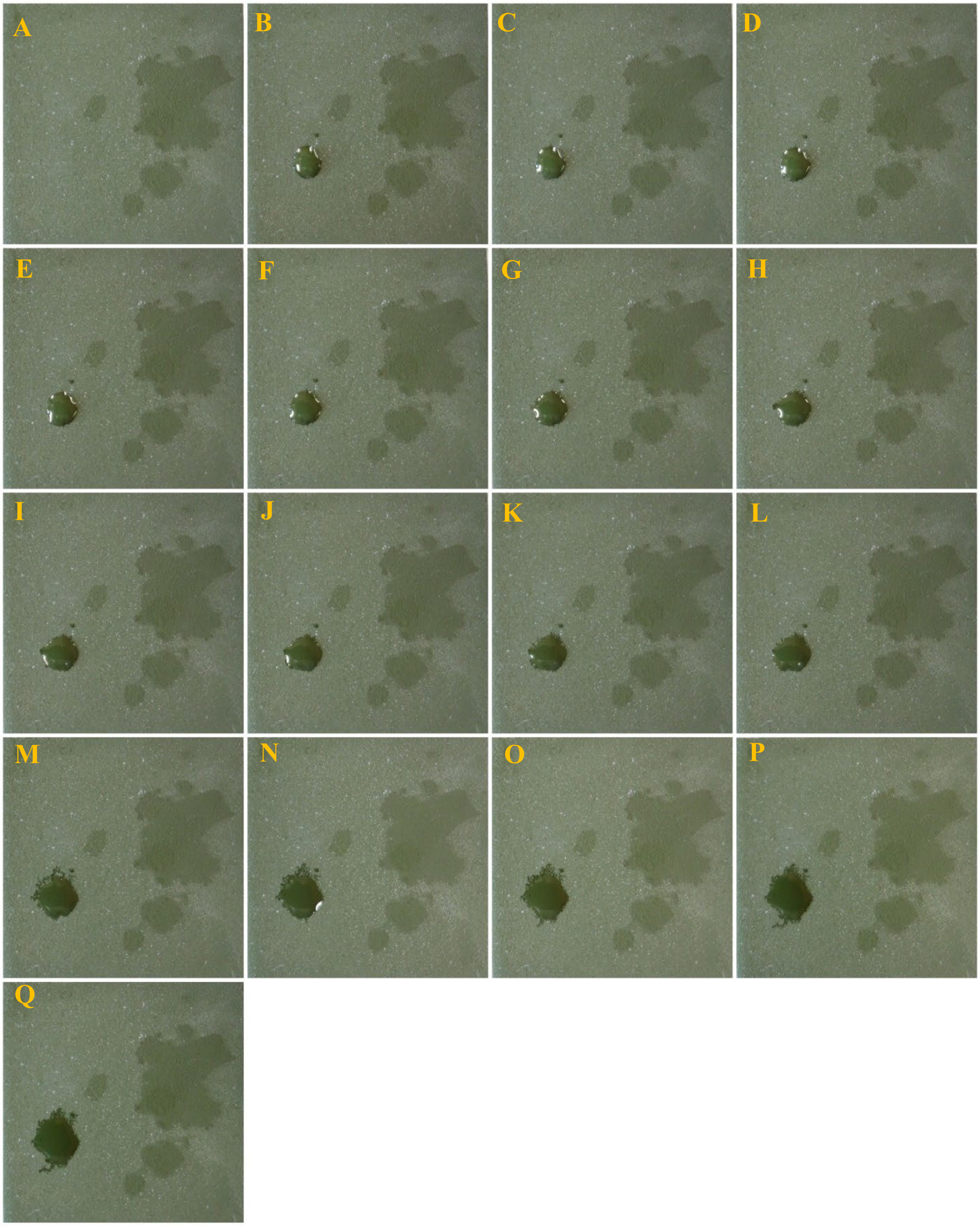
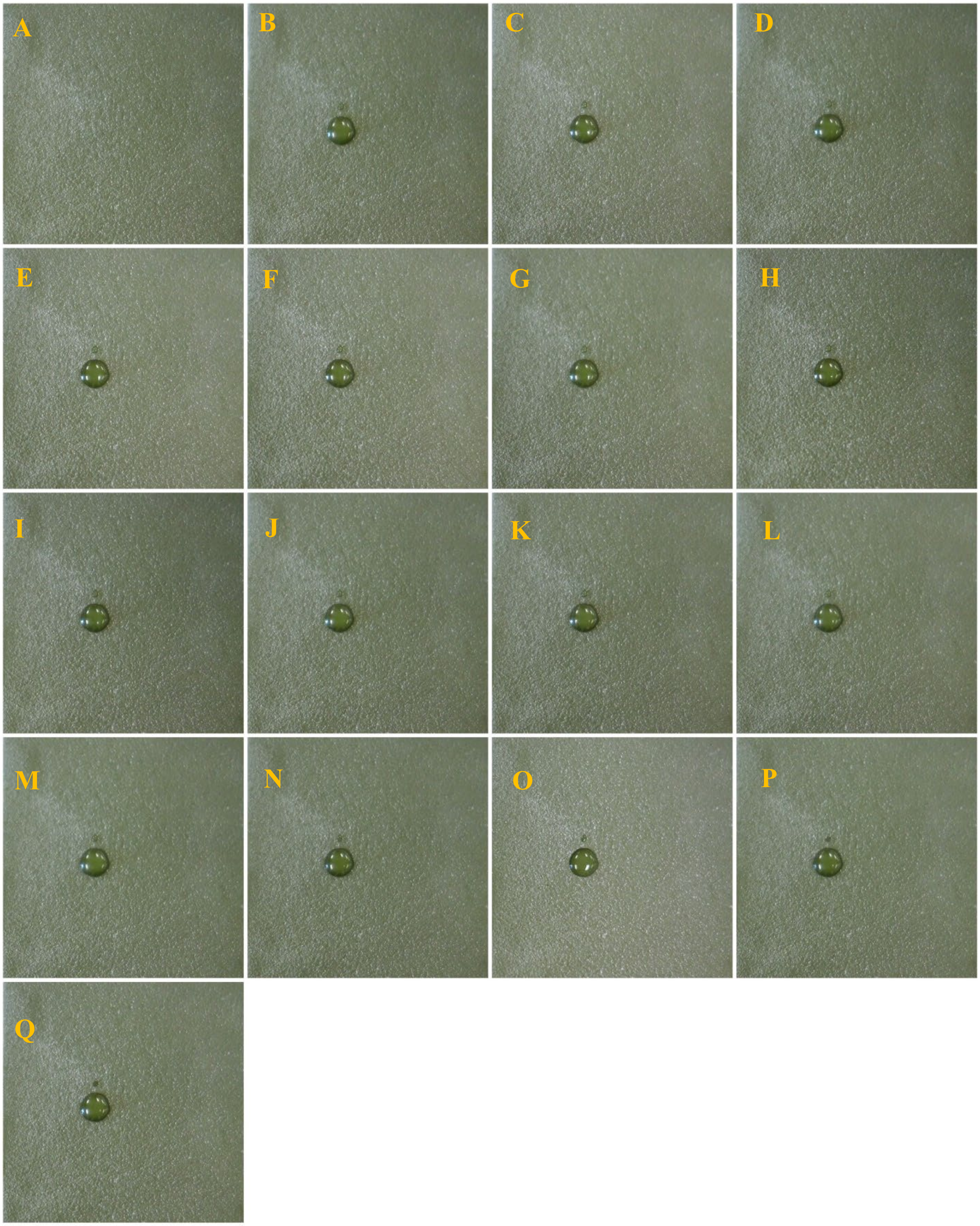


Fig. C3 — DMMP on IPDI-NH2PDMSNH2 2x Mn~3,000 on TEOS. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Appendix D

IPDI-NH2PDMSNH2 2xMn ~5,000 on TEOS COUPON IMAGES

Fig. D1 — DFP on IPDI-NH2PDMSNH2 2xMn ~5,000 on TEOS. 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.

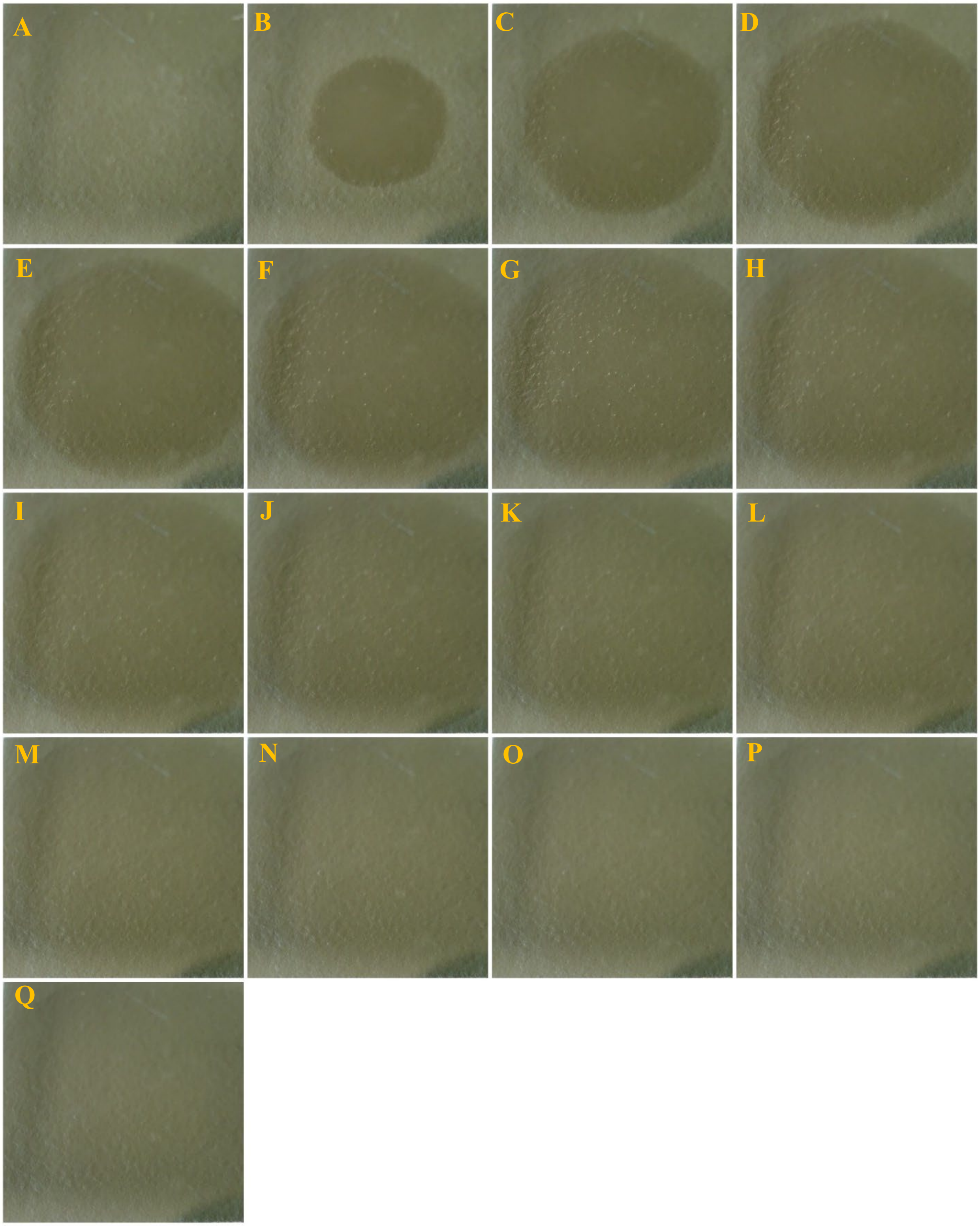


Fig. D2 — MES on IPDI-NH2PDMSNH2 2xMn ~5,000 on TEOS. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

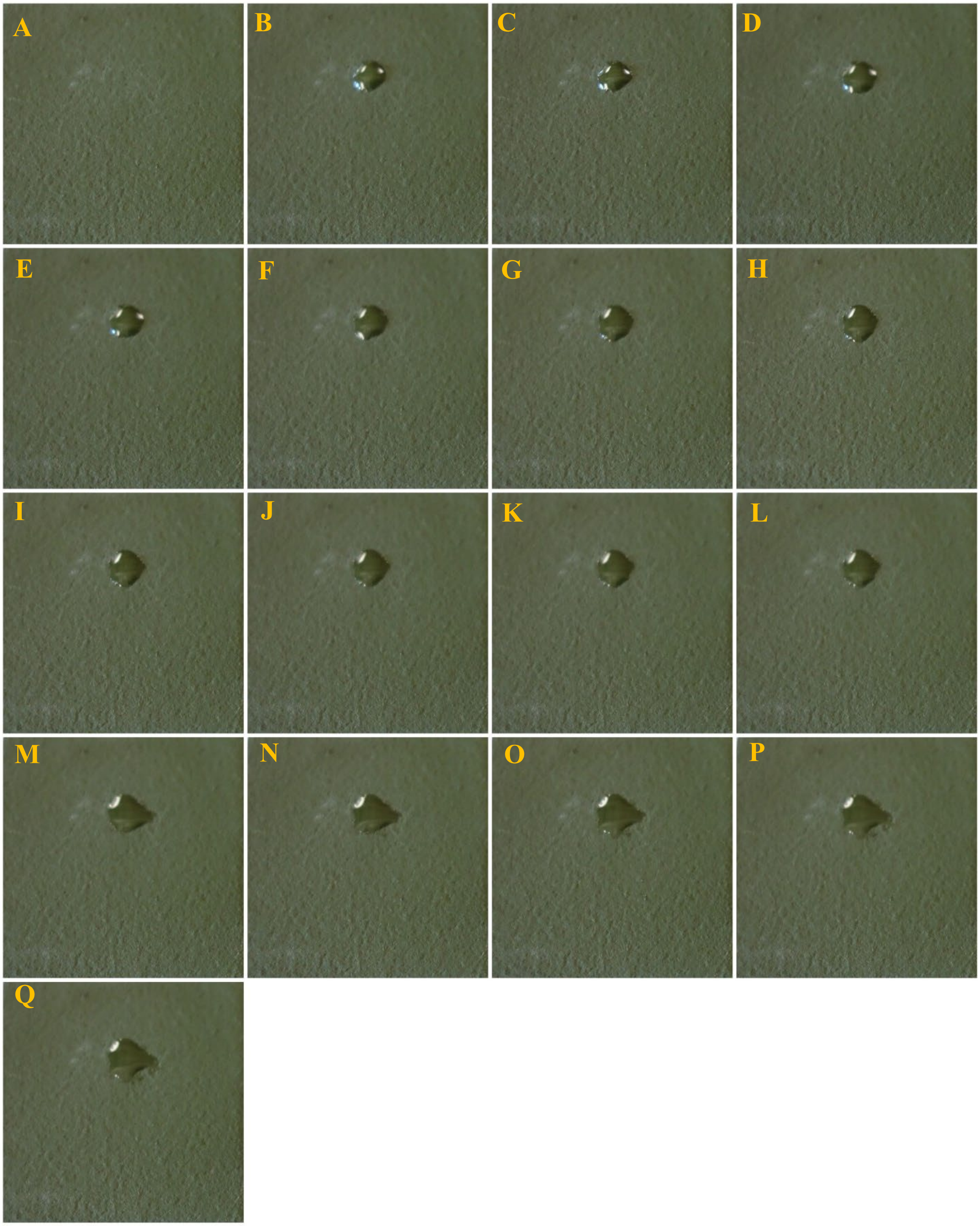


Fig. D3 — DMMP on IPDI-NH2PDMSNH2 2xMn ~5,000 on TEOS. Images of a film supported by painted coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.