Naval Research Laboratory
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Bioinspired Surface Treatments for Improved Decontamination: Icephobic Surfaces

Brandy J. White
Martin H. Moore

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

Anthony P. Malanoski

Laboratory for Biosensor and Biomaterials
Center for Bio/Molecular Science & Engineering

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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 an anti-ice coating developed by the University of Massachusetts Lowell. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphate, and diisopropyl fluorophosphates following treatment of contaminated surfaces with a soapy water solution is reported. Wetting behaviors and target droplet diffusion on the surfaces are also discussed.

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CONTENTS

INTRODUCTION 1
METHODS 2
RESULTS 3
CONCLUSIONS 5
ACKNOWLEDGMENTS 5
REFERENCES 6

APPENDIX – COUPON IMAGES 7

FIGURES

Fig. 1 — Coupon images 2
Fig. 2 — Simulant Droplets 4
Fig. 3 — Droplet Diameters........ 4
Fig. 4 — Simulant retention 5

TABLES

Table 1 — Contact angles 3
Table 2 — Simulant retention 5

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 an anti-ice coating developed by the University of Massachusetts Lowell. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphate, and diisopropyl fluorophosphates following treatment of contaminated surfaces with a soapy water solution is reported. Wetting behaviors for the surfaces are also discussed.

BIOINSPIRED SURFACE TREATMENTS FOR IMPROVED DECONTAMINATION: ICEPHOBIC SURFACES

INTRODUCTION

The DoD Chemical and Biological Defense Program (CBDP) seeks to provide protection of forces in a contaminated environment including contamination avoidance, individual protection, collective protection, and decontamination. In January 2015, the Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) began an effort funded through the Defense Threat Reduction Agency (DTRA, CB10125) with a view toward evaluation and development of top-coat type treatments suitable for application to painted surfaces that would reduce retention of chemical threat agents following standard decontamination approaches. The effort sought to survey relevant and related areas of research and evaluate identified technologies under appropriate methods to determine efficacy, scalability, and durability.

The current document summarizes results for one of the identified technologies. The University of Massachusetts Lowell icephobic materials are based on a system comprised of silica nanoparticles and fluorosilane to produce both texture and hydrophobic properties. [1, 2] The coating technology is reported to produce a water contact angle of greater than 160° with sliding angles <10° classifying the surface as superhydrophobic (water contact angles >150°). The durability of the material was previously evaluated using the cross hatch tape test (ASTM D3359) and the Taber abrasion test (ASTM D4060; 100 cycles) as well as with a wind tunnel test (120 mph). Following the cross hatch tape and wind tunnel durability tests, the surfaces were found to be superhydrophobic; the Taber abrasion test resulted in increased wetting, producing a hydrophobic rather than superhydrophobic surface. The coating technology has previously been deposited on a range of substrates including glass, metal, paper, and polymers. It is amenable to spray-, dip-, and spin-coating deposition processes. For the current study, aluminum coupons painted with a polyurethane paint system were provided to the UMass Lowell Nanomanufacturing Center (Figure 1). UMass Lowell treated these coupons and returned them to NRL for evaluation. The coupons were subjected to the standard evaluations including measurement of sessile, sliding, and shedding contact angles and quantification of retention for simulant compounds.

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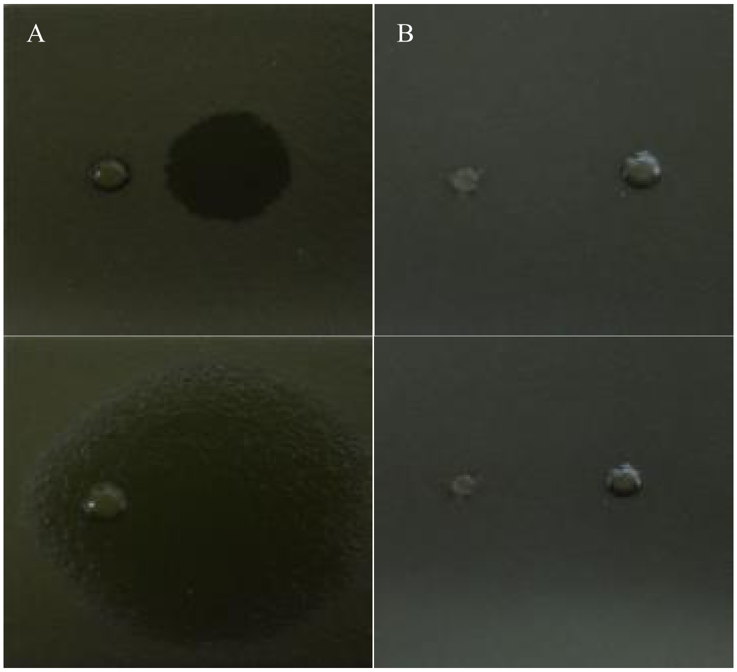

Fig. 1 — Images of a painted coupon and a painted coupon treated with the icephobic formulation with standing droplets of water (left) and methyl salicylate (right) immediately following liquid application (top) and 5 min after liquid application (bottom): painted coupon (A) and icephobic coupon (B).

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 (average of nine measurements for each liquid). 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 visually 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. In order to analyze agent spreading on the surfaces, 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. Droplet diameters were determined using tools provided by Adobe Photoshop CS3. 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 those images.

Standard target exposures utilized a challenge level of 10 g/m^2. The coupons provided by UMass Lowell were 0.002581 m^2; the 10 g/m^2 target challenge was applied to the surfaces as four 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 which was then rinsed with soapy water (0.59 g/L Alconox in deionized water). The coupons were subsequently soaked in isopropanol for 30 min to extract remaining target; this isopropanol extract was analyzed by the appropriate chromatography method to determine target retention on the surface.

For paraoxon analysis, a Shimadzu High Performance Liquid Chromatography (HPLC) system with dual-plunger parallel flow solvent delivery modules (LC-20AD) and an auto-sampler (SIL-20AC; 40 µL injection volume) coupled to a photodiode array detector (SPD-M20A; 277 nm) was used. The stationary phase was a C18 stainless steel analytical column (Luna, 150 mm x 4.6 mm, 3 µm diameter; Phenomenex, Torrance, CA) with an isocratic 45:55 acetonitrile: 1% aqueous acetic acid mobile phase (1.2 mL/min). [3] For analysis of methyl salicylate (MES), diisopropyl fluorophosphates (DFP), and dimethyl methylphosphonate (DMMP), gas chromatography-mass spectrometry (GC-MS) was accomplished using a Shimadzu GCMS-QP2010 with AOC-20 auto-injector equipped with a Restex RTX-5 (30 m x 0.25 mm ID x 0.25 µm df) cross bond 5% diphenyl 95% dimethyl polysiloxane column. A GC injection temperature of 200°C was used with a 1:1 split ratio at a flow rate of 3.6 mL/min at 69.4 kPa. The oven gradient ramped from 50°C (1 min hold time) to 180°C at 15°C/min and then to 300°C at 20°C/min where it was held for 5 min.

RESULTS

Analysis of the painted surfaces alone provides a point of comparison for evaluating the benefits of the surface treatments. Table 1 provides contact angles collected for coupons coated with the polyurethane paint system only as well as those for the icephobic coating. As shown, the icephobic surface treatment significantly increased the wetting angles for both water and ethylene glycol. The samples did not, however, achieve the superhydrophobic water contact angles (>150°) that were previously reported. Heptane wetted all surfaces, producing contact angles below the measurable threshold. Geometric surface energy was reduced by an order of magnitude for coupons with the icephobic treatment. The icephobic surface produced a water sliding angle of less than 10°; sliding angles for both ethylene glycol and heptane were greater than 60°. A shedding angle of 31° was observed for ethylene glycol; heptane did not shed at any angle for this treatment. It should be noted that the samples were not entirely uniform. Water dropped on to the flat icephobic surfaces from 12.5 cm frequently bounces rather than sticking, regardless of the angle of the surface. Each of the analyzed surfaces, however, had regions on which the water droplets would be retained (see sessile angles).

Table 1 – Sessile, Sliding, and Shedding Contact Angles

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	--	>60	>60	
Icephobic	water	144.3 ± 1.9	9.2 ± 4.0	1.1 ± 1.0	8.09 ± 3.09
	ethylene glycol	128.6 ± 3.3	>60	31.2 ± 6.2	
	n-heptane	--	>60	>60	

The tendency of droplets to spread across the surfaces was also evaluated (Figures 2 and 3). For these studies, 5 µL droplets of the simulants were utilized. The spread of the droplets was quantified by measuring the diameter of the droplets in the images over time (Figure 3). A full series of images is provided in the Appendix for each surface / target combination. For the paint only samples, DFP spreads quickly while MES slowly spreads across the surface. DMMP does not spread during the course of the 30 min incubation. The icephobic treatment slows the spread of the DFP as compared to the painted surface alone. MES and DMMP do not spread on this surface.

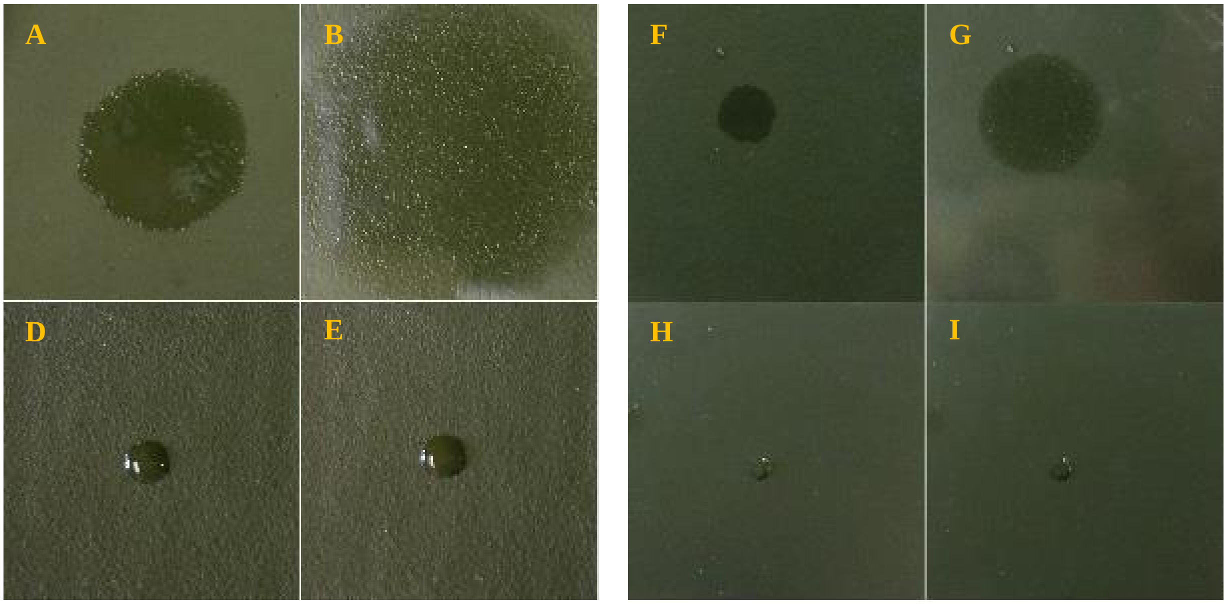

Fig. 2 — Images of a painted coupon and a painted coupon treated with the icephobic formulation with standing droplets of DFP and DMMP: painted coupon with DFP immediately following application (A) and at 2.5 min (B); painted coupon with DMMP immediately following application (C) and at 30 min (D); icephobic coupon with DFP immediately following application (E) and at 2.5 min (F); and icephobic coupon with DMMP immediately following application (G) and at 30 min (H).

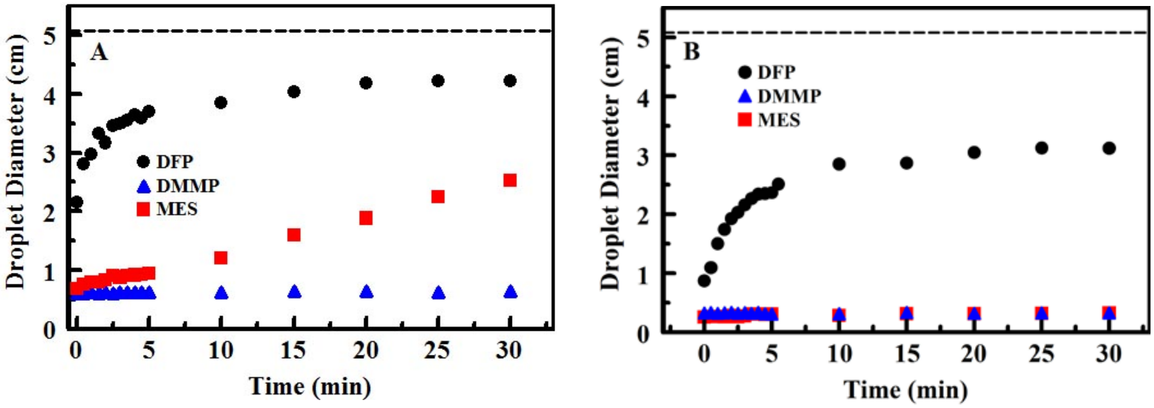

Fig. 3 — Progression of simulant droplet diameters during incubation on the surfaces for DFP (black), DMMP (blue), and MES (red): paint only (A) and icephobic coating (B).

The coupons were subjected to several cycles of simulant exposure, aging, washing, and drying over a period of four weeks. No significant changes in the appearance or wetting characteristics were noted during this period. When the soapy water decontamination process was employed (Figure 4; Table 2), retention of all targets was significantly reduced by the icephobic treatment. Retained DMMP was 0.01 g/m^2. All other targets were retained at less than 0.5 g/m^2, less than 5% of the deposited target. Table 2 presents additional results for coupons that were not rinsed prior to isopropanol. Though the nominal target application was 10 g/m^2, recovery from surfaces was always less than this value. Losses due to evaporation would be expected, especially for DFP. Additional losses likely occur during the rinse steps due to agent interaction with the untreated region of the coupon; the back of these coupons is unpainted aluminum.

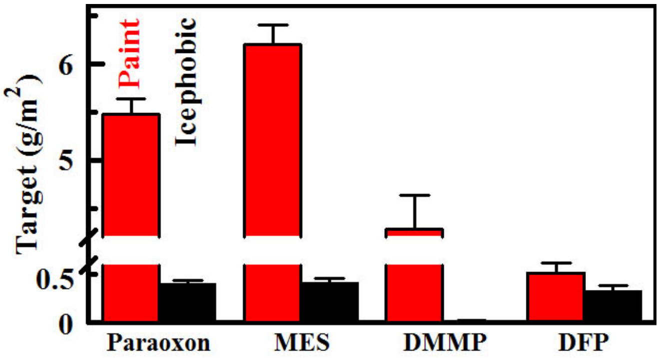

Fig. 4 — Target retention by coupons following treatment with an air stream and rinsing with soapy water.

Table 2 – Target Retention (g/m^2) Following 1 h Aging

Coupon	Target	No Rinse	Air & Soapy Water
Paint Only	paraoxon	9.84	5.48
	MES	9.54	6.20
	DMMP	9.90	4.28
	DFP	7.39	0.52
Icephobic	paraoxon	9.82	0.40
	MES	9.46	0.41
	DMMP	9.22	0.01
	DFP	7.45	0.32

CONCLUSIONS

The samples analyzed for this report yield promising results for improved decontamination. The samples have low surface energy as well as low target retention in simulant studies. Based on work completed by UMass Lowell, the samples likely provide the robust durability necessary for long term protection of painted surfaces. There was no visible difference in color or reflectance between the UMass Lowell icephobic samples and the painted coupons. Additional analysis using spectrophotometric methods should be completed to verify retention of paint signature characteristics following the icephobic treatment.

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Appendix

Coupon Images

Fig. A1 — DFP on the icephobic coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 5.5 (M), 10 (N), 15 (O), 20 (P), 25 (Q), and 30 (R) 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.

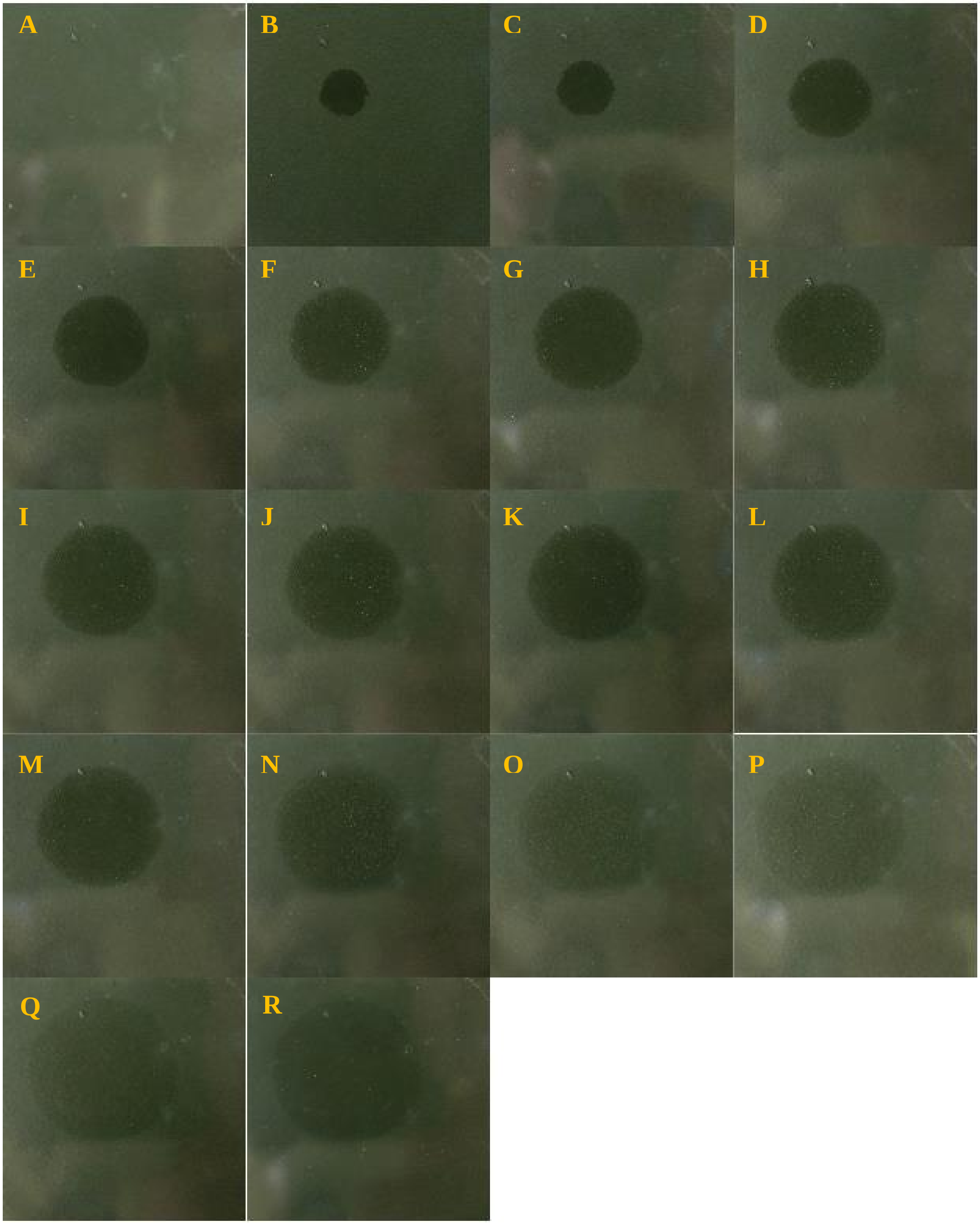

Fig. A2 — MES on the icephobic coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

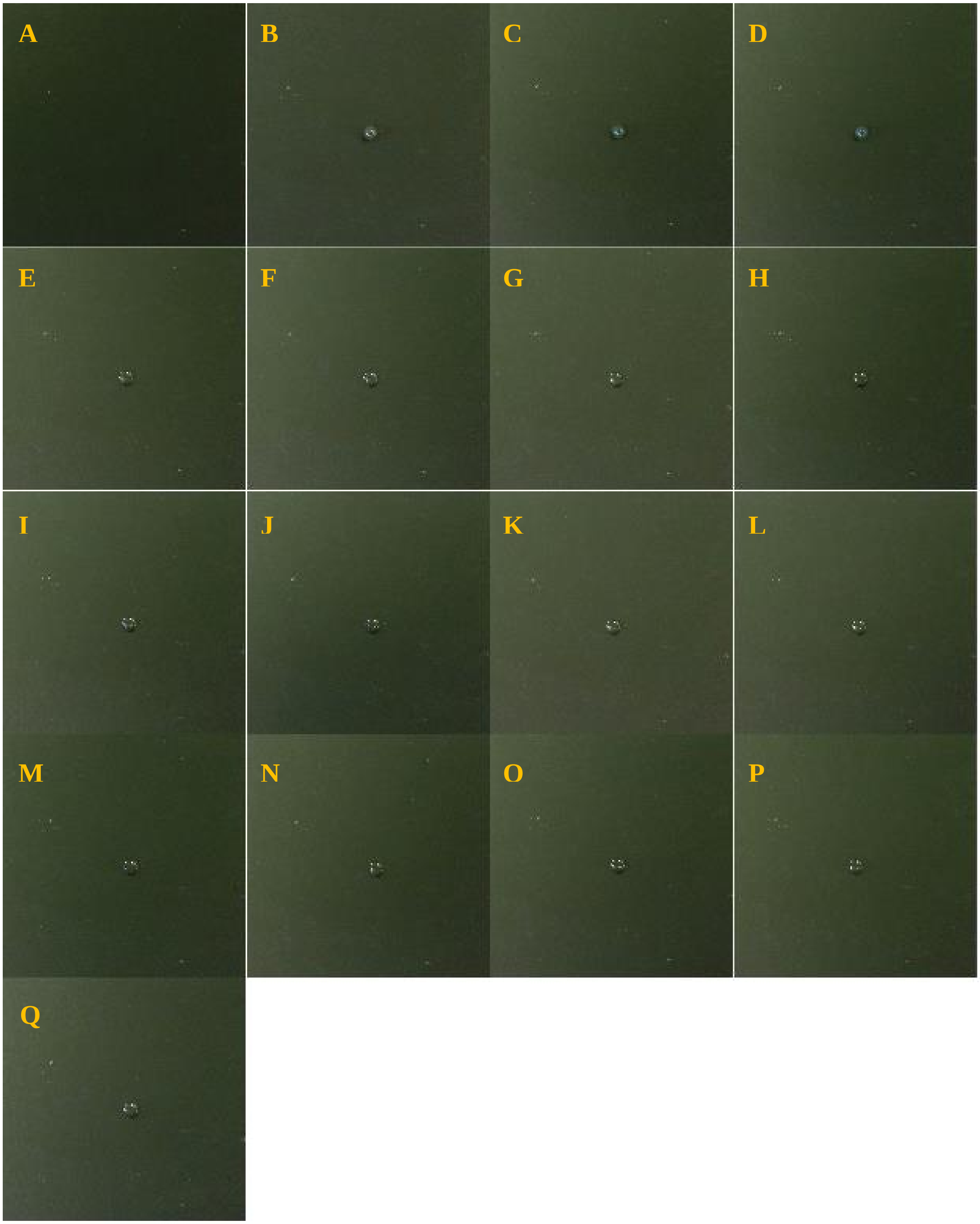

Fig. A3 — DMMP on the icephobic coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

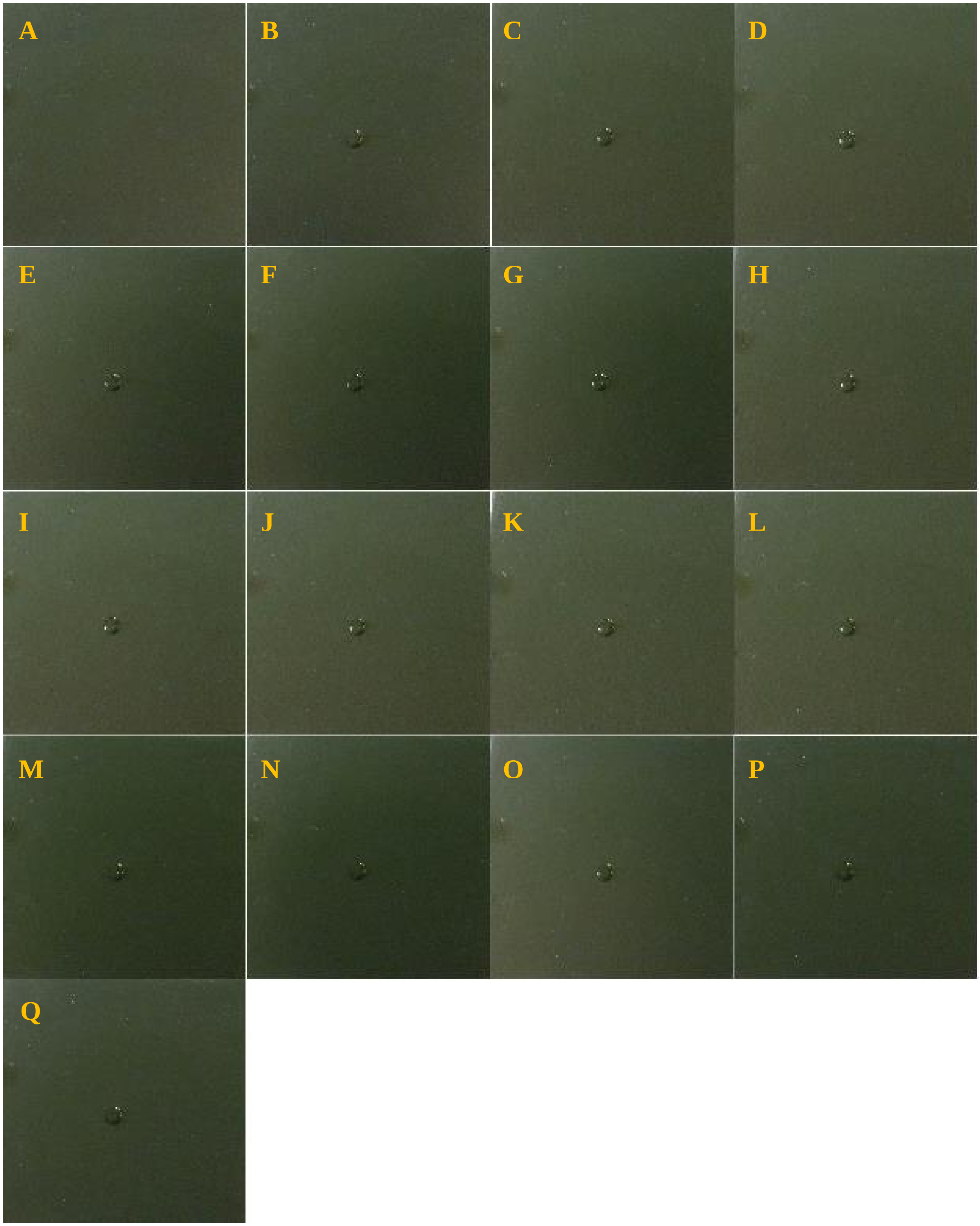

Fig. A4 — DFP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1.0 (D), 1.5 (E), 2.0 (F), 2.5 (G), 3.0 (H), 3.5 (I), 4.0 (J), 4.5 (K), 10 (L), 15 (M), 20 (N), 25 (O), and 30 (P) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

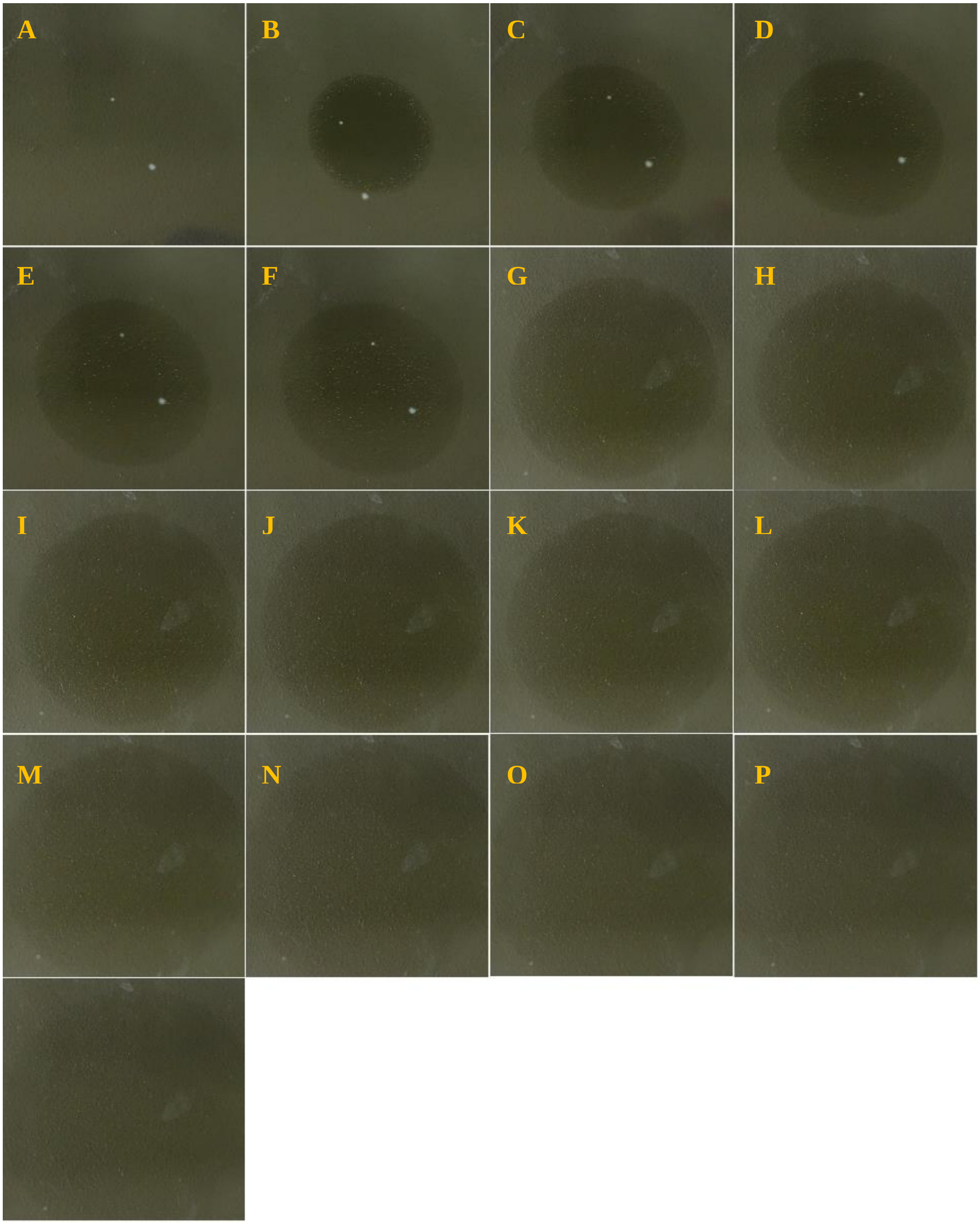

Fig. A5 — MES on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

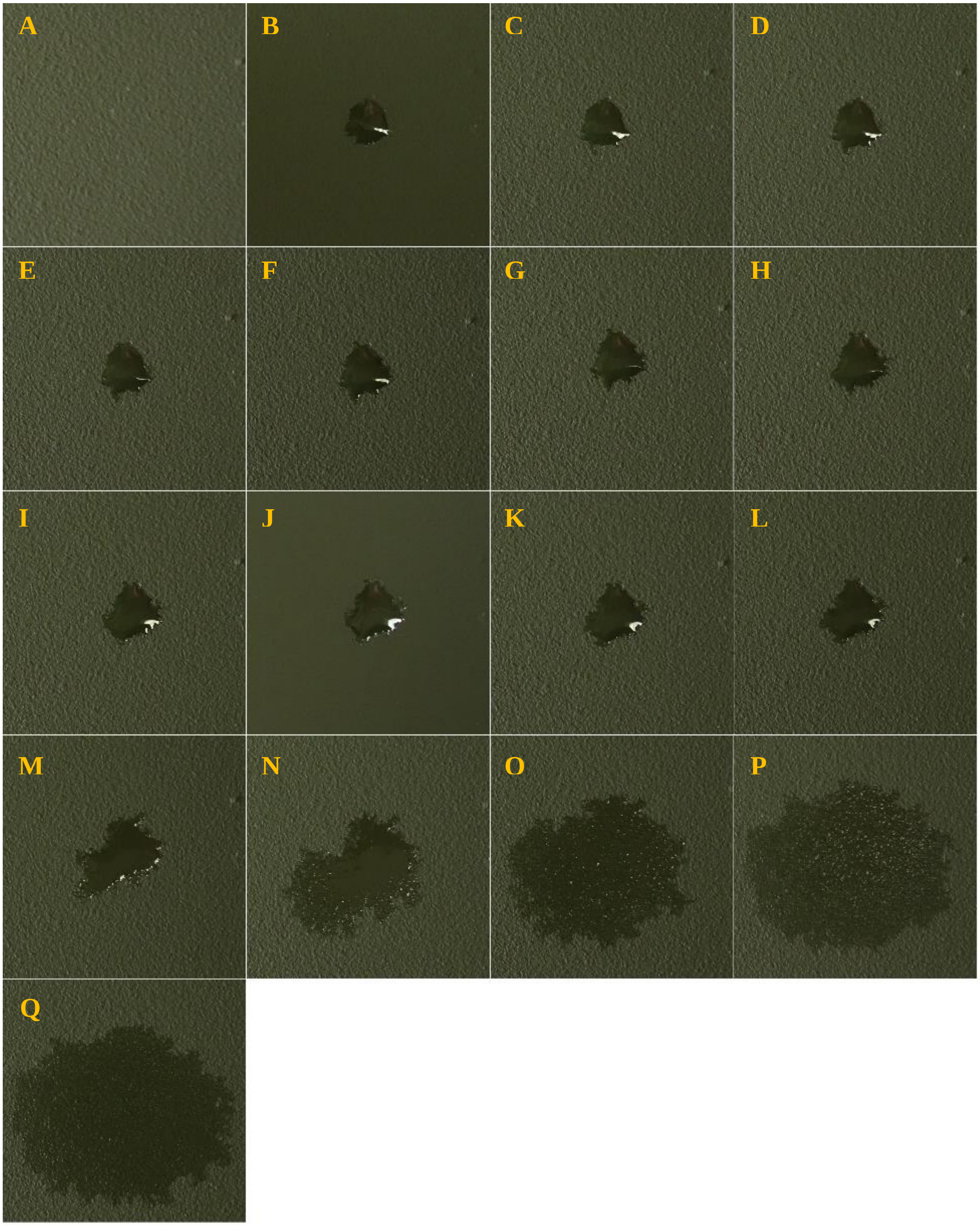

Fig. A6 — DMMP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.