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Bioinspired Surface Treatments for Improved Decontamination: Polyhedral Oligomeric Silsesquioxane (POSS)

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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 polyhedral oligomeric silsesquioxane (POSS) surface treatments. POSS are cage structures of silicon and oxygen that bind to organic polymers producing chains that can serve to reinforce the overall structure. The POSS variants evaluated under this study included a cage structure with methacrylate side chain (MA0702), two variants using a cage structure with polyethylene glycol side chain (PG1192 and PG1193), two variants using the Corin XLS polyimide structure (Corin XLS and Corin 0578) and two cage structures with alkyl groups of differing length (SO1450 and SO1455). The materials were deposited on polyurethane paint coated aluminum coupons. Retention of the simulants paraoxon, methyl salicylate, dimethyl methylphosphonate, and diisopropyl fluorophosphate following treatment of contaminated surfaces with a soapy water solution is reported along with droplet diffusion on the surfaces and wetting angles.

BIOINSPIRED SURFACE TREATMENTS FOR IMPROVED DECONTAMINATION: POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS)

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. In this case, a series of polyhedral oligomeric silsesquioxane (POSS) prepared by J. Lichtenhan of Hybrid Plastics Inc.

In attempts to control surface wetting and penetration of liquids into surfaces, the lotus leaf effect is commonly harnessed. This involves the use of a textured surface providing air-liquid and air-solid interfaces. There are a couple of problems that generally cause failures for this approach. First, at high pressure, liquid will intrude into the textured surface resulting in a defeat of the repellent characteristic. In addition, the surface features that produce this effect tend to be fragile. Several alternatives to the lotus leaf effect have been described. Slippery liquid-infused porous surfaces (SLIPS) offer one such alternative. These coatings comprise a film of lubricating liquid with a textured substrate (micro/nano or both). [1, 2, 3, 4] The results are a surface that is effectively smooth on the molecular scale and a liquid-liquid interaction interface. Typically, these SLIPS treatments offer a self-healing mechanism for damage to the surfaces. The solid and liquid components of a SLIPS system are selected to repel liquids of interest. A shortfall of these SLIPS materials is related to this mobile liquid that can be depleted. Slippery omniphobic covalently attached liquids (SOCAL) [5] offer another alternative. 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. SOCAL and related self-assembled monolayer (SAM) surface treatments can involve complex deposition methods or lead to nondurable coatings. The reported SOCAL treatment also requires a smooth, cleaned silicate substrate for optimum performance.

The study described here builds on the valuable features of the SLIPS and SOCAL coatings, taking a different approach to achieving those characteristics. [6, 7, 8] Polyhedral oligomeric silsesquioxanes (POSS) are cage structures of silicon and oxygen that bind to organic polymers producing large chains that can act as a reinforcing fiber (Figure 1). They are used to enhance the mechanical properties of polymers (scratch resistance or increased modulus, for example) and thermal stability. They can also be used as flow aids, dispersants, lubricants, and surface modifiers. The POSS considered here offer a range of structures including POSS cages with long organic side chains. The expectation is that the POSS may produce effects similar to those observed for the polydimethylsiloxane (PDMS) based SOCAL coating. [7]

For the complete system, aluminum coupons were coated with a polyurethane paint system by NRL and were provided to Hybrid Plastics Inc (Figure 2). Following deposition of the POSS variants, coupons were returned to NRL for evaluation using standard approaches including measurement of sessile, sliding,

and shedding contact angles and quantification of retention for the simulant compounds. The POSS variants included a cage structure with methacrylate side chain (MA0702), two variants using a cage structure with polyethylene glycol side chain (PG1192 and PG1193), two variants using the Corin XLS polyimide structure (Corin XLS and Corin 0578) and two cage structures with different lengths on the alkyl groups (SO1450 and SO1455).

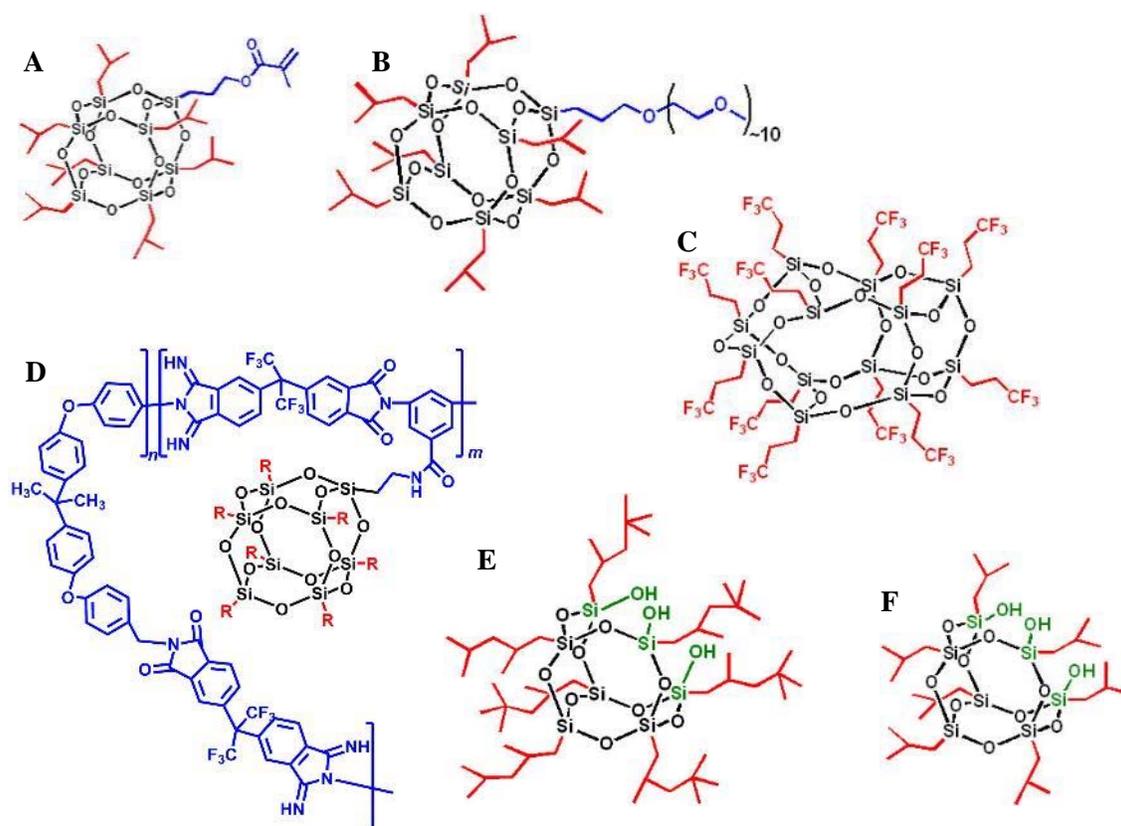


Fig. 1 — Molecular structures for the POSS variants evaluated: methacryloisobutyl POSS (A; MA0702); methoxyPEGisobutyl POSS (B; PG1192); trifluoropropyl POSS (C; FL0578); Corin XLS Polyimide (D); trisilanolisocetyl POSS (E; SO1455); and trisilanolisobutyl POSS (F; SO1450).

MA0702 (CAS 307531-94-8; MW 943) is comprised of the POSS cage structure with isobutyl groups at the corners and a methacrylate group. It is used as a comonomer for increased hydrophobicity and toughness. The material is a white powder soluble in tetrahydrofuran, hexane, and acetone and insoluble in acetonitrile. For the evaluated coating, MA0702 was cast in a 1:2 (g:g) ratio with dichloromethane at 109°C. This approach has been reported to form a monolayer on surfaces with association via the methacrylate group. As shown in Figure 2, this coating gave the appearance of a white residue on the painted surfaces.

PG1192 (MW 1330) is comprised of the POSS cage structure with isobutyl groups at the corners and a PEG-10 (polyethylene glycol) side chain. PG1192 provides an alternative to petroleum and related waxes. It has been used in cosmetics as a moisturizing wax with hydrophobic and hydrophilic properties. The material is a semi-solid wax with pale yellow color soluble in ethanol, aliphatic solvents, and oils. For this study, the compound has been cast from a 1:2 (g:g) solution in dichloromethane. The PEG side chain should provide interaction with the surface while the isobutyl groups provide hydrophobic character. PG1193 is a similar coating. These coatings had little impact on the visible characteristics of the coupons.

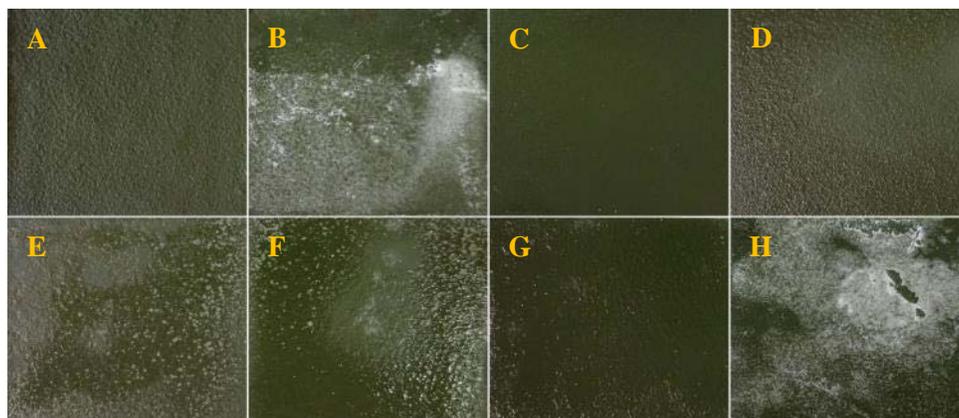


Fig. 2 — Images of a painted coupon (A) and painted coupons with methacryloisobutyl POSS (B; MA0702); methoxyPEGisobutyl POSS (C; PG1192); methoxyPEGisobutyl POSS (D; PG1193); Corin XLS Polyimide (E); Corin XLS Polyimide with trifluoropropyl POSS (F; Corin 0578); trisilanolisooctyl POSS (G; SO1455); and trisilanolisobutyl POSS (H; SO1450).

Corin XLS Polyimide combines the POSS cage structure with fluorinated polyimide. It is a clear, colorless, sprayable coating shown to provide clarity, radiation resistance, and oxidative and solar stability. It has been used in space based solar energy applications and offers a glass transition temperature in excess of 250°C. The material can be supplied as films, solvent-based liquid resin or powder form. For this study, a solution of 12.5% Corin XLS in propylene glycol methyl ether acetate was allowed to equilibrate for one week, producing a translucent, yellow solution. The imide of this material would be expected to bind to the surface with isobutyl POSS cages forming nano-texture with the fluorinated imide offering hydrophobicity. The Corin 0578 coating also used the Corin XLS Polyimide, but the cast solution was diluted with 1% trifluoropropyl POSS (FL0578; Figure 1). FL0578 is incorporated as a mobile surface agent increasing the overall hydrophobicity of the coating. This additive leads to a coating with a wet appearance (Figure 2).

SO1450 (CAS 307531-92-6) is the isobutyl POSS cage common to MA0702 and PG1192 but with an open corner leaving three active silanol groups (Figure 1). It is used for surface modification of metal oxides and other materials and as an additive to thermoplastics to improve moisture resistance. It is soluble in chloroform, hexane, and tetrahydrofuran and insoluble in acetonitrile. For this study, SO1450 was cast in a 1:2 (g:g) solution with dichloromethane. Silanols are expected to provide an interaction with the surface with the isobutyl groups providing hydrophobic character. SO1455 is similar in structure but incorporates isooctyl groups at the cage corners. In addition to the fields of use identified for SO1450, this structure offers potential in skin adhesion, wound closure, and hemostasis applications.

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 mL were applied to the surfaces and images were collected at 30 s intervals for 5 min followed by images at 5 min intervals for a total of 30 min. DFP samples were kept covered for the duration of the experiment to minimize evaporation. In some cases, reflections from the glass cover can be seen in the images.

Simulant exposure and evaluation methods were based on the tests developed by Edgewood Chemical Biological Center referred to as Chemical Agent Resistance Method (CARM). [9] Standard target exposures utilized a challenge level of 10 g/m^2 . The glass coupons were 0.00188 m^2 ; the 10 g/m^2 target challenge was applied to the surfaces as four equally sized neat droplets. The painted coupons were 0.00101 m^2 ; the 10 g/m^2 target challenge was applied to the surfaces as two equally sized neat droplets. Following application of the target, coupons were aged 1 h prior to use of a gentle stream of air to expel target from the surface. Samples were then rinsed with soapy water (0.59 g/L Alconox in deionized water). The rinsed coupons were soaked in isopropanol for 30 min to extract remaining target; this isopropanol extract was analyzed by the appropriate chromatography method to determine target retention on the surface.

For 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; $40 \mu\text{L}$ 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, $150 \text{ mm} \times 4.6 \text{ mm}$, $3 \mu\text{m}$ diameter; Phenomenex, Torrance, CA) with an isocratic 45:55 acetonitrile: 1% aqueous acetic acid mobile phase (1.2 mL/min). [10] For analysis of methyl salicylate (MES), diisopropyl fluorophosphate (DFP), and dimethyl methylphosphonate (DMMP), gas chromatography-mass spectrometry (GC-MS) was accomplished using a Shimadzu GCMS-QP2010 with AOC-20 auto-injector equipped with a Restex Rtx-5 ($30 \text{ m} \times 0.25 \text{ mm ID} \times 0.25 \mu\text{m df}$) 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 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 oiled painted aluminum coupon. With the exception of PG1193, application of the POSS coatings to the painted surfaces reduced the surface energy (Table 1 and Figure 3). The methacrylate modified isobutyl POSS structure (MA0702) yielded the lowest surface energy with wetting behaviors similar to those of the SO1450. The Corin coatings had the highest observed water contact angles, but were slightly more wetted by ethylene glycol than the MA0702 coating. Addition of the mobile fluorinated group FL0578 to the Corin XLS polyimide (Corin 0578) did result in greater hydrophobicity but lead to an overall higher surface energy. All of the POSS surfaces were fully wetted by heptane. No sliding or shedding from the surfaces was noted below an incline of 60° .

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) |
|-------------------------|-----------------|---------------|---------------|----------------|---|
| 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 | |
| MA0702 | water | 90.2 ± 0.4 | >60 | >60 | 18.1 ± 0.2 |
| | ethylene glycol | 79.0 ± 0.5 | >60 | >60 | |
| | n-heptane | -- | -- | -- | |
| PG1192 | water | 54.9 ± 0.3 | >60 | >60 | 56.3 ± 0.4 |
| | ethylene glycol | 41.2 ± 0.9 | >60 | >60 | |
| | n-heptane | -- | -- | -- | |
| PG1193 | water | -- | -- | -- | -- |
| | ethylene glycol | 8.7 ± 0.2 | -- | -- | |
| | n-heptane | -- | -- | -- | |
| Corin XLS Polyimide | water | 105.0 ± 0.5 | >60 | >60 | 21.5 ± 0.5 |
| | ethylene glycol | 80.6 ± 0.2 | >60 | >60 | |
| | n-heptane | -- | -- | -- | |
| Corin 0578 | water | 103.1 ± 1.0 | >60 | >60 | 24.0 ± 1.4 |
| | ethylene glycol | 76.9 ± 0.6 | >60 | >60 | |
| | n-heptane | -- | -- | -- | |
| SO1450 | water | 91.8 ± 0.3 | >60 | >60 | 20.1 ± 0.5 |
| | ethylene glycol | 73.3 ± 0.8 | >60 | >60 | |
| | n-heptane | -- | -- | -- | |
| SO1455 | water | 73.8 ± 1.1 | >60 | >60 | 29.8 ± 0.7 |
| | ethylene glycol | 58.6 ± 0.3 | >60 | >60 | |
| | n-heptane | -- | -- | -- | |

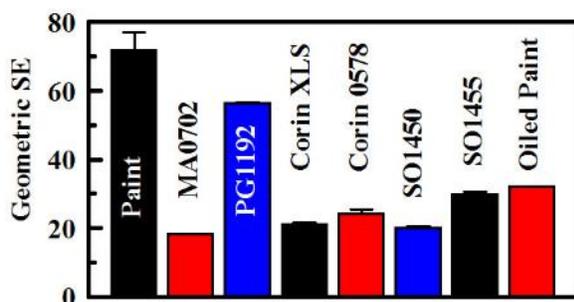


Fig. 3 — Geometric surface energy (mJ/m²) for the evaluated coatings. PG1193 was fully wetted by water and heptane preventing calculation of values for these surfaces.

The tendency of droplets to spread across the surfaces was also evaluated (Figure 4; Appendix A). For these studies, droplets of the simulants (5 μ L) were utilized. The spread of the droplets was quantified by measuring the diameter of the droplets in the images over time (Figure 5). 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 POSS materials produced a wide range of results. The MA0702 coating reduced the spread of DFP and MES but increased spread of DMMP. SO1455 prevented spread of DMMP and reduced the spread of MES; DFP was not visible after the first few minutes of the experiment. PG1192 showed similar behavior to that of SO1455. PG1193, on the other hand, had little impact on spread of MES or DFP and increased spread of DMMP. DFP spread on SO1450 was initially slowed, but DMMP and MES spread rapidly across this surface. Spread of the three simulants was nearly completely prevented by the Corin XLS and Corin 0578 coatings.

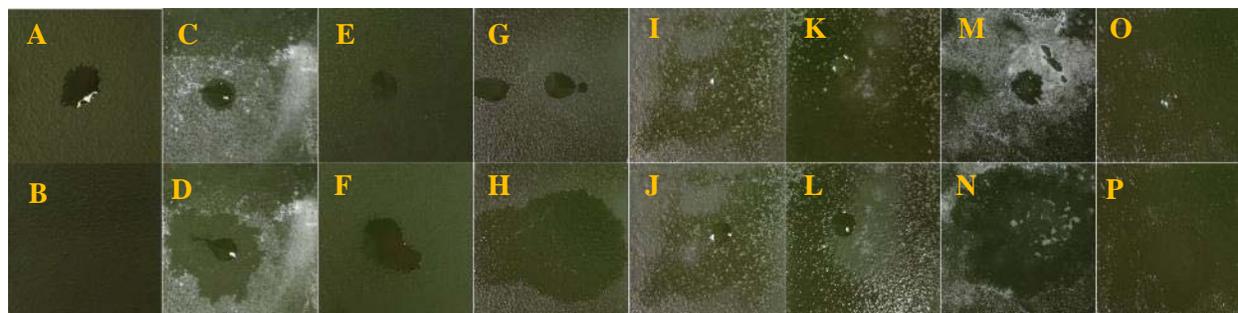


Fig. 4 — Images of coupons at 0 and 30 min following MES exposure: painted coupon (A & B) and painted coupon with MA0702 (C & D), PG1192 (E & F), PG1193 (G & H), Corin XLS Polyimide (I & J), Corin XLS Polyimide and FL0578 (K & L), SO1450 (M & N), and SO1455 (O & P).

The coupons were subjected to several cycles of simulant exposure (10 g/m^2), aging, washing, and drying over a period of several weeks. DFP exposure resulted in significant marking of the Corin and MA0702 treated coupons (Figure 6). The PG1192, PG1193, and SO1455 series treatments showed little change in the appearance or wetting characteristics. The Corin coatings and MA0702 showed significant damage and SO1450 appears to have been removed from the surface completely. When the soapy water process was employed (Figure 7; Table 2), retention of all targets was less for the Fomblin Y lubricated paint treatments than for the paint only surfaces. The MA0702 coating reduced retention of DMMP and paraoxon but increased retention DFP as compared to the painted surface. The PG1192 and PG1193 coatings reduced retention of paraoxon, DMMP, and MES but had little impact on DFP retention. The Corin coatings reduced paraoxon and DMMP retention, but increased DFP and MES retention. The SO1450 and SO1455 coatings reduced paraoxon and DMMP retention but had little impact on retention of MES and DFP.

Overall, all of the treatments reduced paraoxon and DMMP retention as compared to the painted coupon. Only PG1193 and SO1455 reduced retention of all simulants as compared to the painted coupon. None of the coatings outperformed the Fomblin Y coatings for all targets; PG1193 performed the best across all of the targets. 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.

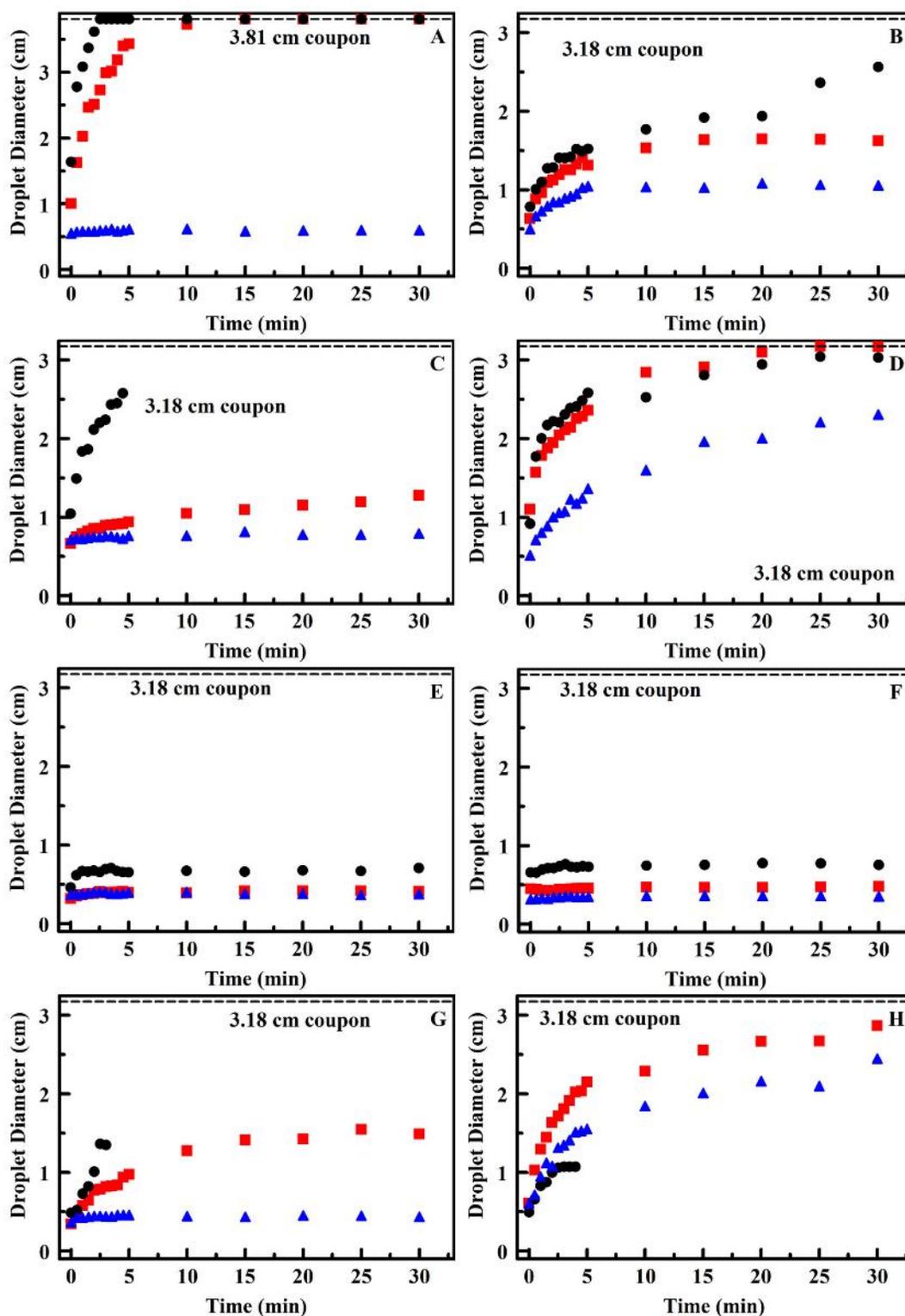


Fig. 5 — Droplet diameters over time following exposure to DFP (black), MES (red), and DMMP (blue) for a painted coupon (A) and painted coupons with methacryloisobutyl POSS (B; MA0702); methoxyPEGisobutyl POSS (C; PG1192); methoxyPEGisobutyl POSS (D; PG1193); Corin XLS Polyimide (E); Corin XLS Polyimide with trifluoropropyl POSS (F; Corin 0578); trisilanolisocetyl POSS (G; SO1455); and trisilanolisobutyl POSS (H; SO1450).

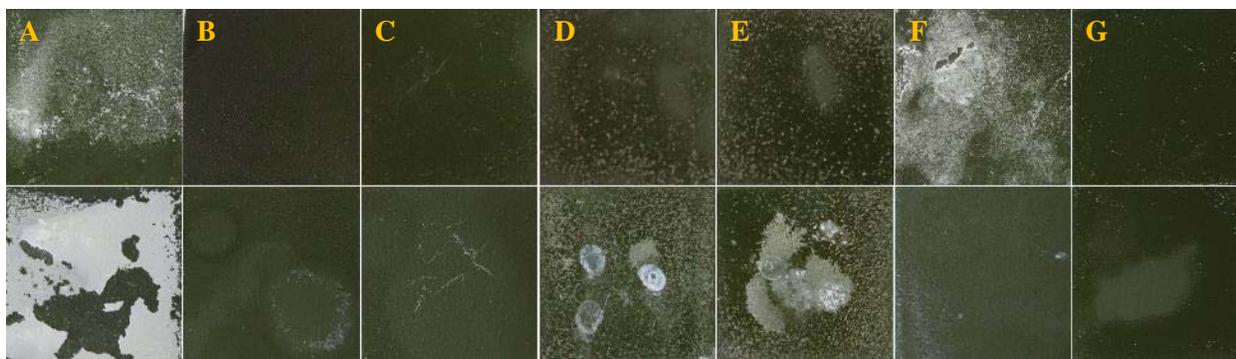


Fig. 6 — Images of coupons before (top) and after (bottom) analysis of target retention cycles: painted coupon with MA0702 (A), PG1192 (B), PG1193 (C), Corin XLS Polyimide (D), Corin XLS Polyimide and FL0578 (E), SO1450 (F), and SO1455 (G).

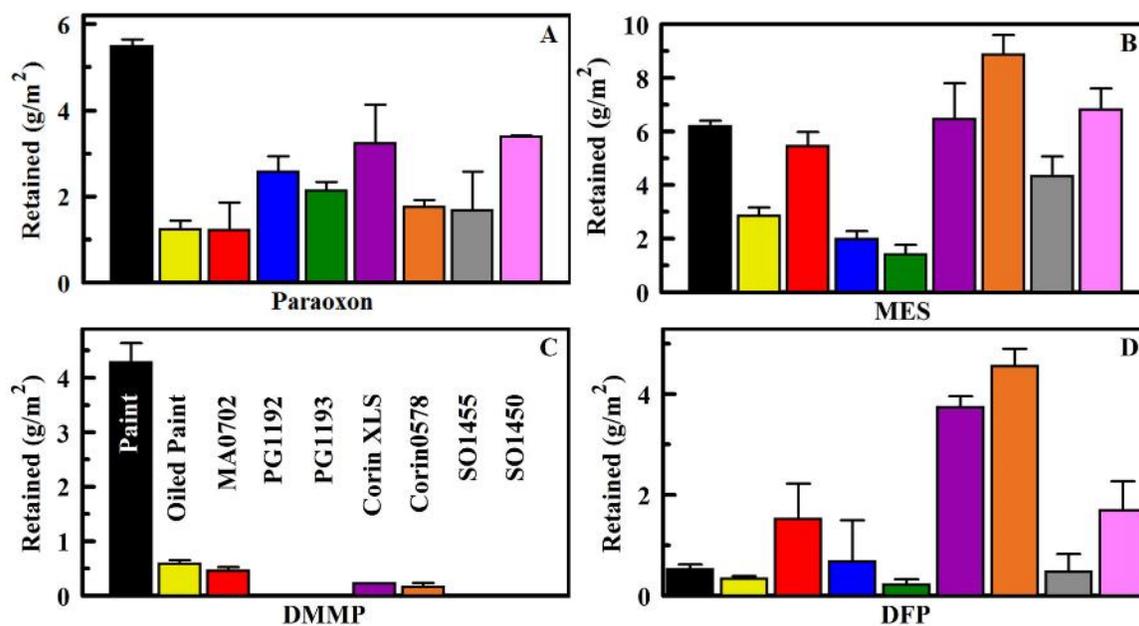


Fig. 7 — Target retention by coupons following treatment with an air stream and rinsing with soapy water: (A) painted (black), MA0702 (red), PG1192 (blue), PG1193 (green), Corin XLS (purple), Corin 0578 (orange), SO1455 (gray), SO1450 (pink), and Fomblin Y oiled paint (yellow).

Table 2 – Target Retention (g/m²) Following 1 h Aging on Aluminum Supports

| Coupon | Paraoxon | MES | DMMP | DFP |
|-------------------------|----------|------|------|------|
| Aluminum Support | | | | |
| Paint Only | 5.48 | 6.2 | 4.28 | 0.52 |
| Fomblin Y Oiled Paint | 1.24 | 2.85 | 0.59 | 0.34 |
| MA0702 | 1.22 | 5.45 | 0.46 | 1.52 |
| PG1192 | 2.58 | 1.98 | ND | 0.68 |
| PG1193 | 2.14 | 1.41 | ND | 0.22 |
| Corin XLS | 3.23 | 6.46 | 0.22 | 3.74 |
| Corin 0578 | 1.76 | 8.87 | 0.16 | 4.55 |
| SO1455 | 1.67 | 4.33 | ND | 0.48 |
| SO1450 | 3.40 | 6.82 | ND | 1.70 |

ND = not detected

CONCLUSIONS

These samples provide interesting results with wetting and target retention behaviors varying widely across the coating types. Different coatings provided better resistance to retention of individual targets, but do not provide overall improved performance. The approach does offer interesting potential as the process for application of the materials can be simple. Given the damage noted on repeated use, the materials are likely applicable only in strippable or temporary scenarios. Application of several of the coatings produces a visible change in appearance for the painted surfaces (Figure 2 and Appendix). Spectrophotometric analysis is necessary to determine the overall impact on color and reflectivity. It may be of interest to consider alternative compositions that combine the FL0578 as a mobile lubricant with the better performing PG1193 or SO1455.

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Appendix
COUPON IMAGES

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

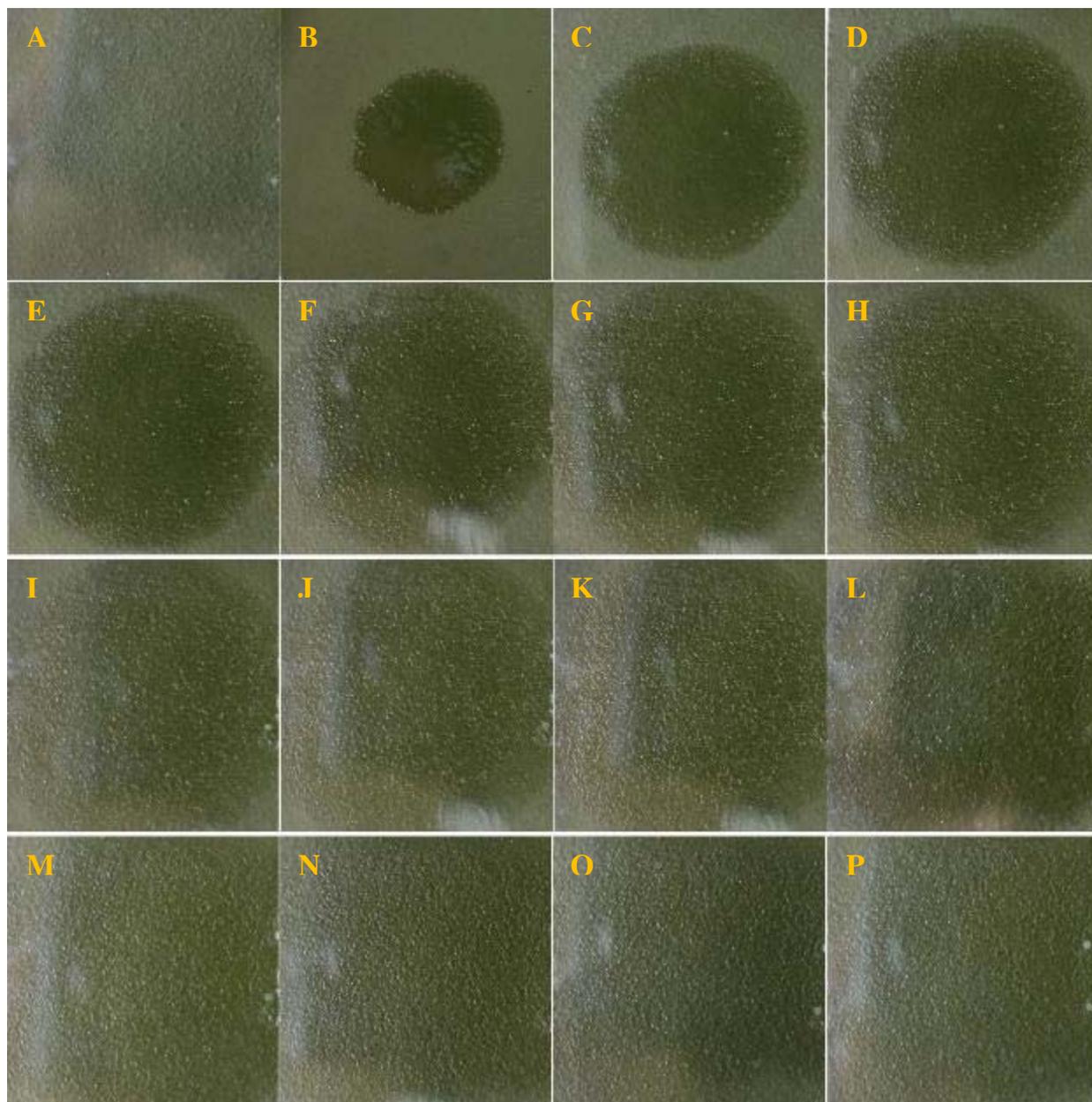


Fig. A2 — MES on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

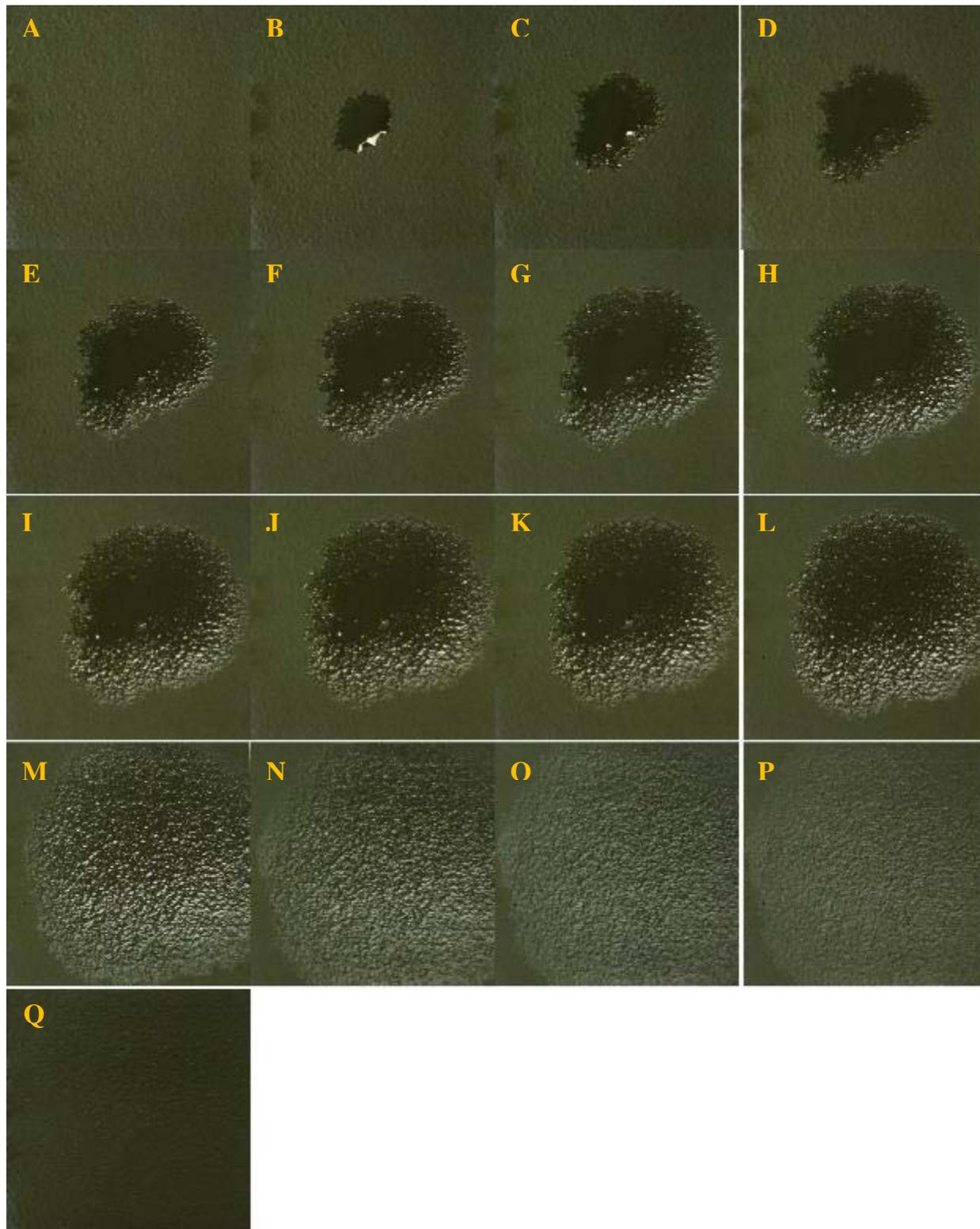


Fig. A3 — DMMP on paint. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

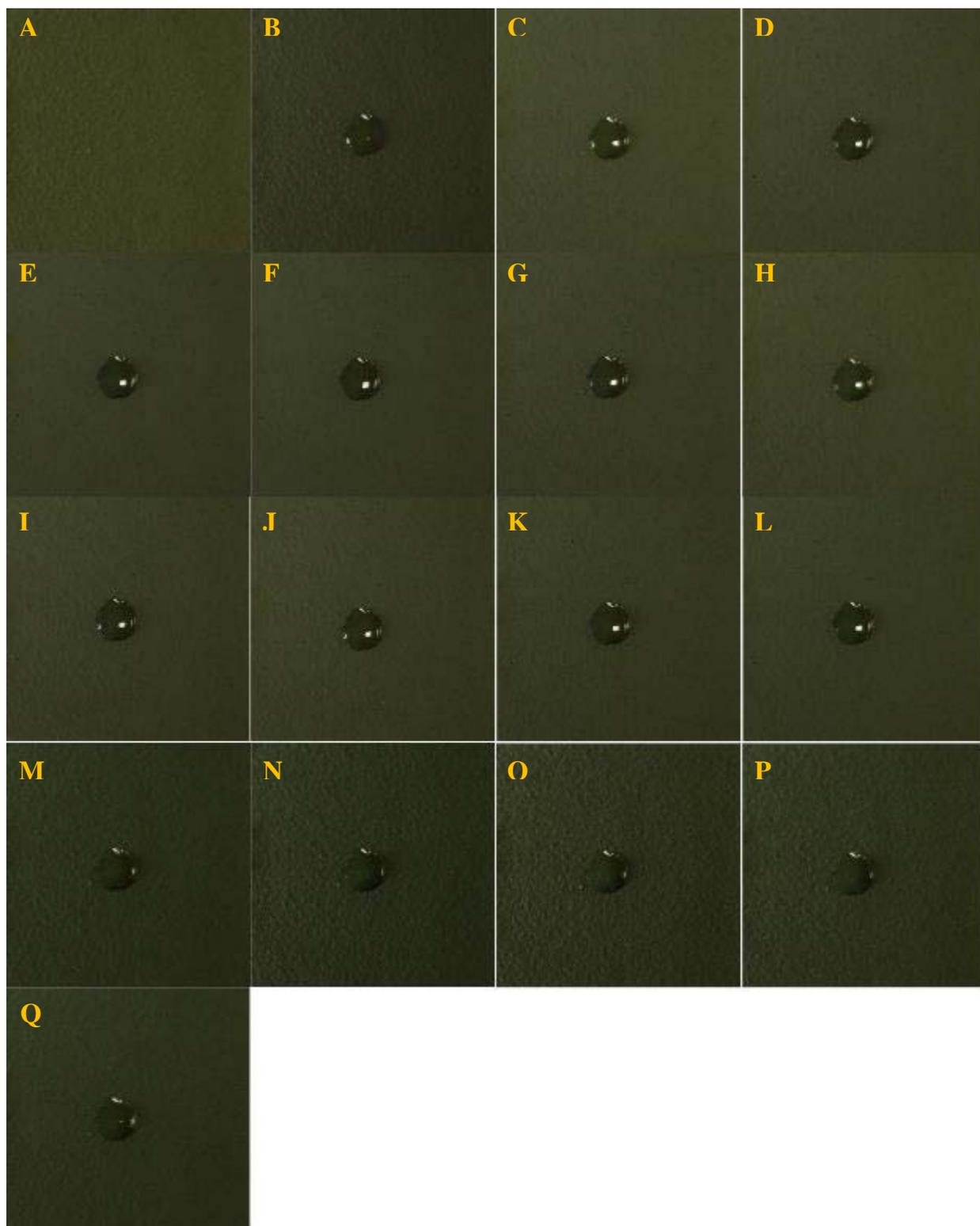


Fig. A4 — DFP MA0702 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

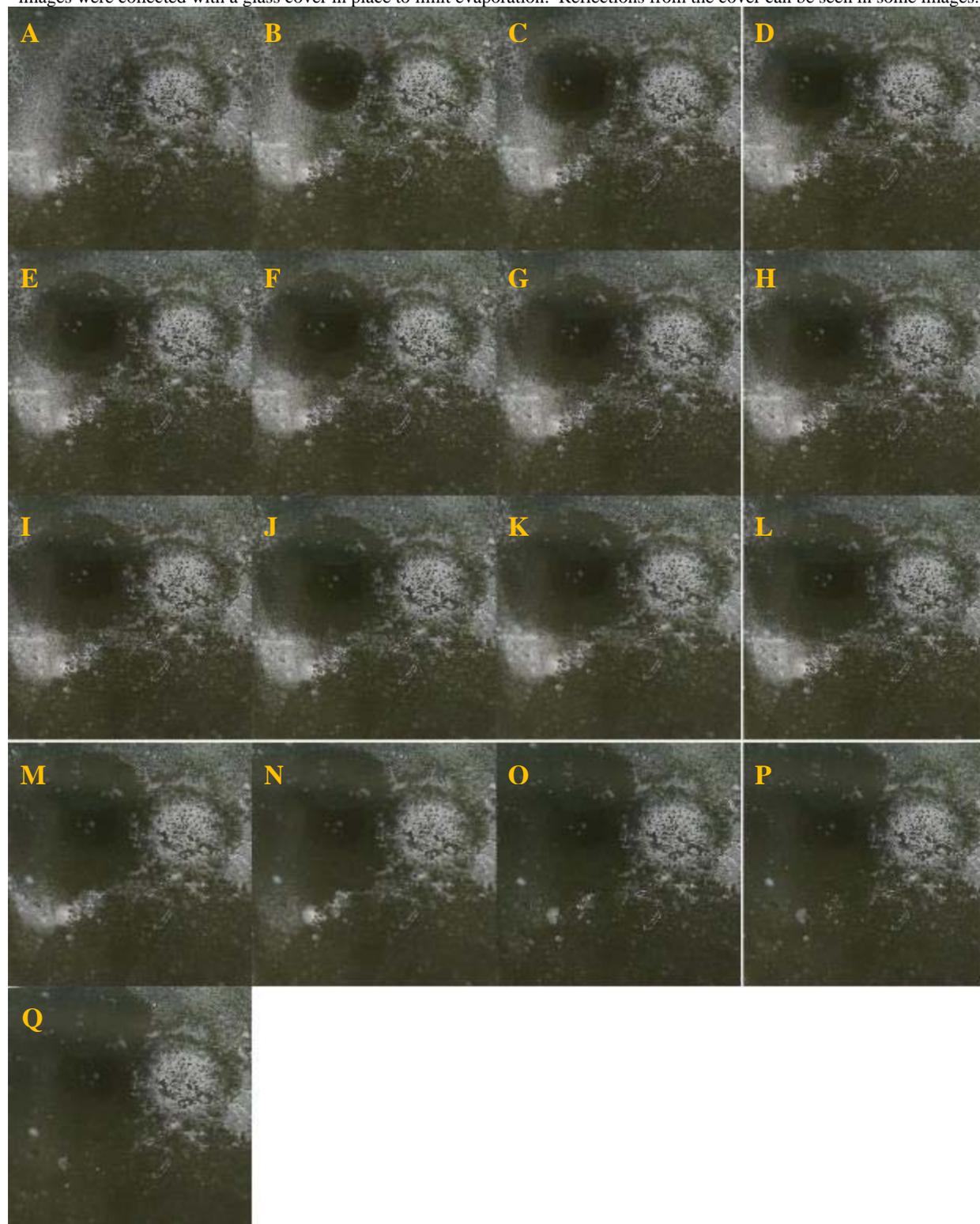


Fig. A5 — MES on the MA0702 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

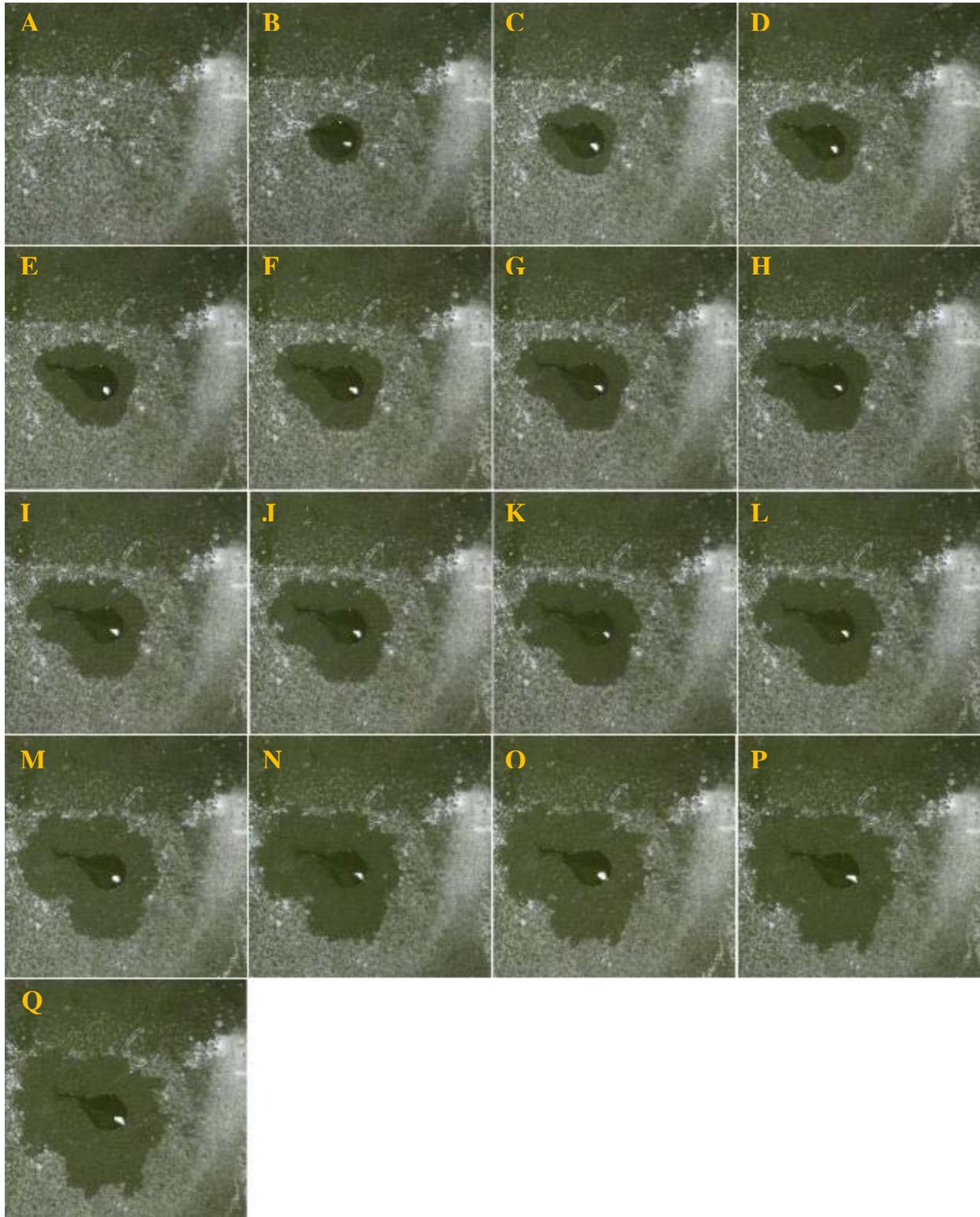


Fig. A6 — DMMP on the MA0702 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

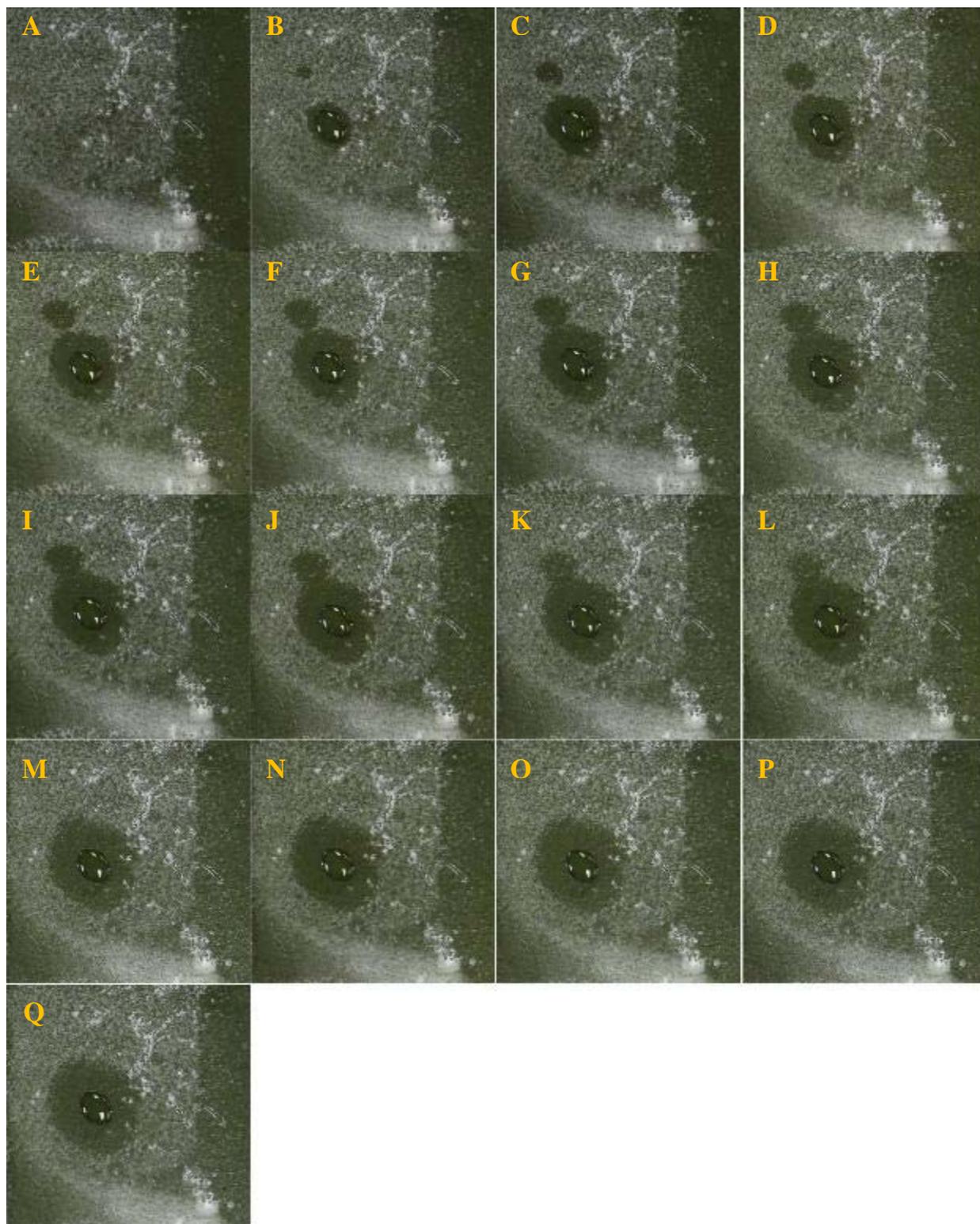


Fig. A7 — DFP on the Corin XLS coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

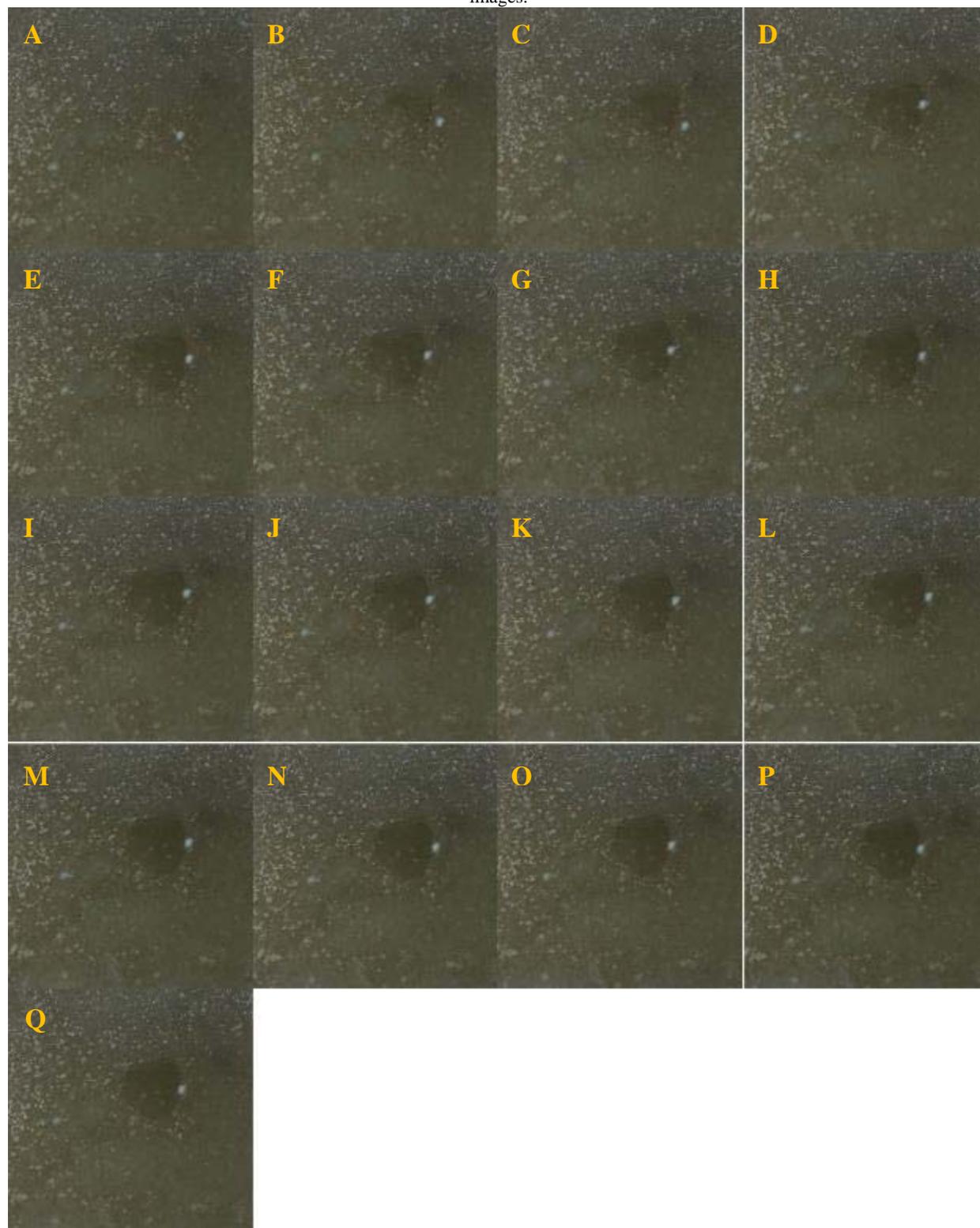


Fig. A8 — MES on the Corin XLS coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

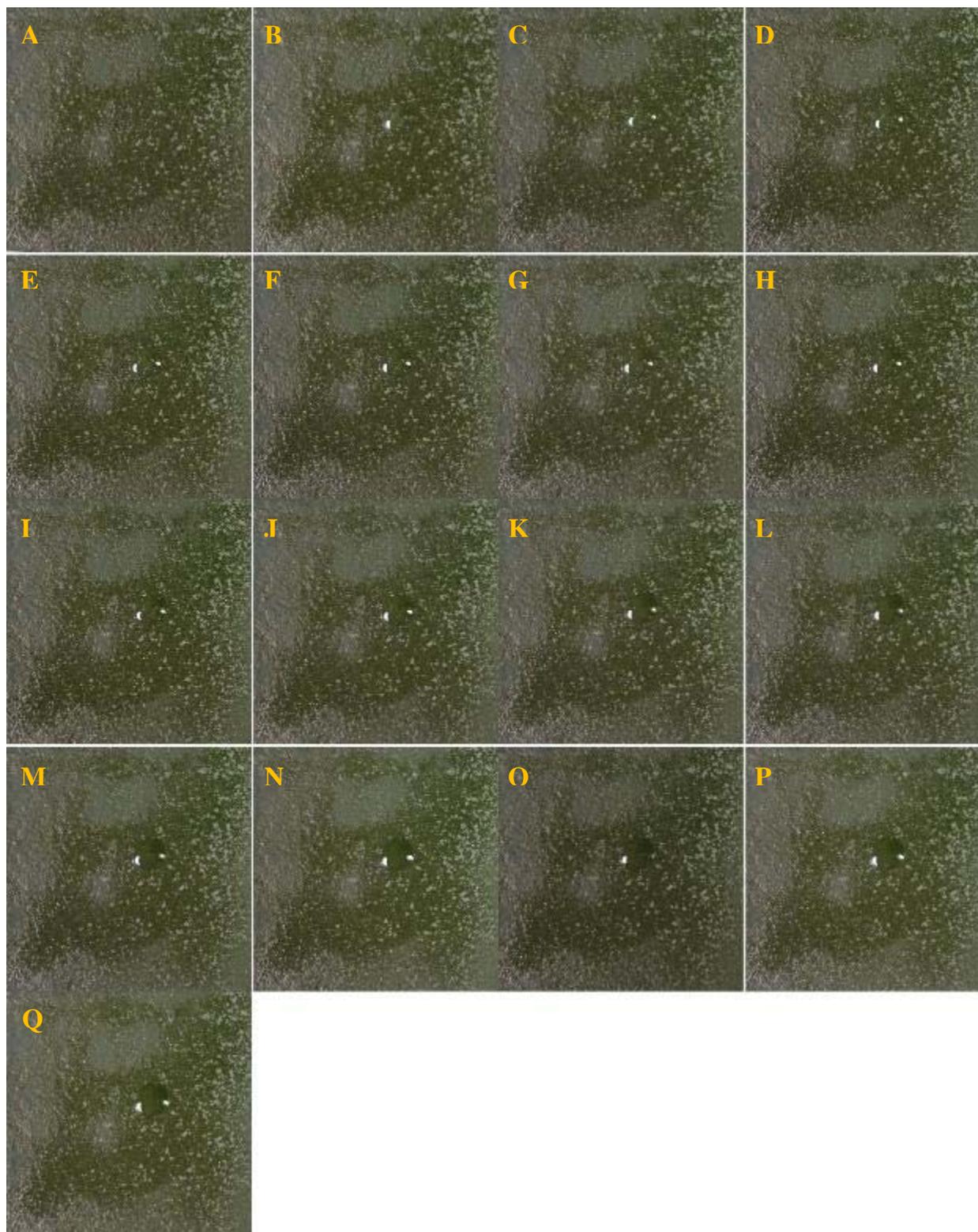


Fig. A9 — DMMP on the Corin XLS coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

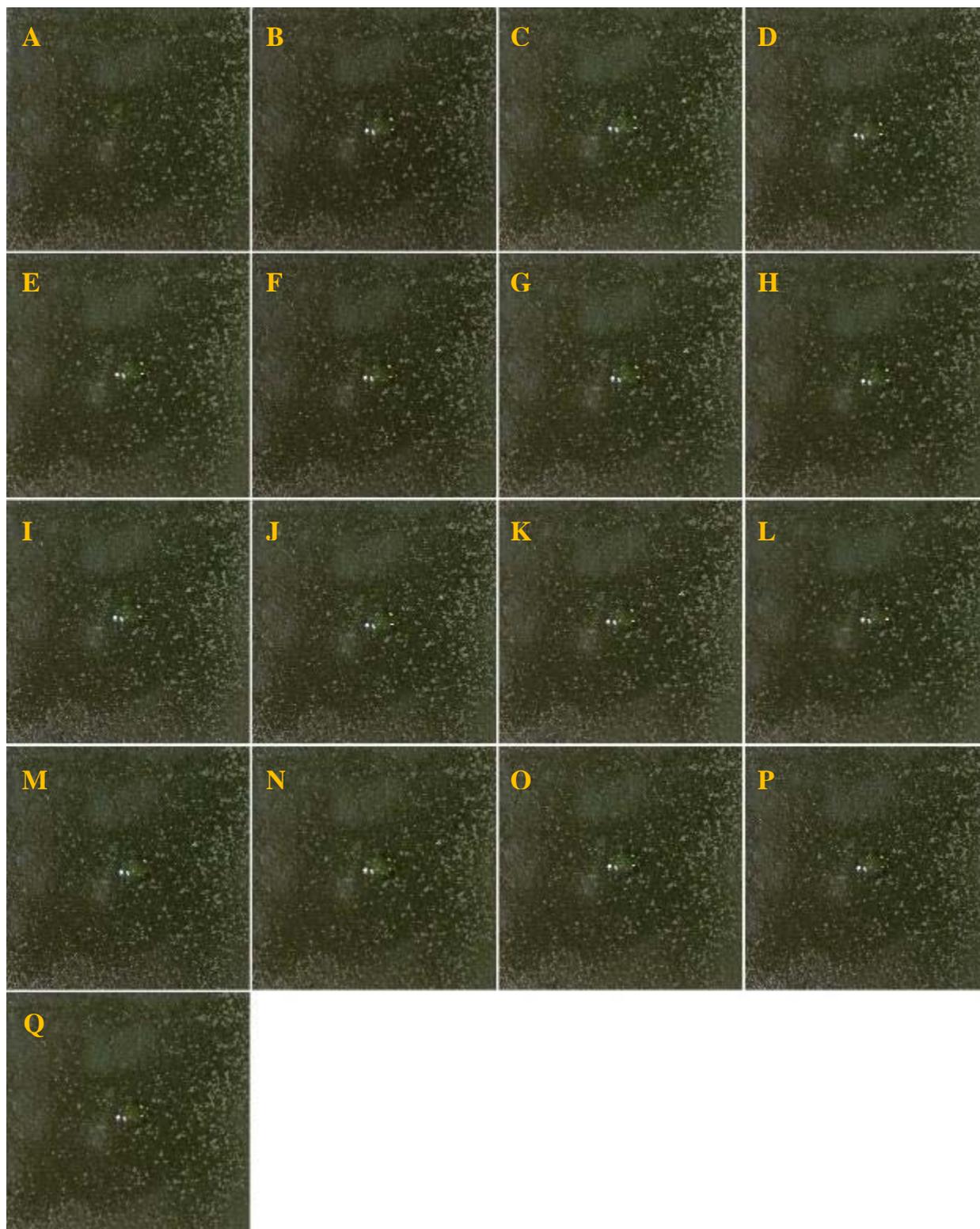


Fig. A10 — DFP on the Corin 0578 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

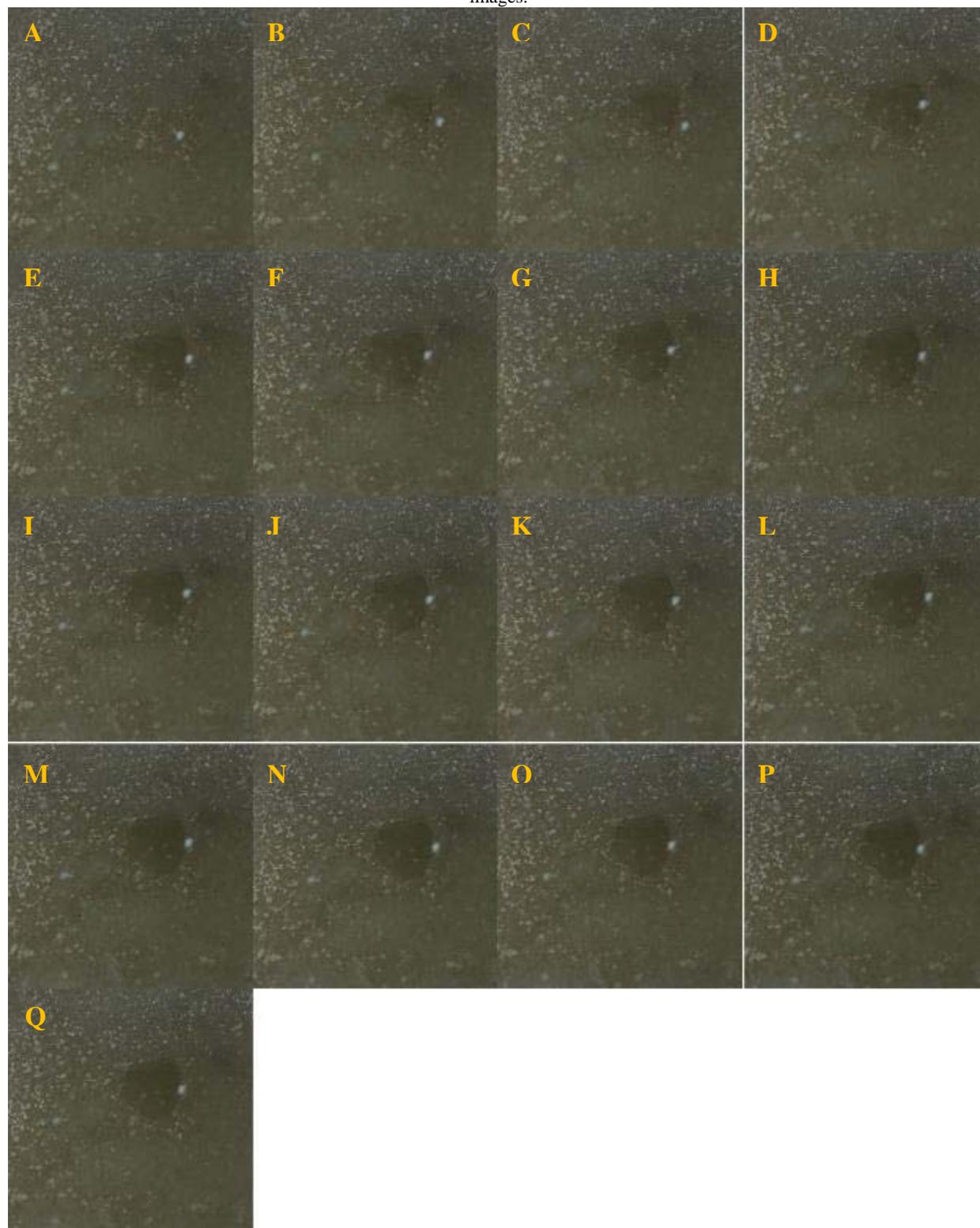


Fig. A11 — MES on the Corin 0578 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.



Fig. A12 — DMMP on the Corin 0578 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.

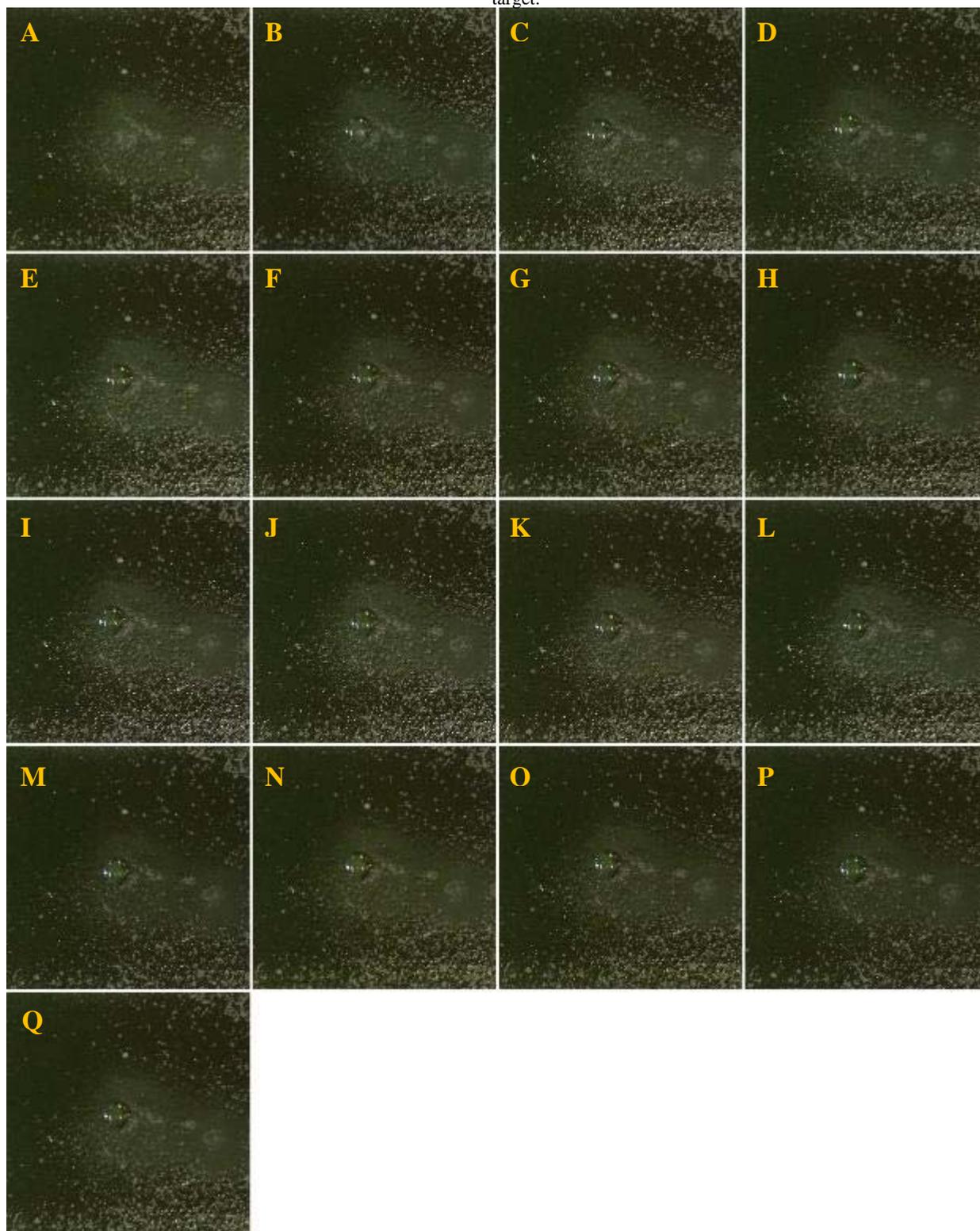


Fig. A13 — DFP on the PG1192 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.



Fig. A14 — MES on the PG1192 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.

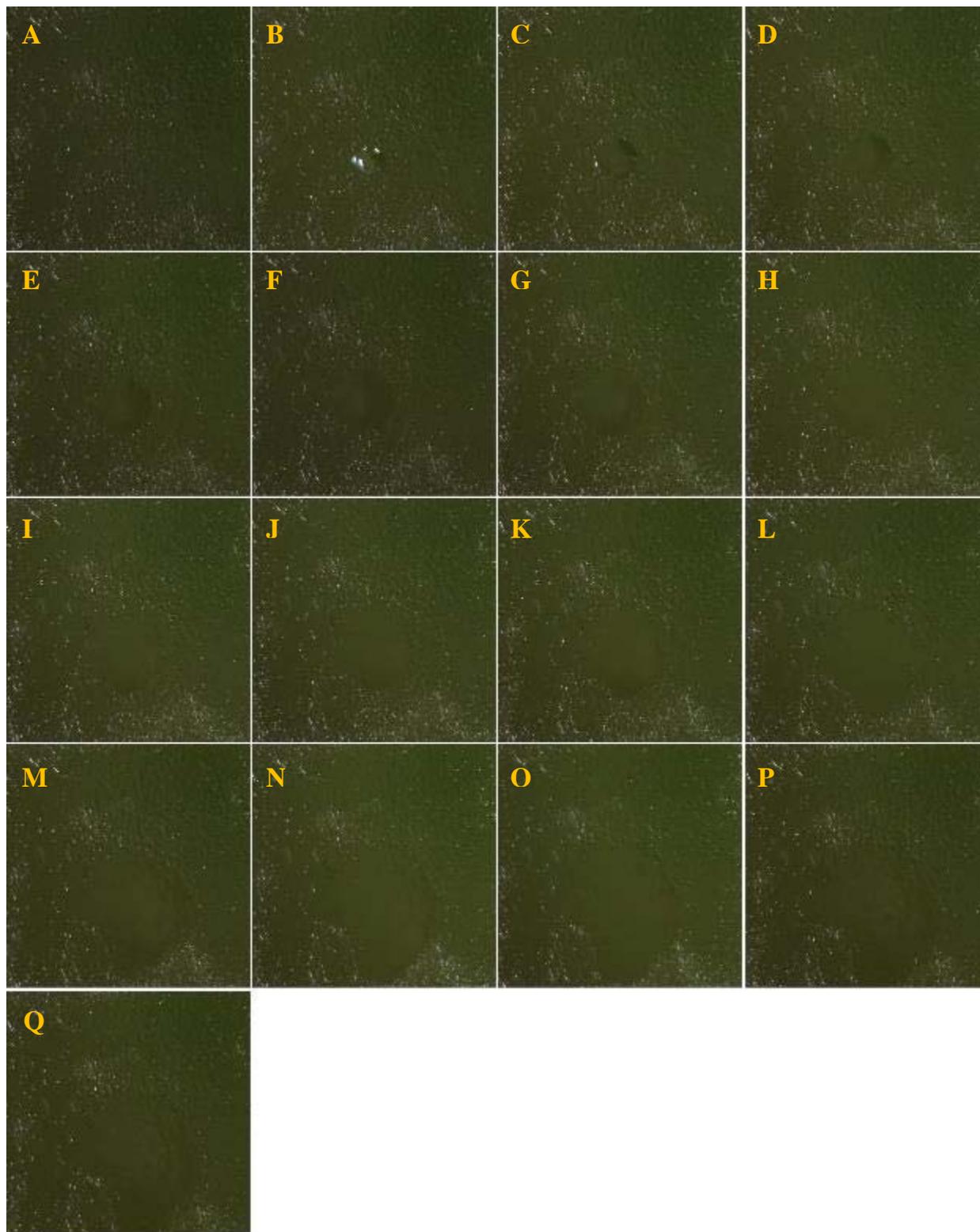


Fig. A15 — DMMP on the PG1192 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

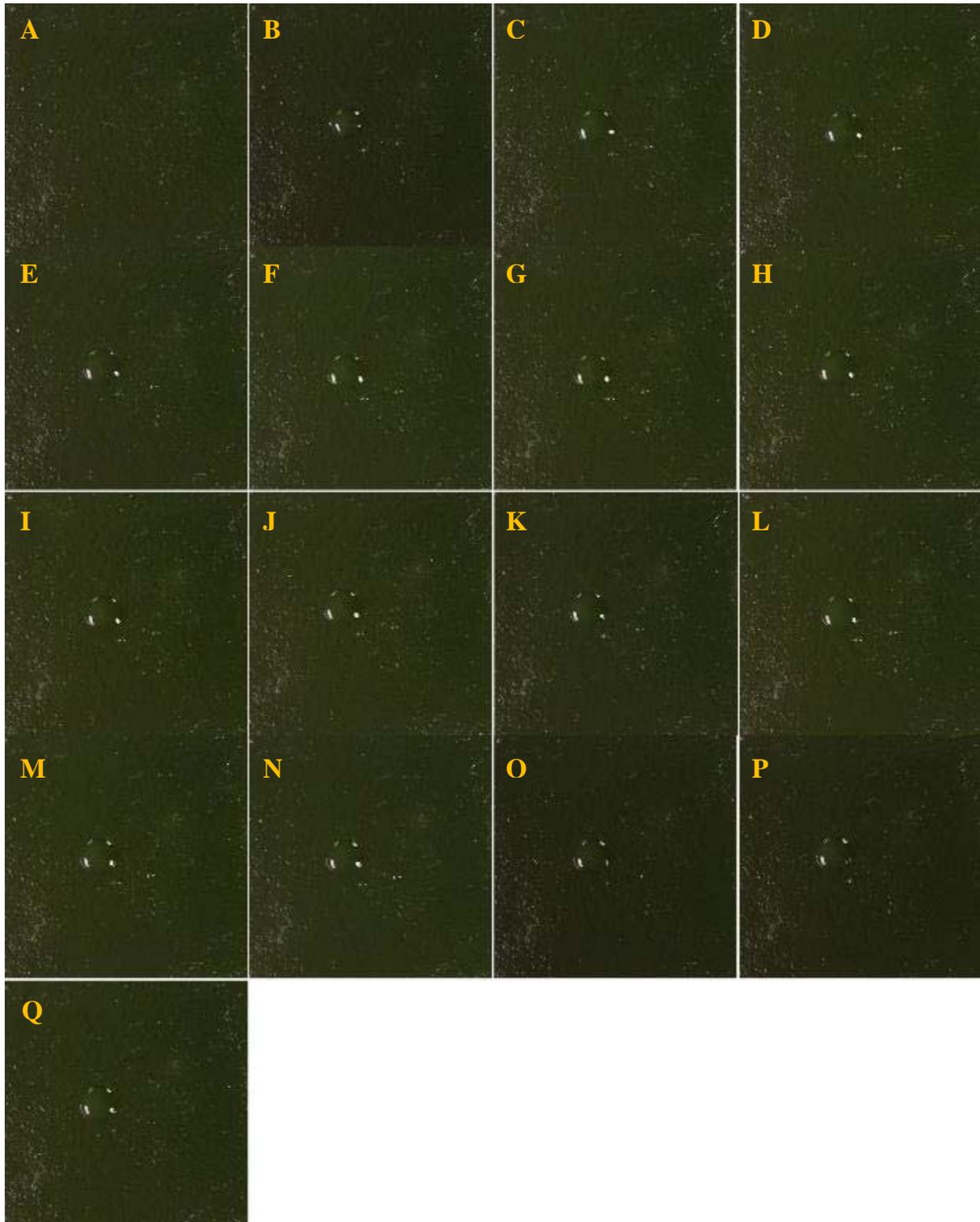


Fig. A16 — DFP on the PG1193 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

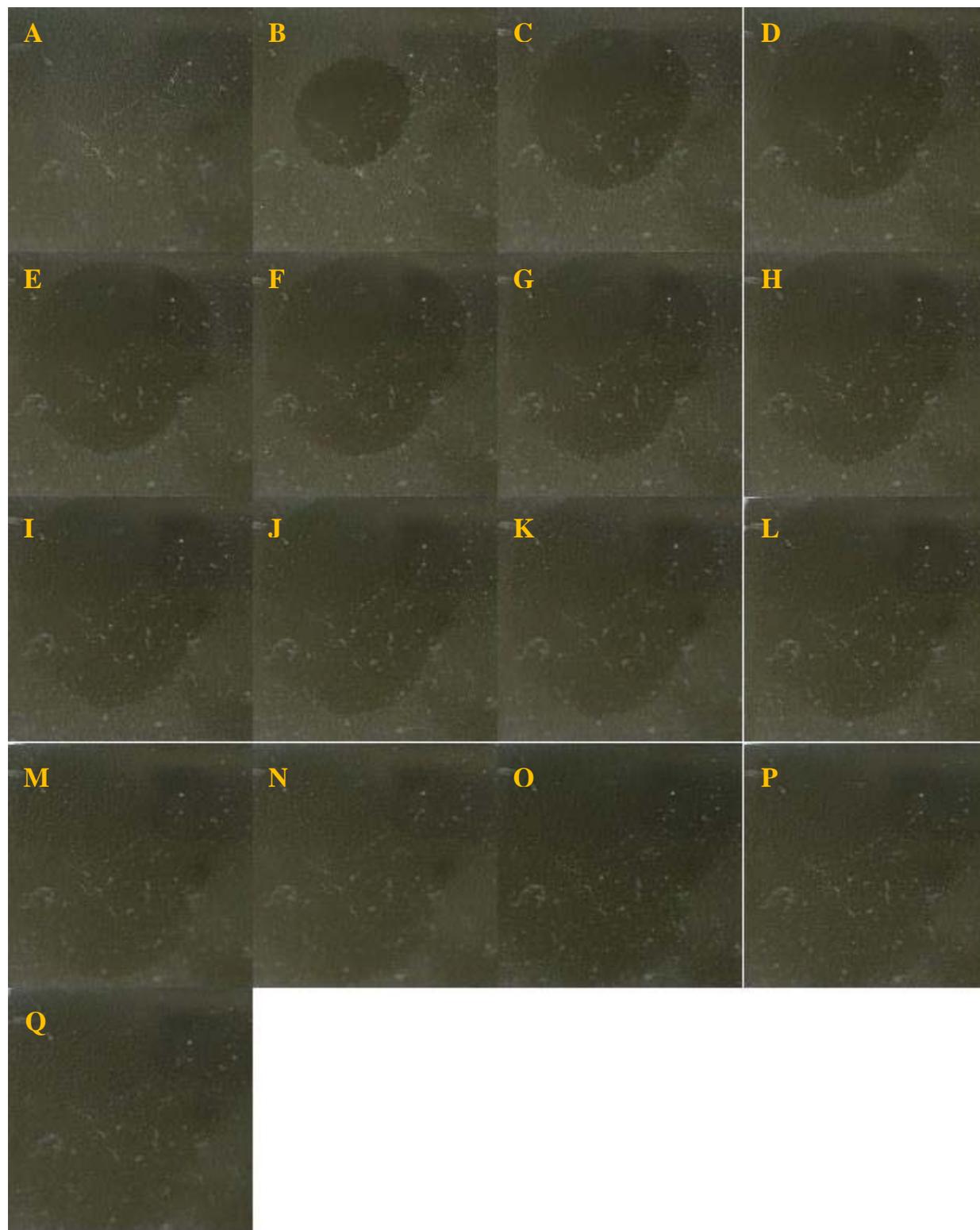


Fig. A17 — MES on the PG1193 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

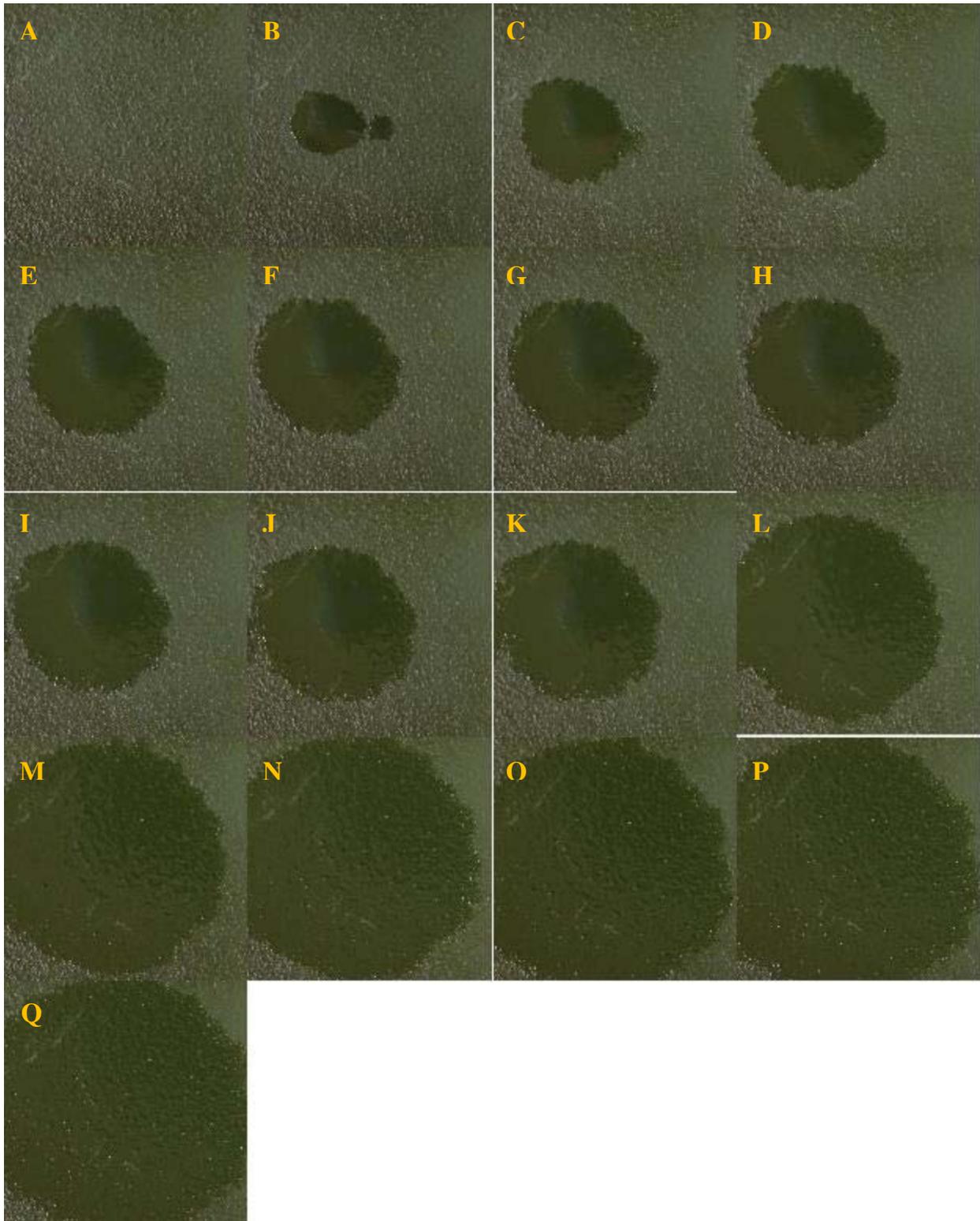


Fig. A18 — DMMP on the PG1193 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

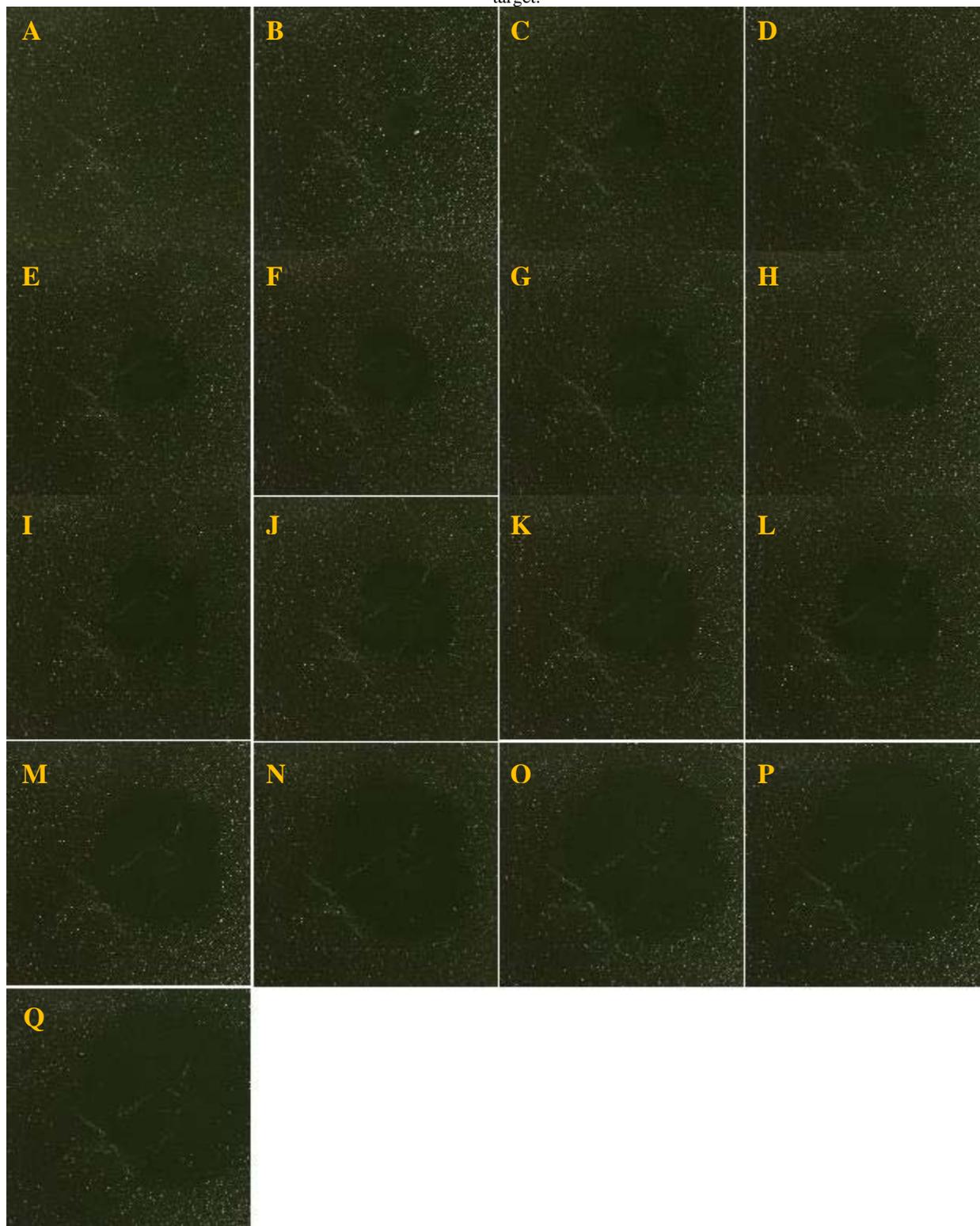


Fig. A19 — DFP on the SO1450 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.

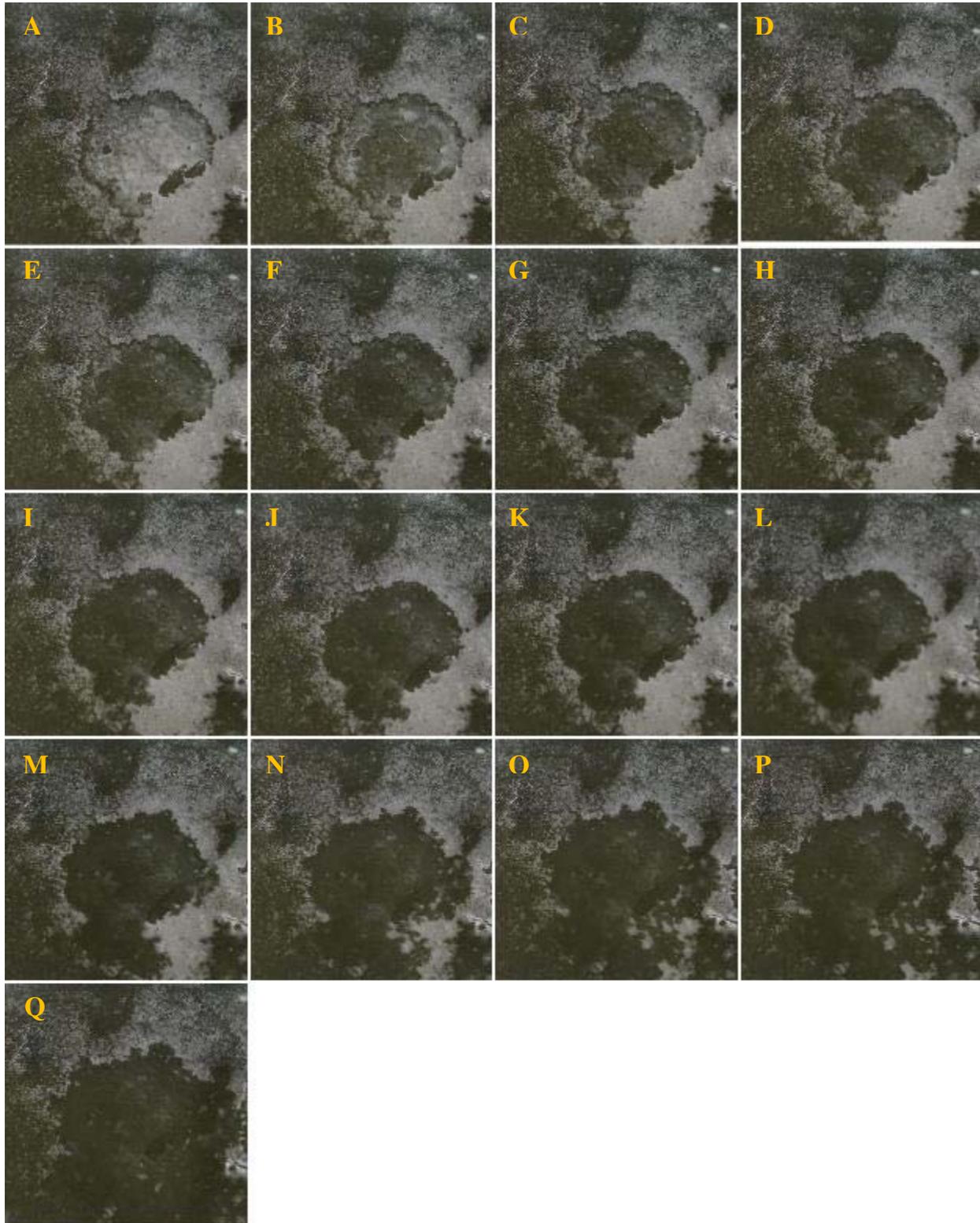


Fig. A20 — MES on the SO1450 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

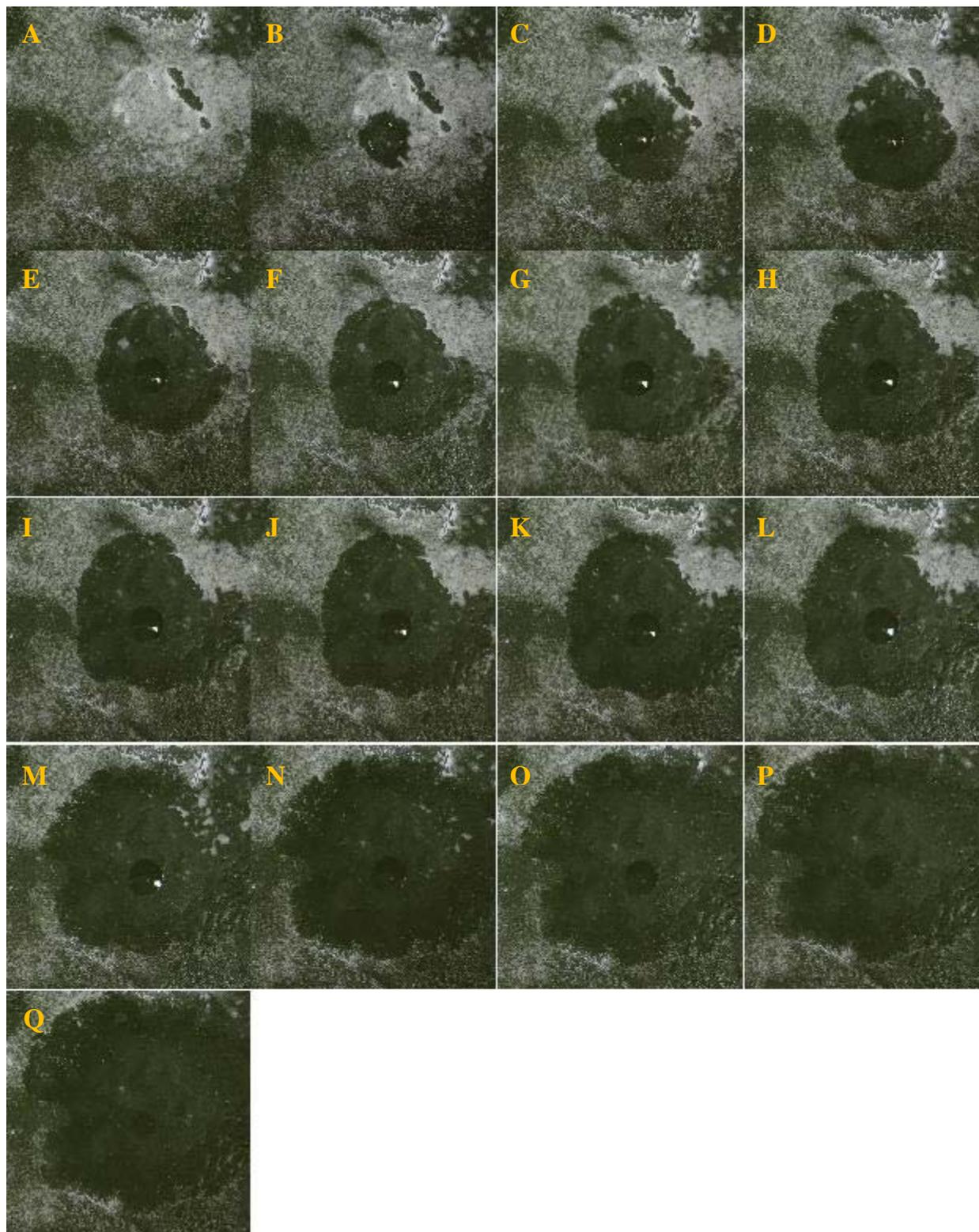


Fig. A21 — DMMP on the SO1450 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

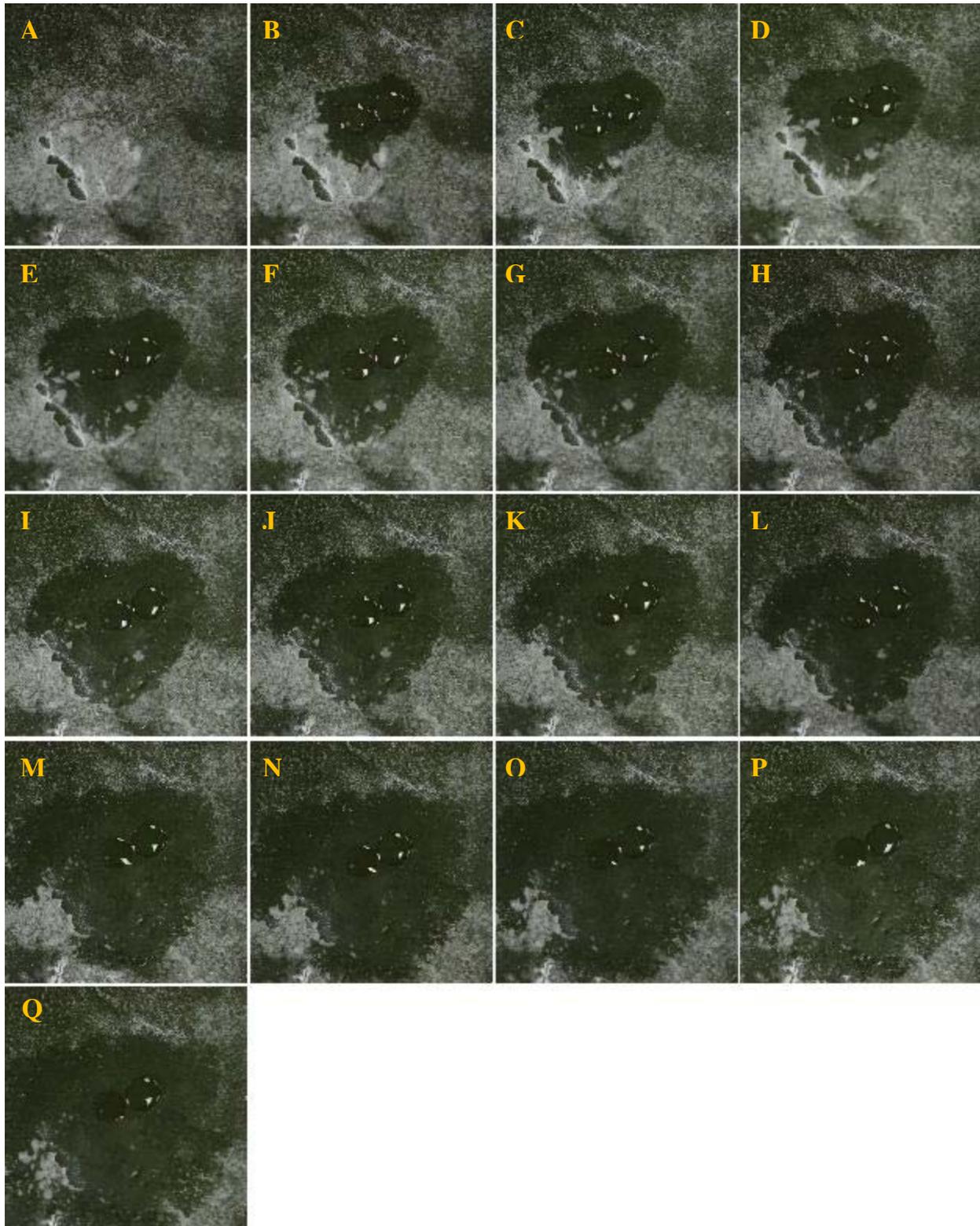


Fig. A22 — DFP on the SO1455 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target. These images were collected with a glass cover in place to limit evaporation. Reflections from the cover can be seen in some images.



Fig. A23 — MES on the SO1455 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.

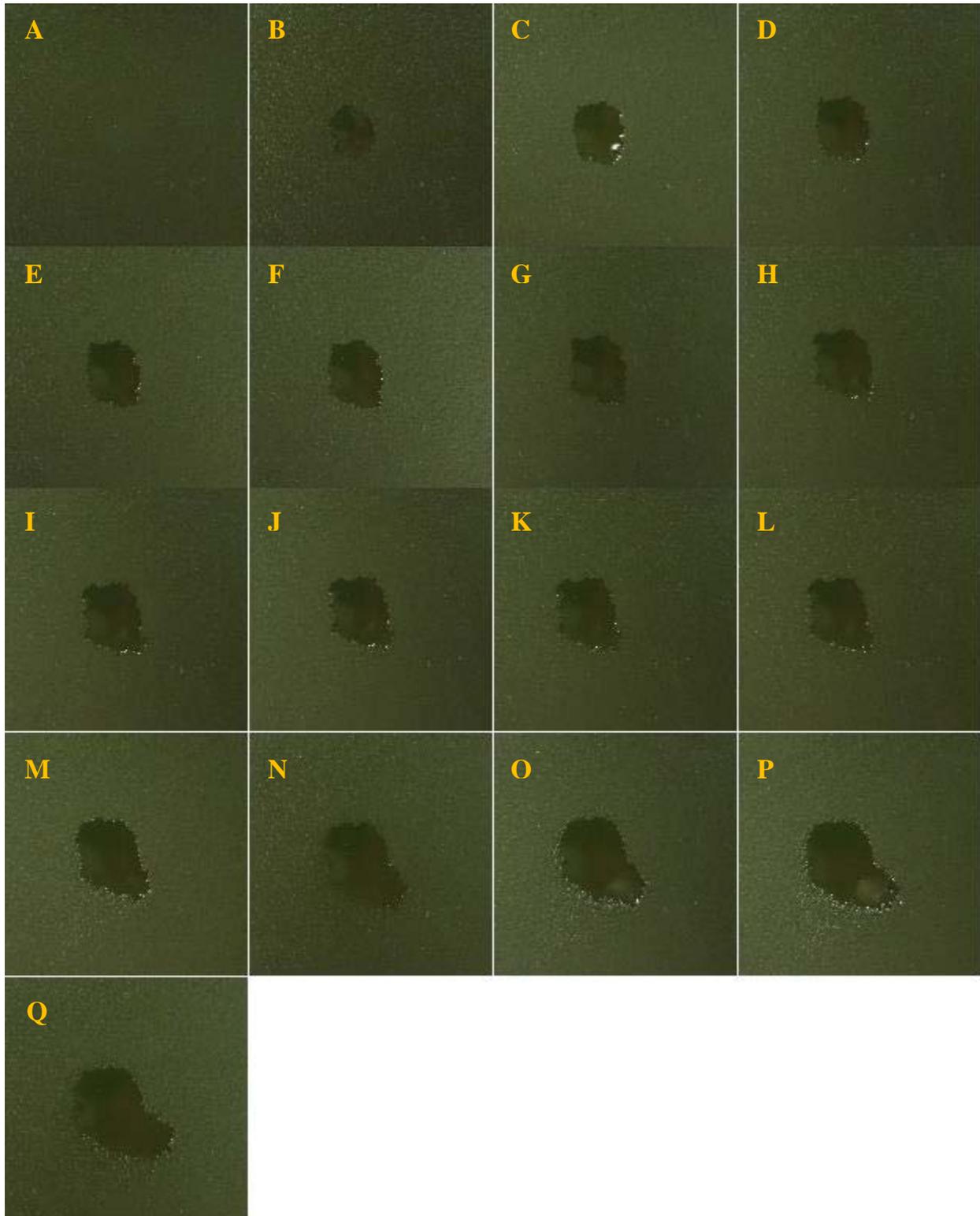


Fig. A24 — DMMP on the SO1455 coating. Images of a coupon before application (A) and at 0 (B), 0.5 (C), 1 (D), 1.5 (E), 2 (F), 2.5 (G), 3 (H), 3.5 (I), 4 (J), 4.5 (K), 5 (L), 10 (M), 15 (N), 20 (O), 25 (P), and 30 (Q) min following application of the target.

