

*ARMY RESEARCH LABORATORY*



**Mechanisms of Military Coatings Degradation: Accelerated  
and Outdoor Exposure Evaluations**

**by John A. Escarsega, William S. Lum, and Philip H. Patterson**

**ARL-TR-3085**

**September 2003**

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**Weapons and Materials Research Directorate, ARL**

## Report Documentation Page

*Form Approved*  
OMB No. 0704-0188

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<b>1. REPORT DATE (DD-MM-YYYY)</b> September 2003		<b>2. REPORT TYPE</b> Final		<b>3. DATES COVERED (From - To)</b> April 2000–December 2002	
<b>4. TITLE AND SUBTITLE</b> Mechanisms of Military Coatings Degradation: Accelerated and Outdoor Exposure Evaluations				<b>5a. CONTRACT NUMBER</b>	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> John A. Escarsega, William S. Lum, and Philip H. Patterson				<b>5d. PROJECT NUMBER</b> AH84	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> U.S. Army Research Laboratory ATTN: AMSRL-WM-MA Aberdeen Proving Ground, MD 21005-5069				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b> ARL-TR-3085	
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b>				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>	
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b>	
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> Approved for public release; distribution is unlimited.					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> The Weapons and Materials Directorate of the U.S. Army Research Laboratory (ARL) has completed a 4-year research investigation on identifying and quantifying key degradation mechanisms of legacy and newly developed coatings systems used by the U.S. Army, Marine Corps, and Air Force. This study has incorporated numerous analytical tools and methods in an effort to better understand the fundamental principles of environmental degradation that lead to coating failures. These environmentally related failures are broadly characterized in two different ways: one as minor, such as appearance changes (color loss/fade), and the other as catastrophic, such as film protection changes (substrate corrosion). This report will summarize the coatings' appearance performances when exposed to enhanced ultraviolet radiation and to outdoor static weathering. Specifically discussed are the results obtained on the coatings' change in color and specular gloss. These evaluations will serve as a performance baseline providing the knowledge required to formulate more durable military coatings. Additionally, when correlated with results obtained from other techniques, a failure analysis model can be established predicting a coating's actual field service life.					
<b>15. SUBJECT TERMS</b> coatings, weathering, color degradation, gloss					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>  UL	<b>18. NUMBER OF PAGES</b>  38	<b>19a. NAME OF RESPONSIBLE PERSON</b> John A. Escarsega
<b>a. REPORT</b> UNCLASSIFIED	<b>b. ABSTRACT</b> UNCLASSIFIED	<b>c. THIS PAGE</b> UNCLASSIFIED			<b>19b. TELEPHONE NUMBER (Include area code)</b> 410-306-0693

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

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## Contents

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<b>List of Figures</b>	<b>iv</b>
<b>List of Tables</b>	<b>iv</b>
<b>Acknowledgments</b>	<b>v</b>
<b>1. Introduction</b>	<b>1</b>
<b>2. Experimental</b>	<b>2</b>
<b>3. Conditions and Evaluations</b>	<b>3</b>
<b>4. Results and Discussions: Appearance Characterization</b>	<b>4</b>
<b>5. Conclusions and Observations</b>	<b>9</b>
<b>6. References</b>	<b>14</b>
<b>Distribution List</b>	<b>16</b>

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## List of Figures

---

Figure 1. A typical camouflage coating system.....	1
Figure 2. QUV exposure data: color change of coating systems.....	7
Figure 3. Florida exposure data: color change of coating systems.....	8
Figure 4. Arizona exposure data: color change of coating systems.....	8
Figure 5. Gloss values after 27 weeks of QUV exposure.....	11
Figure 6. Gloss values after 97 weeks of Arizona exposure.....	11
Figure 7. Gloss values after 97 weeks of Florida exposure.....	12
Figure 8. Photographs displaying coating systems after 48 weeks of UV exposure.....	12

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## List of Tables

---

Table 1. QUV exposure data: NBS color change from initial color.....	5
Table 2. Florida exposure data: color change (Delta E) from initial color.....	6
Table 3. Arizona exposure data: color change (Delta E) from initial color.....	6
Table 4. Summary QUV exposure data (averaged): color change from initial color.....	6
Table 5. Summary of Florida exposure data (averaged): color change from initial color.....	7
Table 6. Summary of Arizona exposure data (averaged): color change from initial color.....	7
Table 7. Summary of gloss values for QUV after 27 weeks, radiant energy UV: 671.13 MJ/m <sup>2</sup> .....	10
Table 8. Summary of gloss values for Arizona after 97 weeks, radiant energy UV: 603.52 MJ/m <sup>2</sup> .....	10
Table 9. Summary of gloss values for Florida after 97 weeks, radiant energy UV: 501.37 MJ/m <sup>2</sup> .....	10

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## **Acknowledgments**

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This coating research was supported in part by the U.S. Department of Defense through the Strategic Environmental Research and Development Program under the task area of pollution prevention (PP-1133). The authors gratefully acknowledge the principal investigator, Ms. Wendy Kosik of the U.S. Army Research Laboratory, for her efforts in coordinating and managing the many facets of the program.

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# 1. Introduction

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The U.S. Army, Marine Corps, and Air Force use polyurethane coatings as camouflage “topcoats” and epoxy coatings as “primers” on all tactical vehicles and aircraft. Pretreatments for the substrates vary depending upon the composition of the vehicle or aircraft and whether it is a refurbished item or a piece of original equipment from the manufacturer (OEM). In either case, it is typically a chromated wash primer for refurbished equipment and an alodine-based conversion coating for aluminum (Al) or zinc phosphate based material for ferrous substrates for OEMs. This “coating system” not only serves to provide camouflage for vehicles and aircraft but also provides protection against chemical warfare agents for the U.S. Army and Marine Corps with their chemical agent resistant coatings (CARCs). A visual schematic of the system is shown in figure 1. The coatings must retain their physical properties over a broad temperature range in widely varying climatic environments. The coating system is the first line of defense in preventing corrosion, thereby extending the life cycle of a military vehicle or aircraft. In an effort to specifically minimize overall vehicle corrosion and reduce costly refurbishment and maintenance expenditures, an ongoing tri-service research effort has been established to examine the mechanism and relationships involving the coatings’ degradation. Four polyurethane topcoat and epoxy primer coating systems representing the U.S. Army, Marine Corps, and Air Force were selected. Standard specification, as well as newly developed, “greener” materials, were evaluated. This report will present data on gloss, color, and general appearance changes occurring in samples exposed in Arizona and Florida, as well as in an accelerated ultraviolet light (QUV)\* chamber. The weathering effects on topcoat degradation and “coating system” interaction will be discussed.

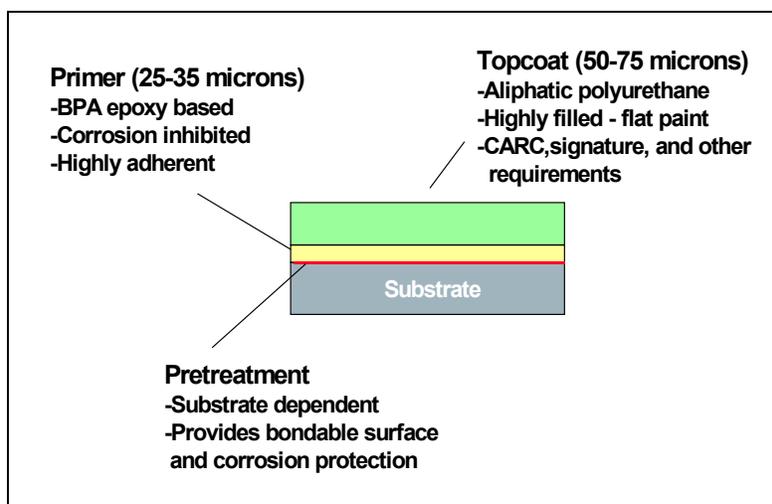


Figure 1. A typical camouflage coating system.

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\* QUV is a registered trademark of the Q-Panel Company.

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## 2. Experimental

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The coatings were sprayed onto two different metal substrates, cold-rolled steel (SAE 1008) panels pretreated with zinc phosphate (Bondrite 37<sup>\*</sup>) and a chromate sealer (Parcoolene 60<sup>†</sup>) conforming to TT-C-490 (1) and 2024 T3 Al alloy panels pretreated with a chemical conversion (Iridite 14-2<sup>‡</sup>) conforming to MIL-C-5541 (2). Free films were also prepared with only the topcoats sprayed onto a low surface tension Tedlar polyvinyl fluoride (DuPont Inc., Buffalo, NY) release film. Additionally, a primer and topcoat system were also prepared onto a stainless steel mesh substrate for additional thermal analysis conducted by the Marine Corps. Only color data from the QUV exposures were obtained for these samples, due to their irregular surface. The panels and free films were sprayed to a dry film thickness of 50–65  $\mu\text{m}$  for the topcoats and 25–37  $\mu\text{m}$  for the epoxy primers (applied to the metal panels only). Film thickness for the stainless steel mesh required additional primer and topcoat to adequately eliminate any surface defects and resulted in a total film thickness of 155  $\mu\text{m}$ . The topcoat formulations reported in this paper were pigmented to conform with U.S. Army color number 34094 (Green 383) as stated in MIL-C-46168 (3), the military's specification for two-component, chemical agent resistant, polyurethane coatings, and Air Force color number 36375 (Medium Gray) as referenced in MIL-PRF-85285 (4), the military's specification for high-solids polyurethane coatings.

The water-dispersible formulations are identified as Systems "B" and "D." The solvent-based formulations are designated as "A" and "C." The Army's water-dispersible topcoat (Part of System "B") is formulated with water-dispersible hydroxy-functional polyurethane and a water-dispersible polyisocyanate. The coating's pigment package includes prime pigments used to make the Army's camouflage color number 34094 (Green 383), as well as polymeric-type extenders for flattening purposes. While the water-dispersible topcoat of System "D" uses no polymeric flattening agents and is pigmented to Air Force color number 36375 (Medium Gray). The solvent based topcoats also use nonpolymeric flattening agents and incorporate their respective prime pigments for the Army color number 34094 (Green 383), System "A," and the Air Force color number 36375 (Medium Gray), System "C."

Summary of Coating Systems:

- **A = MIL-C-46168, Army Control System**  
Top Coat: MIL-C-46168 TYPE IV solvent-based polyurethane (siliceous extender)

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\* Bondrite 37 is a registered trademark of ACT Laboratories, Inc.

† Parcoolene 60 is a registered trademark of ACT Laboratories, Inc.

‡ Iridite 14-2 is registered trademark of the Q-Panel Company.

Primer: MIL-P-53022 (5) solvent-based epoxy  
Surface Treatment: TT-C-490 zinc phosphate on a steel substrate

- **B = MIL-DTL-64159-TYPE II, Zero Hazardous Air Pollutants With Polymeric Flattening Agents (6, 7)**

Top Coat: Water Dispersible CARC polyurethane (polymeric bead extenders)  
Primer: MIL-P-53030 (8) water-based epoxy  
Surface Treatment: TT-C-490 zinc phosphate on a steel substrate

- **C = MIL-PRF-85285, Navy Control System**

Top Coat: MIL-PRF-85285 solvent-based polyurethane  
Primer: MIL-PRF-23377 (9) solvent-based epoxy  
Surface Treatment: MIL-C-5541 chemical conversion on Al substrate

- **D = MIL-PRF-85285 TYPE III (Zero VOC Top Coat)**

Top Coat: Zero VOC top coat water-based polyurethane  
Primer: MIL-PRF-85582 (10) water-based epoxy  
Surface Treatment: MIL-C-5541 chemical conversion on an Al substrate

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### 3. Conditions and Evaluations

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Three types of exposures were conducted, two at separate outdoor weathering locations (Florida and Arizona) and one in an accelerated UV weathering (QUV) chamber. The test procedures established for the Arizona and South Florida exposures conform to American Society for Testing and Materials (ASTM) G-7 (11) and ASTM G-147 (12). The exposure testing was performed in Miami, FL (26° N) and New River, Arizona (34° N) in accordance with the ASTM Governing Standards at a tilt angle of 5° from the horizontal facing south. The exposure intervals ranged from 7 to 97 weeks. The accelerated UV testing was conducted using a weathering chamber operated under the requirements established by ASTM G-53 (13). Cycling involved total UV light exposure with no condensation or water spray. A series of UVA 340 lamps were used as the light source set to emit a spectral irradiance of 0.77 W/m<sup>2</sup>. An automatic sensor controller kept this irradiance level measured at 340 nm, stable throughout the testing and was calibrated after every 400 hr of lamp operation. An exposure temperature of 60 °C was maintained inside the weathering chambers. The study was conducted following an elapsed time schedule, with the samples exposed to continuous UV over the intervals of 3–48 weeks. With each timed interval, the solar UV energy dosage was recorded as well.

After each exposure interval, the samples were rinsed with deionized water and allowed to dry before color and gloss measurements were made. During the performance testing, all specimens were carefully handled to avoid marring, and the operators wore lint-free gloves in order to keep coating surfaces clean.

For the outdoor exposures, color measurements were performed on a Hunterlab Ultrascan Colorimeter with a 6-in integrating sphere. Color measurements for the QUV exposures were made using a Data Color Chroma Sensor Spectrophotometer equipped with an 8-in integrating sphere. In both cases, the spheres were set up to include the specular component of the sample's reflectance. All of the color readings were made in accordance to ASTM D-2244 (14) using a 2° observer under illuminant C.

Gloss measurements were made in accordance with ASTM D-523 (15) using a BYK Gardner GB4606 Haze-Gloss Reflectometer. The measurements were taken at 60 and 85°. The instrument was calibrated using the manufacturer's reflectometer standard gloss tile. A BYK-Gardner Micro-Tri-Gloss portable glossmeter was used for the outdoor exposures.

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#### **4. Results and Discussions: Appearance Characterization**

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The results from all of color measurements made on the samples' QUV, Florida, and Arizona exposures are provided in tables 1–3, respectively. Tables 4–6 are averaged measurements provided to simplify the data. Additionally, the averaged data are shown in figures 2–4. It should be noted that listed in the last eight columns of table 1 are color data obtained from specifically prepared samples. These coatings were prepared as either free films (T designation) or having a screen mesh (B designation) as its substrate.

From reviewing table 4, it is apparent that of the four coating systems evaluated, System “A,” using the MIL-C-46168 solvent-based polyurethane topcoat, shows the most pronounced signs of appearance degradation due to accelerated UV exposure. Severe color fade/degradation (3.23 color-difference units) occurs after just 6 weeks/149.1 MJ/m<sup>2</sup> (UV dosage) of exposure. The change is primarily due to an increase in the brightness of the coating's color. It is interesting to note that this degradation trend continues throughout the remaining exposure intervals. Conversely, the UV color stability is best for the topcoats used in the water-based systems (“B” and “D”). This weathering characteristic is almost certainly related to the coatings' extender pigment content for the topcoats (16). A comparison of the pigment to binder (resin) ratio is greatest for the System “A” topcoat (2:1 pigment/binder ratio), and the least is System “B” with “C” and “D” falling in between.

The test results from Florida and Arizona outdoor weathering provide insight to the effects of humidity and moisture on the exposed coatings. Because the Arizona environment has very little humidity or moisture (i.e., rain), degradation effects are primarily the result of UV radiation. However, the Florida environment has a significant amount of humidity and moisture in conjunction with UV radiation that often accelerates the degradation of organic coatings.

As table 5 shows, the System “B” topcoat, MIL-PRF-64159 (17), water dispersible polyurethane, exhibited the smallest change in color of all the coatings exposed in South Florida. This

Table 1. QUV exposure data: NBS color change from initial color.

Exposure Time, Radiant UV Energy	Sample Code																			
	AA	BA	CA	DA	AN	BN	CN	DN	AM	BM	CM	DM	AMT	AMB	BMT	BMB	CMT	CMB	DMT	DMB
3 weeks, 74.57 MJ/m <sup>2</sup>	0.45	0.44	0.33	0.46	0.57	0.67	0.27	0.45	0.38	0.55	0.32	0.39	0.34	0.70	0.62	0.72	0.31	0.46	0.40	0.34
6 weeks, 149.14 MJ/m <sup>2</sup>	3.50	0.54	0.26	0.56	3.40	0.53	0.28	0.54	2.8	0.63	0.4	0.47	3.30	2.50	0.74	0.76	0.37	1.80	0.35	0.32
12 weeks, 298.28 MJ/m <sup>2</sup>	5.30	0.67	0.28	0.69	6.30	0.72	0.47	0.71	5.9	0.87	1.40	0.65	7.90	7.70	0.8	0.98	1.70	6.40	0.41	0.44
18 weeks, 447.42 MJ/m <sup>2</sup>	8.60	0.82	0.26	0.78	7.75	0.98	1.38	0.77	7.85	0.89	2.09	0.75	8.59	8.49	0.86	0.91	8.20	3.02	0.52	0.51
27 weeks, 671.13 MJ/m <sup>2</sup>	10.37	0.82	No data	No data	10.68	0.93	3.36	1.01	11.35	0.95	No data	No data	—	—	—	—	—	—	—	—
36 weeks, 894.84 MJ/m <sup>2</sup>	12.10	0.93	No data	No data	12.59	1.16	4.96	1.01	12.00	1.03	No data	No data	—	—	—	—	—	—	—	—
48 weeks, 1193.12 MJ/m <sup>2</sup>	12.86	1.04	5.47	0.74	13.30	1.34	5.99	1.15	13.35	1.30	6.13	0.68	—	—	—	—	—	—	—	—

Notes: sample code key:

First letter: A = Coating System “A,” B = Coating System “B,” C = Coating System “C,” and D = Coating System “D.”

Second letter: A = Test Sample 1, N = Test Sample 2, and M = Test Sample 3.

Third letter: T = samples tested as a free film, and B = sample films applied and tested on grid substrate.

Table 2. Florida exposure data: color change (Delta E) from initial color.

Exposure Time, Radiant UV Energy	Sample Code											
	AA	BA	CA	DA	AN	BN	CN	DN	AM	BM	CM	DM
7 weeks, 75.03 MJ/m <sup>2</sup>	0.11	0.90	0.39	0.96	0.13	0.95	0.35	0.99	0.20	0.78	0.39	0.86
13 weeks, 91.15 MJ/m <sup>2</sup>	0.54	1.12	0.34	1.31	0.42	1.1	0.44	1.32	0.42	1.15	0.18	1.28
25 weeks, 151.41 MJ/m <sup>2</sup>	2.60	1.12	0.59	1.34	2.31	1.22	0.42	1.43	2.73	1.26	0.42	1.34
49 weeks, 270.65 MJ/m <sup>2</sup>	4.90	1.32	0.79	3.33	4.67	1.32	0.87	2.73	5.14	1.22	0.92	3.91
97 weeks, 501.37 MJ/m <sup>2</sup>	7.70	1.53	2.74	2.70	7.31	1.57	2.61	3.25	7.26	1.59	2.52	2.83

Table 3. Arizona exposure data: color change (Delta E) from initial color.

Exposure Time, Radiant UV Energy	Sample Code											
	AA	BA	CA	DA	AN	BN	CN	DN	AM	BM	CM	DM
7 weeks, 65.29 MJ/m <sup>2</sup>	0.33	0.59	0.14	0.23	0.51	0.76	0.165	0.21	0.65	0.71	0.16	0.21
13 weeks, 120.08 MJ/m <sup>2</sup>	0.59	0.81	0.27	0.61	0.54	0.91	0.18	0.64	0.55	0.91	0.28	0.63
25 weeks, 203.40 MJ/m <sup>2</sup>	3.02	1.23	0.46	0.95	3.46	1.24	0.52	0.95	3.29	1.30	0.48	0.87
49 weeks, 305.37 MJ/m <sup>2</sup>	4.89	1.28	1.75	0.40	4.60	1.27	1.28	0.51	4.81	1.33	1.65	0.48
97 weeks, 603.52 MJ/m <sup>2</sup>	9.03	1.30	4.12	1.98	9.39	1.30	3.80	1.45	9.31	1.32	3.59	1.75

Table 4. Summary QUV exposure data (averaged): color change from initial color.

Exposure Time, Radiant UV Energy	Coating System			
	A	B	C	D
3 weeks, 74.57 MJ/m <sup>2</sup>	0.47	0.55	0.31	0.43
6 weeks, 149.14 MJ/m <sup>2</sup>	3.23	0.57	0.31	0.52
12 weeks, 298.28 MJ/m <sup>2</sup>	5.83	0.75	0.72	0.68
18 weeks, 447.42 MJ/m <sup>2</sup>	8.07	0.90	1.24	0.77
27 weeks, 671.13 MJ/m <sup>2</sup>	10.80	0.90	3.36	1.01
36 weeks, 894.84 MJ/m <sup>2</sup>	12.23	1.04	4.96	1.01
48 weeks, 1193.12 MJ/m <sup>2</sup>	13.17	1.23	5.86	0.86

Table 5. Summary of Florida exposure data (averaged): color change from initial color.

Exposure Time, Radiant UV Energy	Coating System			
	A	B	C	D
7 weeks, 75.03 MJ/m <sup>2</sup>	0.15	0.88	0.38	0.94
13 weeks, 91.15 MJ/m <sup>2</sup>	0.46	1.12	0.32	1.30
25 weeks, 151.41 MJ/m <sup>2</sup>	2.55	1.2	0.48	1.37
49 weeks, 270.65 MJ/m <sup>2</sup>	4.92	1.29	0.86	3.32
97 weeks, 501.37 MJ/m <sup>2</sup>	7.42	1.56	2.62	2.93

Table 6. Summary of Arizona exposure data (averaged): color change from initial color.

Exposure Time, Radiant UV Energy	Coating System			
	A	B	C	D
7 weeks, 65.29 MJ/m <sup>2</sup>	0.50	0.69	0.16	0.22
13 weeks, 120.08 MJ/m <sup>2</sup>	0.56	0.88	0.24	0.63
25 weeks, 203.4 MJ/m <sup>2</sup>	3.26	1.26	0.49	0.92
49 weeks, 305.37 MJ/m <sup>2</sup>	4.77	1.29	1.56	0.46
97 weeks, 603.52 MJ/m <sup>2</sup>	9.24	1.31	3.84	1.73

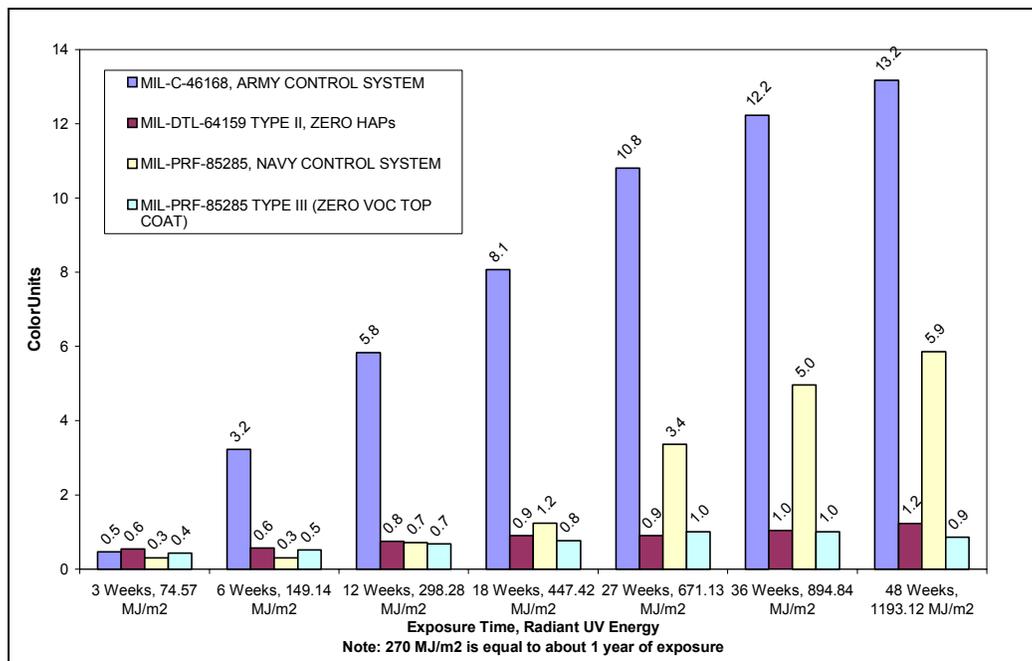


Figure 2. QUV exposure data: color change of coating systems.

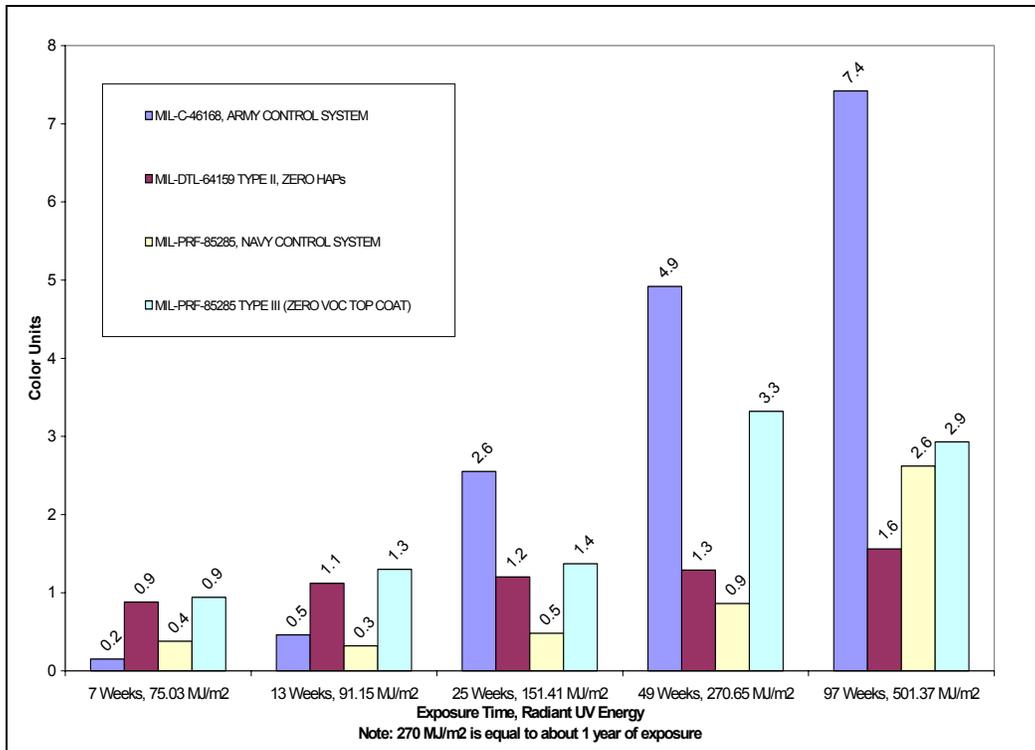


Figure 3. Florida exposure data: color change of coating systems.

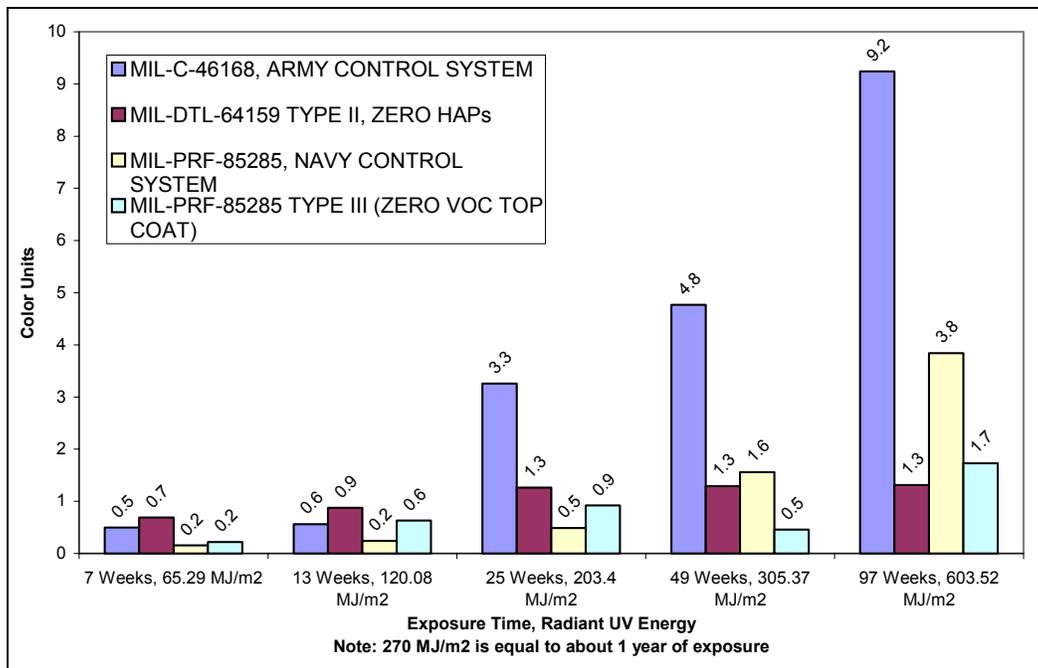


Figure 4. Arizona exposure data: color change of coating systems.

subtropical environment was most detrimental (loss of color retention) to the System “A” coating, which displayed a color difference value of 7.42 units at the final weathering interval. Also, at this interval, the topcoats from both System “C” and “D” showed significant color degradation (~3 units). The color retention for the System “D” topcoat was actually compromised at the previous exposure interval, 49 weeks/270.6 MJ/m<sup>2</sup> (UV dosage), whereas with System “C,” the color remained stable. It should be noted, this behavior for coating “D” did not manifest itself under the Arizona or the QUV exposures. This is an example of how humidity and moisture combined with UV radiation synergistically increase the degradation of a specific coating.

As summarized in table 6, the color retention is good for all of the coating systems through the first 13 weeks of weathering in Arizona. It is not until 25 weeks /203.4 MJ/m<sup>2</sup> (UV dosage) of exposure that the degradation trends begin to appear. As with the QUV exposures, the topcoat of System “A” is the first to show a visually significant color change (3.26 units). System “C,” using the MIL-PRF-85285, solvent-based polyurethane topcoat, was the second most susceptible coating to color degradation, with a major color change (3.84 units) occurring after 97 weeks/603.5 MJ/m<sup>2</sup> (UV dosage) of exposure. Overall, the degradation trend and performance ranking for these coatings are in line with the results obtained from the QUV exposures.

The coatings’ gloss values for both 60 and 85° are summarized in tables 7–9 and charted in figures 5–7. The data were taken from the final evaluation interval (97 weeks) for the outdoor exposures and 27 weeks for the QUV exposure. This QUV interval was chosen to match, as closely as possible, the total UV energy dosage to that of the outdoor exposures. The gloss changes for the low matte samples, Systems “A” and “B” is minimal. Even the change in the 85° gloss reading (1.2 unit increase) for the “System “B” topcoat, under the Florida exposure, is an acceptable difference. For the higher gloss coatings, Systems “C” and “D,” all of the weathering results show a similar gloss change trend; that is, a decrease in 60° gloss and an increase in the 85° gloss. The one exception to this trend was the loss of 85° gloss for System “D” in Florida, although in its previous exposure interval (49 weeks), the 85° reading did indeed rise. No explanation for this data reversal is readily apparent. These gloss degradation trends are best explained by the way in which formulators generally use larger particle-sized pigments to lower the 85° gloss reading. As the coating film weathers and the binder degrades, these pigments are lost and a new surface topography develops that is generally smoother, thus giving rise to the 85° reading and a lowering of the 60° reading.

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## 5. Conclusions and Observations

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- The protective film properties of all of the “Coating Systems” remained intact. No catastrophic failures (i.e., cracking, checking, blistering, and delaminating) occurred under any of the exposure conditions.

Table 7. Summary of gloss values for QUV after 27 weeks, radiant energy UV: 671.13 MJ/m<sup>2</sup>.

<b>QUV</b>	<b>Initial</b>	<b>Final</b>	<b>Initial</b>	<b>Final</b>
System	Gloss 60°	Gloss 60°	Gloss 85°	Gloss 85°
A	0.6	0.7	2.9	2.5
B	0.7	0.8	1.6	2.2
C	2.3	1.6	3.6	3.8
D	2.1	1.4	4.4	4.3

Table 8. Summary of gloss values for Arizona after 97 weeks, radiant energy UV: 603.52 MJ/m<sup>2</sup>.

<b>Arizona</b>	<b>Initial</b>	<b>Final</b>	<b>Initial</b>	<b>Final</b>
System	Gloss 60°	Gloss 60°	Gloss 85°	Gloss 85°
A	0.6	0.6	3.6	3.4
B	0.6	0.6	2.2	2.5
C	2.1	1.4	4.1	8.7
D	2.0	1.3	5.4	6.6

Table 9. Summary of gloss values for Florida after 97 weeks, radiant energy UV: 501.37 MJ/m<sup>2</sup>.

<b>Florida</b>	<b>Initial</b>	<b>Final</b>	<b>Initial</b>	<b>Final</b>
System	Gloss 60°	Gloss 60°	Gloss 85°	Gloss 85°
A	0.6	0.5	3.2	4.4
B	0.7	0.6	2.2	2.8
C	2.2	1.6	4.5	6.4
D	1.9	1.0	5.3	3.7

- The water dispersible coatings “B” and “D” provided much better resistance to color changes than their solvent-based counterparts, “A” and “C,” when weathered under the QUV conditions (figure 8). The Arizona results paralleled these findings, an indication that the coatings’ degradation pathways (i.e., photolysis) are similar.
- For the Florida exposures, as with the other two exposure conditions, coating “B” outperformed coating “A” for color retention. However, for the Air Force systems, coating “D” reversed its excellent color retention behavior, as seen in the Arizona/QUV exposures. This system was actually the first of all the coatings to show significant color deterioration. This reversal indicates that for this coating, the subtropical environment created or enhanced a degradation mechanism that adversely impacted color durability greater than that of the arid exposures.

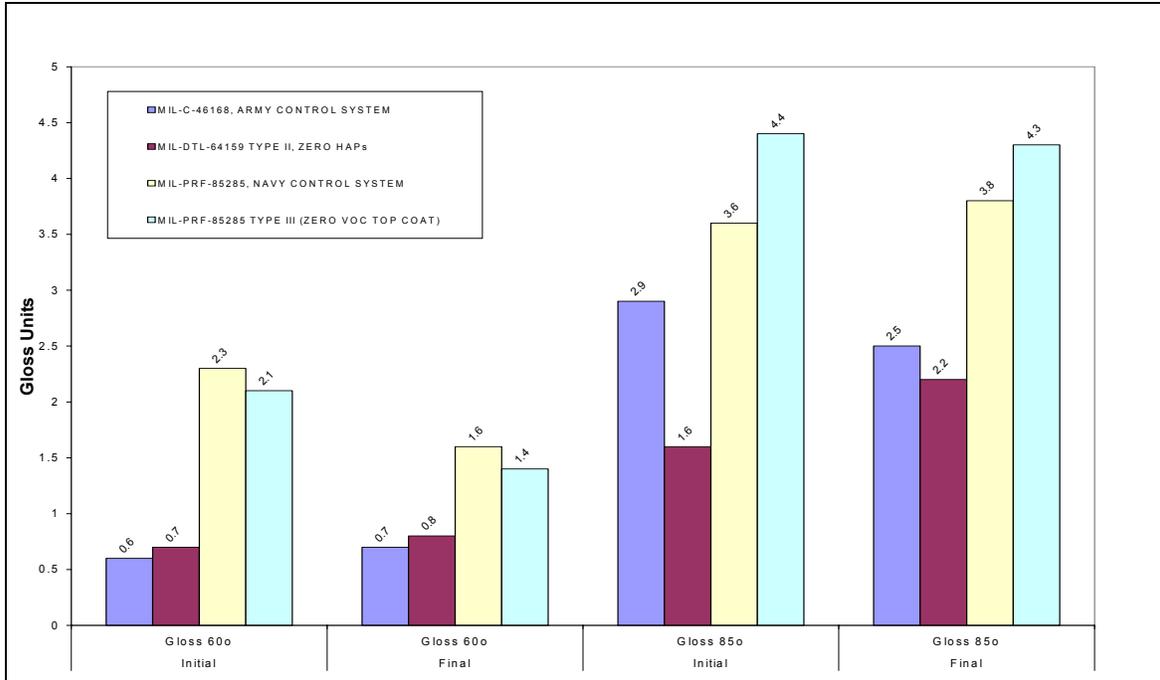


Figure 5. Gloss values after 27 weeks of QUV exposure.

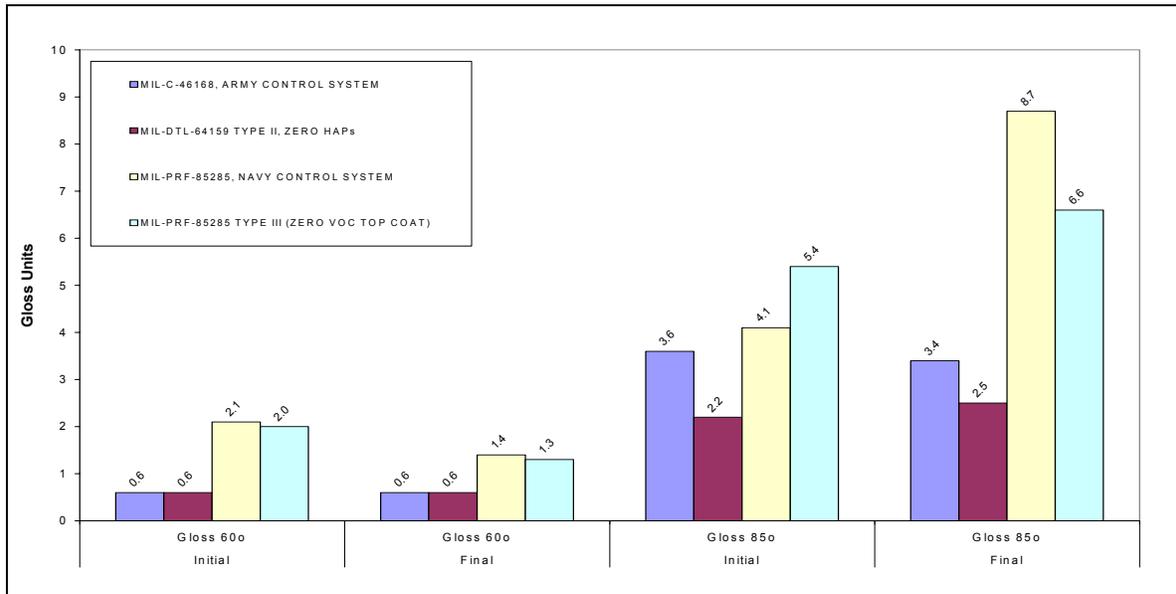


Figure 6. Gloss values after 97 weeks of Arizona exposure.

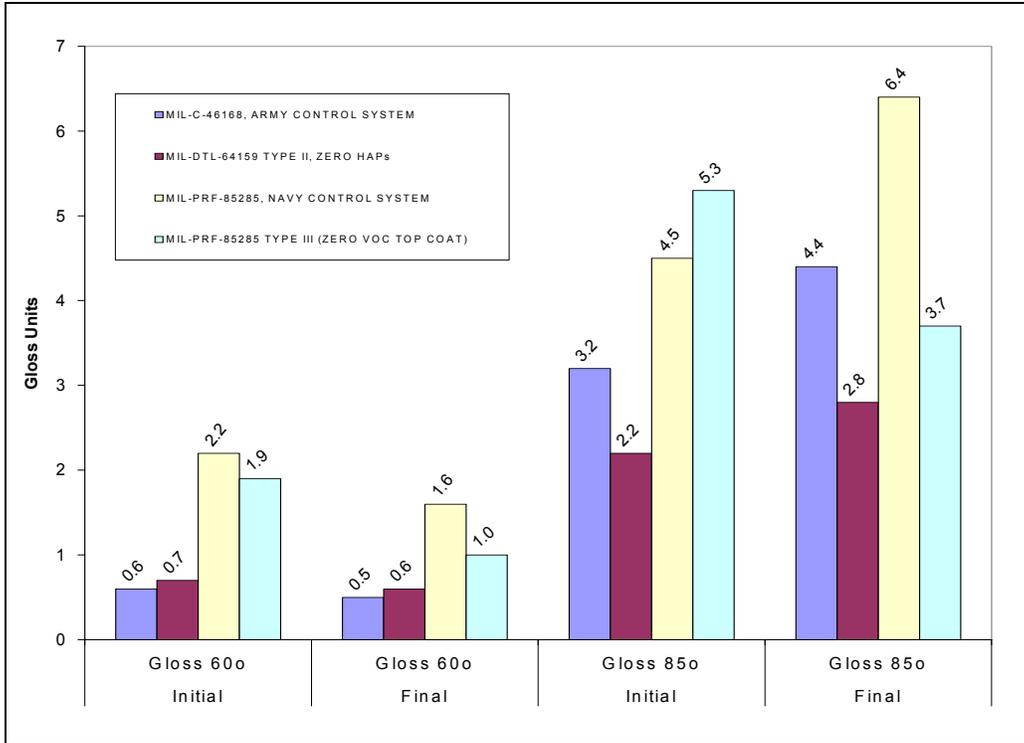


Figure 7. Gloss values after 97 weeks of Florida exposure.



Figure 8. Photographs displaying coating systems after 48 weeks of UV exposure.

- The topcoat formulation with the lowest pigment to binder ratio (System “B”) provided the best overall appearance stability. The performance of this camouflage coating was not enhanced by the addition of UV inhibitors or Hindered Amine Light Stabilizers, but rather through the selection of durable and effective flattening agents (extender pigments) that kept the gloss down while maintaining the low pigment-to-binder ratio.
- Overall, the weathering exposures had little significant impact on the gloss behavior of the coating systems. The gloss changes that did occur, in most instances, were within the tolerances as set forth in the coating’s respective specification.
- Systems “A” and “B” (383 Green pigmentation) have lower reflectance values than “C” and “D” (Air Force Medium Gray color number 36375). It is generally accepted that higher reflectance properties result in lower ambient operating temperatures (18). Therefore, by formulating a topcoat “B” binder system with medium gray pigmentation and polymeric flattening agents, color retention would improve due to higher pigment reflectance properties and to superior polymer durability.
- The changes in surface appearance properties affected by environmental exposures are but one way of evaluating a coating’s durability. Changes can occur on the surface that may or may not impact the bulk of the material. This research included additional degradational analysis that measured some of the coatings’ intrinsic properties. The details of the instrumental analysis characterizing the functional changes involving the coatings’ chemical and mechanical properties will be discussed in a future technical report.

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