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Evaluation of Chemical Agent Resistant Coatings That Are Exposed to Ultraviolet Radiation

by William S. Lum and James A. Kidd, Jr.

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14. ABSTRACT The U.S. Army Research Laboratory (ARL) has the lead research and development responsibility for chemical agent resistant coatings (CARC) and manages the relevant specifications that govern the topcoats, primers, and pretreatments for CARC systems. In striving to optimize coating durability and to extend the life cycle of vehicles and weapon systems that use CARC materials, ARL evaluated several CARC topcoats for ultraviolet (UV) resistance. After samples were subjected to UV irradiance in laboratory weathering chambers, several instruments were used to quantify four parameters that indicate the degradation of a material.				
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1. Introduction

Approximately 99% of solar radiation at the surface of the Earth is within the wavelength region of 295–3000 nm. This report focuses on the exposure of several military coatings to light with a wavelength that is shorter than that for visible light. Ultraviolet (UV) radiant energy is light with a wavelength that ranges from ~295 to 385 nm. Although UV light comprises only 3.3% of the wavelength region for solar radiation, it represents the most energy-intensive region; generally, photon energy is inversely proportional to the wavelength. Short wavelength light can have sufficient energy to break chemical bonds (1, 2).

Since the beginning of Fiscal Year 1985, U.S. Army Regulation 750-1 mandates the use of chemical agent resistant coatings (CARC) systems on all tactical equipment. Additionally, U.S. Army doctrine directs coatings research and development towards three primary principles: survivability, durability (meet or exceed operational requirements and resistance to corrosion and ultraviolet exposure), and environmental compliance.

The U.S. Army Research Laboratory (ARL) is the lead research and development activity for (CARC) and is the approving authority of CARC products for the Department of Defense (DOD). A typical CARC system consists of a pretreatment, primer, and topcoat. The overall coating system is formulated to provide proper substrate protection while maintaining minimal detection in the visible (~385–780 nm) and near infrared (~780–1400 nm) range (2).

Compositionally, a CARC topcoat is formulated to have ~44% primary pigments and inorganic extenders, 24% resins, 30% solvent, and 2% additives. Recent advances in raw material development have lead formulators to change from inorganic to polymeric-based extenders in order to enhance the barrier properties of the topcoat. These improved formulations help to reduce the cost of material degradation for the DOD. Additionally, recent air pollution regulations have required reformulation of the coating's solvent content to reduce the emission of hazardous air pollutants (HAPs). The primary focus of this research effort is quantifying the affect of these changes in composition on the durability of CARC.

2. Procedure

2.1 Parameters for Accelerated Weathering

Accelerated weathering is an important screening practice that is used to ensure that newly developed formulations will adequately provide the necessary performance with respect to colorfastness, retention of low gloss, and long-term protective film integrity. Performance data

for exposures in an accelerated weathering chamber using fluorescent ultraviolet light (QUV) will be presented.

The 12-hr cycle for accelerated weathering exposures was performed using a UV condensation screening chamber for 8 hr followed by 4 hr of condensate without UV. Fluorescent UVA-340 bulbs emitting a spectral irradiance of 0.77 W/m² measured at 340 nm with a 60 °C (140 °F) temperature setting during the UV cycle and 50 °C (122 °F) temperature setting for the condensation were used. The coating specimens were weathered conforming to the requirements in ASTM G-154, “Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials” (3). The chambers were equipped with an automatic sensor controller that maintained the irradiance at a constant level throughout the testing. The controller was calibrated after every 400 hr of lamp operation.

The total radiant exposure (295–385 nm) in units of energy/area was calculated for each exposure interval using a spectral power distribution table supplied by the chamber manufacturer. Table 1 provides the QUV interval schedule for the 12-hr weathering cycle.

Table 1. Exposure schedule for UV radiation.

Duration (hr)	300	500	600	700	800	1000	1200
Cumulative UV Radiation, $\frac{\text{MJ}}{\text{m}^2}$	44.39	73.98	88.78	103.57	118.37	147.96	177.56

One week, 168 hr, of QUV exposure (4) is the equivalent of 24.857 MJ/m². As demonstrated in equation 1, the second entry in column 2 of table 1 can be derived from this value.

$$300 \text{ Hour} \left(\frac{\text{week}}{168 \text{ hour}} \right) \left(\frac{24.857 \frac{\text{MJ}}{\text{m}^2}}{\text{week}} \right) = 44.387 \frac{\text{MJ}}{\text{m}^2}. \quad (1)$$

If the QUV exposure was for one year, the cumulative ultraviolet radiation would be approximately

$$1 \text{ year} \left(\frac{52 \text{ week}}{\text{year}} \right) \left(\frac{24.857 \frac{\text{MJ}}{\text{m}^2}}{\text{week}} \right) = 1,292.56 \frac{\text{MJ}}{\text{m}^2}. \quad (2)$$

Annual outdoor weathering exposure in Arizona (2) is ~350 MJ/m²; this is approximately the equivalent of 3.25 months of QUV exposure, or 1 year of QUV exposure is the equivalent of 3.7 years of natural weathering in Arizona.

For Arizona, the average direct-beam UV irradiance, based on a diurnal cycle, can be estimated as follows:

$$I_{UV} = \frac{350 \frac{\text{MJ}}{\text{m}^2}}{\text{year}} \left(\frac{\text{year}}{365 \text{ day}} \right) \left[\frac{\frac{\text{MW}}{\text{m}^2} (\text{second})}{\frac{\text{MJ}}{\text{m}^2}} \right] \left(\frac{\text{hour}}{3,600 \text{ second}} \right) \left(\frac{\text{day}}{24 \text{ hour}} \right). \quad (3)$$

$$I_{UV} = \frac{350}{365} \left[1(10)^6 \frac{\text{W}}{\text{m}^2} \right] \left(\frac{1}{3,600} \right) \left(\frac{1}{24} \right) = 11.10 \frac{\text{W}}{\text{m}^2}. \quad (4)$$

Annual outdoor weathering exposure in southern Florida (2) is ~280 MJ/m²; this is approximately the equivalent of 2.56 months of QUV exposure, or 1 year of QUV exposure is the equivalent of 4.6 years of natural weathering in southern Florida.

For southern Florida, the average direct-beam UV irradiance, based on a diurnal cycle, can be estimated as follows:

$$I_{UV} = \frac{280 \frac{\text{MJ}}{\text{m}^2}}{\text{year}} \left(\frac{\text{year}}{365 \text{ day}} \right) \left[\frac{\frac{\text{MW}}{\text{m}^2} (\text{second})}{\frac{\text{MJ}}{\text{m}^2}} \right] \left(\frac{\text{hour}}{3,600 \text{ second}} \right) \left(\frac{\text{day}}{24 \text{ hour}} \right) = 8.88 \frac{\text{W}}{\text{m}^2}. \quad (5)$$

These values for Arizona and Florida can be compared to the direct-beam UV irradiance that is delivered in the QUV chamber. Although the QUV uses a 12-hr cycle, for this calculation a 24 hour/day must be used.

$$I_{UV} = \frac{24.857 \frac{\text{MJ}}{\text{m}^2}}{\text{week}} \left[\frac{\frac{\text{MW}}{\text{m}^2} (\text{second})}{\frac{\text{MJ}}{\text{m}^2}} \right] \left(\frac{\text{hour}}{3,600 \text{ second}} \right) \left(\frac{\text{day}}{24 \text{ hour}} \right) \left(\frac{\text{week}}{7 \text{ day}} \right). \quad (6)$$

$$I_{UV} = 24.857 \left[1(10)^6 \frac{\text{W}}{\text{m}^2} \right] \left(\frac{1}{3,600} \right) \left(\frac{1}{24} \right) \left(\frac{1}{7} \right) = 41.10 \frac{\text{W}}{\text{m}^2}. \quad (7)$$

This value for direct-beam UV irradiance is 3.7 times as intense as that for Arizona and 4.6 times that for southern Florida.

For a topcoat that is exposed to intense irradiance to maintain its design camouflage properties, both the color change and the specular gloss must be minimized.

2.2 Sample Preparation

Two cold rolled steel panels, 4 × 12 in, with a zinc phosphate pretreatment and epoxy primer were used for each manufacturer's color. After each panel was sprayed and the coating had cured, the panels were cut in half transversely and then trimmed to 3 × 6 in size so that they

could be placed into the weathering chamber. Therefore, four separate panels represented each color from all suppliers. Four different color topcoats were tested. As specified in paragraphs 4.6.11 and 4.6.12 of MIL-DTL-53039B (5), all panels were sprayed to a dry film thickness of 1.8–2.2 mils and cured at room temperature for 7 days.

2.3 Performance Testing for Color Fastness

Representative results for each of the four colors are tabulated using National Bureau of Standards (NBS) color difference vs. total hours of exposure; all of the results for color change are graphed. Samples were tested for a baseline value at the seven successive intervals shown in table 1. A sample is considered to be acceptable if the color change from the initial value or the change from the center of the ellipse does not exceed 2.5 NBS units after 800 hr of accelerated weathering. This requirement is summarized in paragraph 3.6.11 of MIL-DTL-53039B for color change limit is used for moisture cure polyurethanes. To collect data beyond the required period of exposure, samples were tested for an additional 400 hr.

2.4 Performance Testing of Specular Gloss

The color and infrared reflectance measurements were performed using a visible/near-IR spectrophotometer equipped with an 8 in diameter integrating sphere and a halogen tungsten light source. The readings were taken in accordance with the requirements in MIL-DTL-53039B. The spectrophotometer was calibrated before each series of analyses using the manufacturer's standard color tile (serial no. 2621).

Gloss is associated with the capacity of a surface to reflect more light in some directions than in others. The directions associated with mirror or specular reflection normally have the highest reflectances. The gloss scale is such that the larger the number, the higher the gloss. A highly polished, plane, black glass with a specified refractive index is assigned a specular gloss of 100 for each geometry; this is the maximum value for the scale. If a surface is devoid of reflectance, the specular gloss is zero. The test method for specular gloss is contained in ASTM D-523 (6). Gloss measurements were made in accordance with ASTM D-523 using a Haze-Gloss Reflectometer*, Model 4606. The measurements were taken at two different angle geometries, 60° and 85°. The 60° geometry is used for comparing most specimens. The 85° geometry is for comparing the sheen or near-grazing shininess of specimens; typically, it is used when specimens have 60° gloss values that are <10. Using the manufacturer's standard reference tile (serial no. 9017715), the instrument's performance was verified for accuracy and consistency before each series of measurements. A series consists of one color for each manufacturer measured for both angles; therefore, the instrument was verified for a total of nine groups of gloss measurements.

* Haze-Gloss Reflectometer is a registered trademark of BYK-Gardner, Columbia, MD.

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 degradation (substrate corrosion and chemical debonding). The applicable requirements from MIL-DTL-53039B for specular gloss are listed in table 2.

Table 2. Coating requirements for specular gloss.

Color	Maximal Allowed Value	
	60°	85°, Sheen
Green 383	1.0	3.5
Tan 686A	1.6	4.0
Brown 383	1.0	3.5
Black 37030	1.0	3.5

3. Results

The results for this evaluation are presented in tables 3–6 for representative samples of four different camouflage colors. The numerical designation for color corresponds with paragraph 1.2.2 in MIL-DTL-53039B and the qualified products list for the same document. The numerical designation for the system is an ARL code that indicates the manufacturer. For the third column in each table, the reference point at the center of each ellipse is zero; each value, including the initial reading, represents a concentric ellipse that indicates the change from the reference point. One data point is collected from each of the four panels described in section 2.2; therefore, each averaged value is the mean of four data points.

Table 3. Averaged performance measurement of system 0003, green 383.

Duration of Exposure (hr)	Average Performance Measurement			
	Color Change, NBS Units		Specular Gloss	
	Change From Initial Value	Change From Center of Ellipse	60°	85°
Initial	0.00	1.88	0.5	2.2
300	0.55	1.93	0.5	1.6
500	0.37	1.99	0.5	1.7
600	0.59	1.96	0.5	1.7
700	0.47	2.03	0.5	1.7
800	0.42	2.12	0.5	1.7
1000	0.58	2.24	0.5	1.9
1200	0.99	2.53	0.6	2.8

Table 4. Averaged performance measurement system 3063, tan 686A.

Duration of Exposure (hr)	Average Performance Measurement			
	Color Change, NBS Units		Specular Gloss	
	Change From Initial Value	Change From Center of Ellipse	60°	85°
Initial	0.00	0.70	1.5	1.4
300	0.16	0.79	1.3	1.2
500	0.21	0.87	1.2	1.2
600	0.53	1.16	1.2	1.2
700	0.76	1.43	1.2	1.2
800	1.36	1.68	1.2	1.2
1000	2.56	3.19	1.2	1.2
1200	3.98	4.58	1.4	1.9

Table 5. Averaged performance measurement system 3083, brown 383.

Duration of Exposure (hr)	Average Performance Measurement			
	Color Change, NBS Units		Specular Gloss	
	Change From Initial Value	Change From Center of Ellipse	60°	85°
Initial	0.00	0.60	1.6	1.9
300	0.18	0.68	1.3	1.3
500	0.19	0.78	1.3	1.4
600	0.27	0.85	1.3	1.4
700	0.38	0.96	1.3	1.5
800	0.50	1.05	1.3	1.5
1000	0.92	1.49	1.2	1.5
1200	1.88	2.42	1.5	2.2

Table 6. Averaged performance measurement, system 3073, black 37030.

Duration of Exposure (hr)	Average Performance Measurement			
	Color Change, NBS Units		Specular Gloss	
	Change From Initial Value	Change From Center of Ellipse	60°	85°
Initial	0.00	0.35	0.2	1.3
300	1.04	1.26	0.3	1.0
500	1.21	1.37	0.3	1.0
600	2.64	2.80	0.4	1.0
700	2.82	2.98	0.4	1.0
800	3.04	3.18	0.4	1.1
1000	4.20	4.33	0.4	1.0
1200	4.65	4.77	0.5	1.6

To avoid redundancy, all of the collected data is not shown in the previous four tables. Data was taken on green 383 from three selected manufacturers. Two suppliers provided the samples of tan 686A, brown 383, and black 37030. The results of all of the tests are summarized in figures 1–6. As indicated for the previous tables, each result is the mean of four data points.

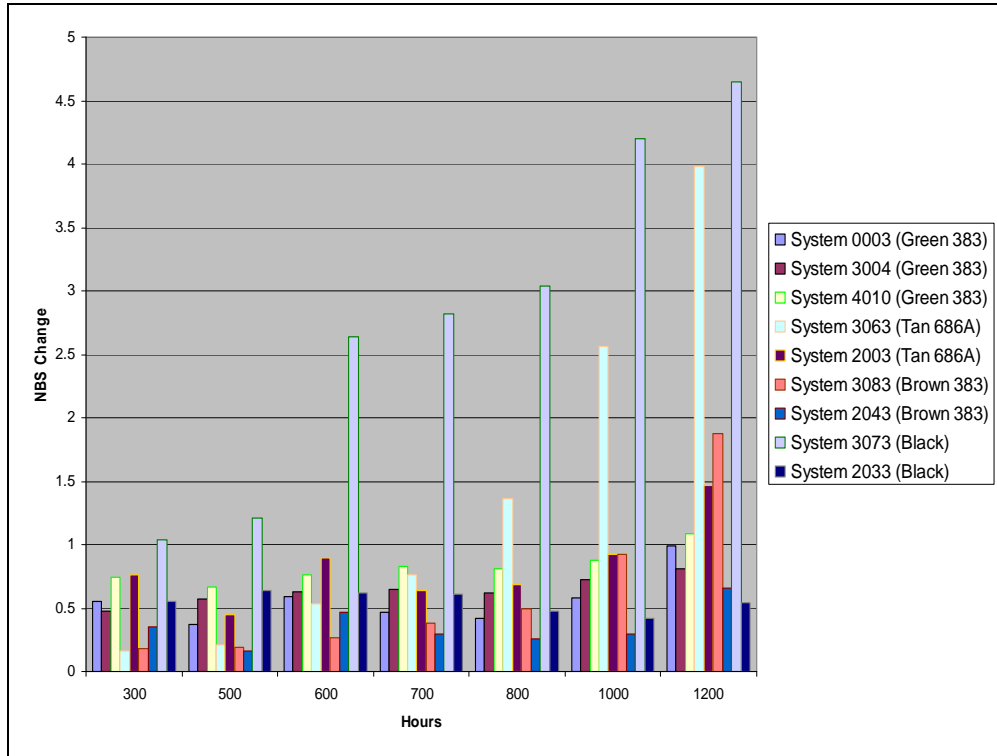


Figure 1. CARC topcoats, color change from initial value.

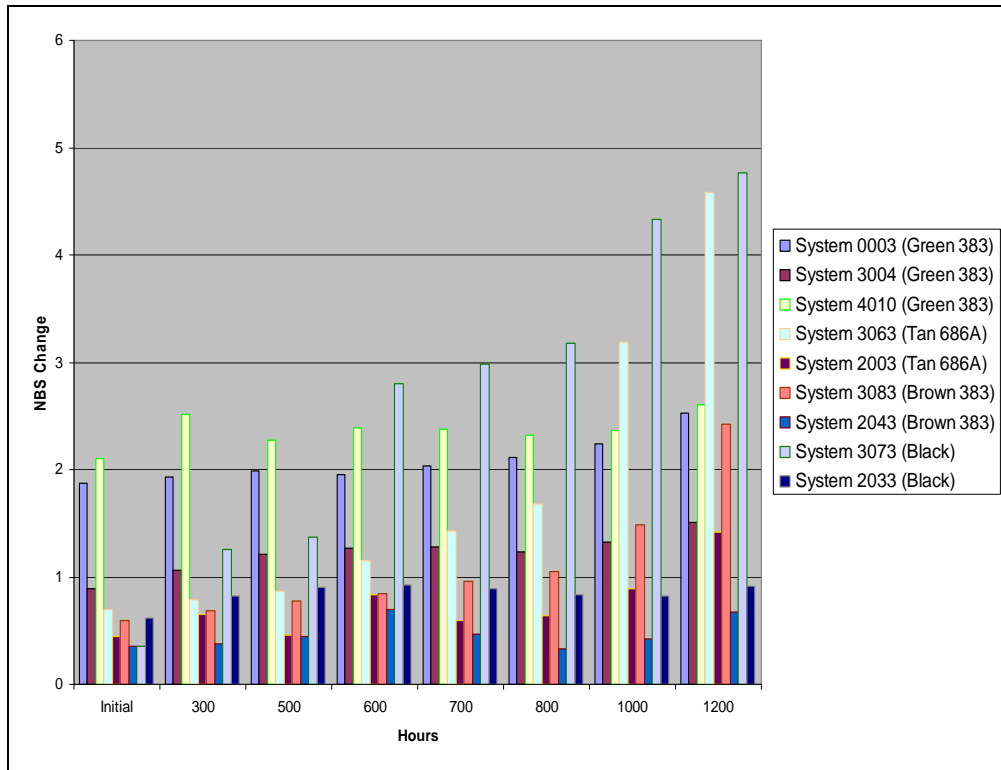


Figure 2. CARC topcoats, color change from center of ellipse.

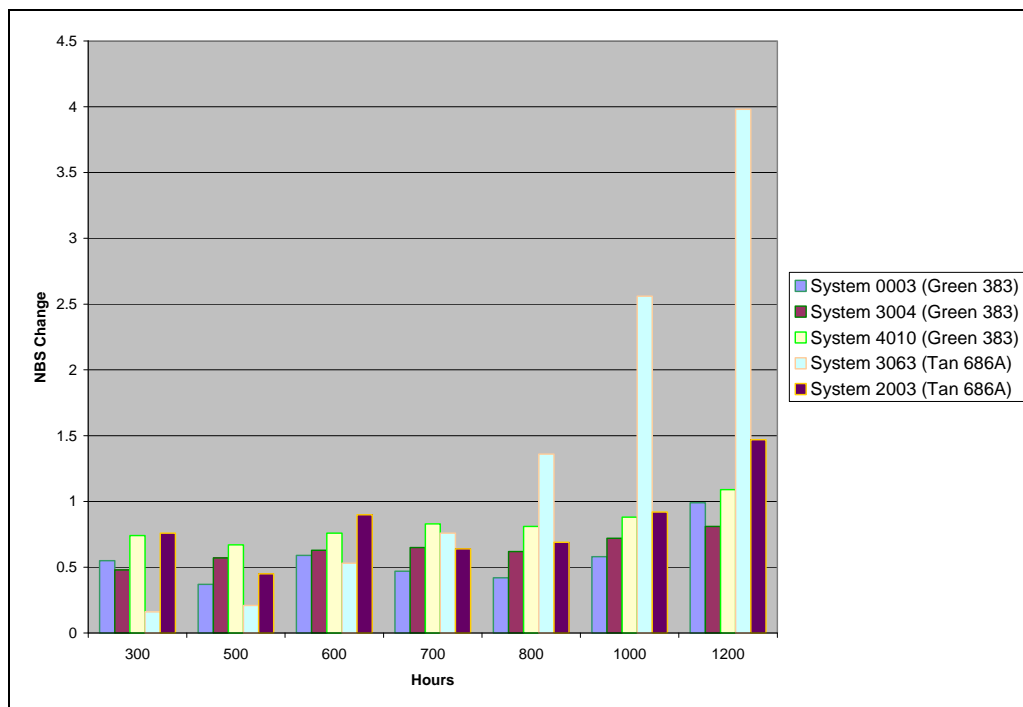


Figure 3. CARC topcoats, color change from initial value for green and tan.

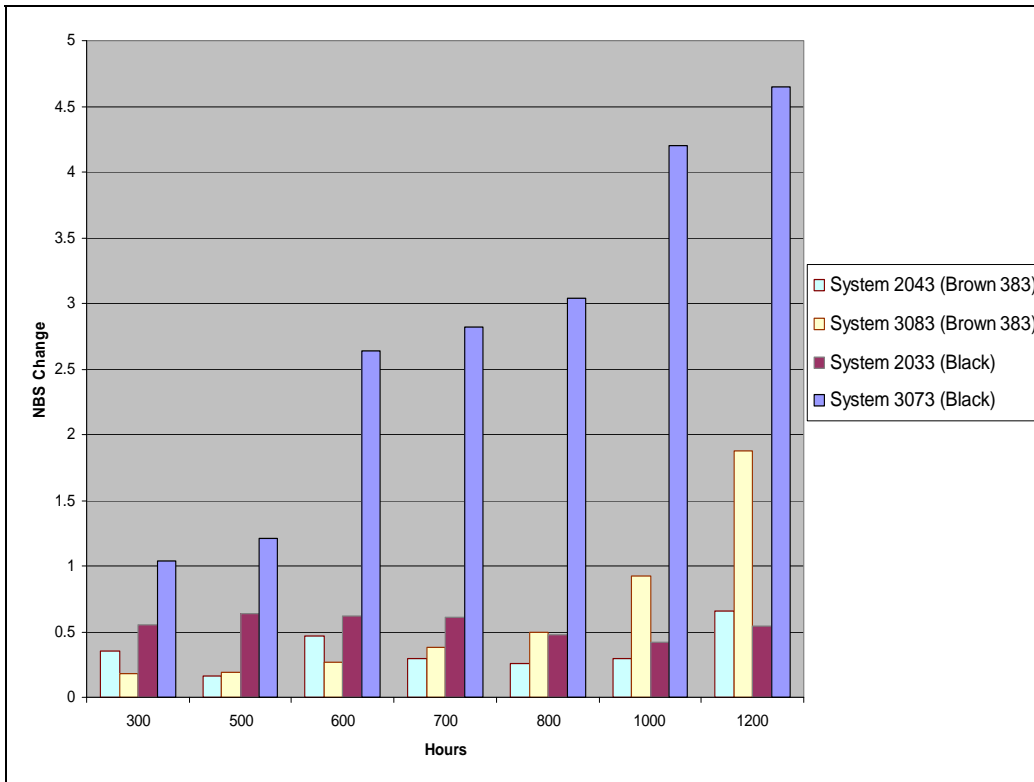


Figure 4. CARC topcoats, color change from initial value for brown and black.

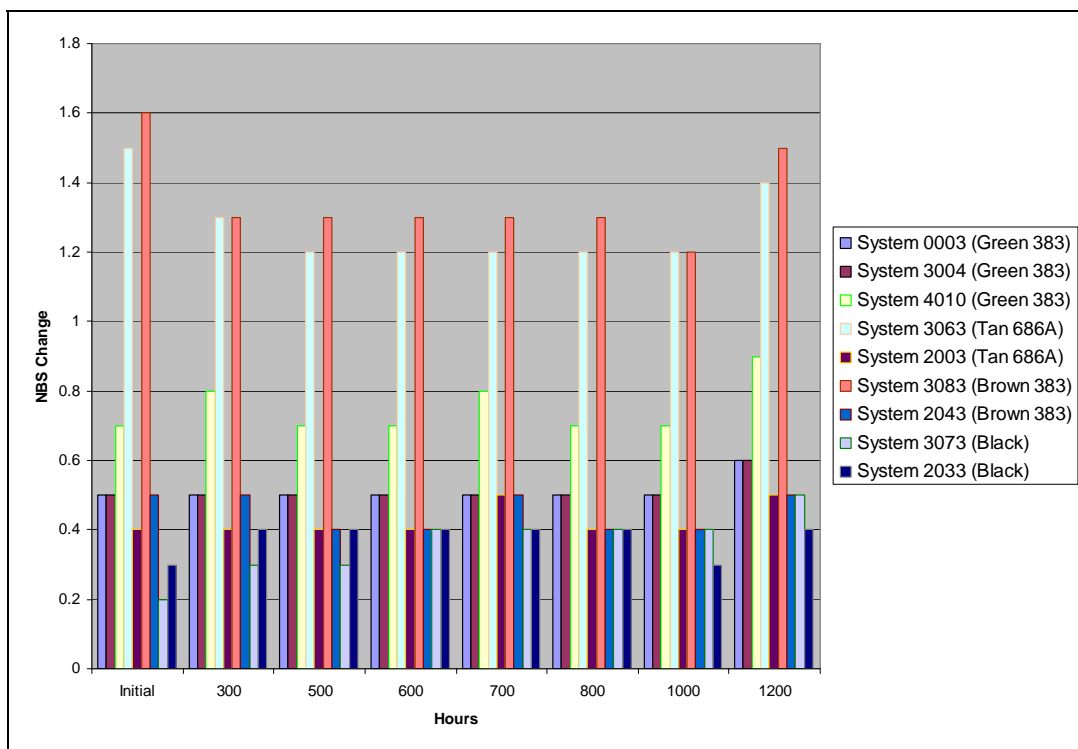


Figure 5. CARC topcoats, gloss at 60°.

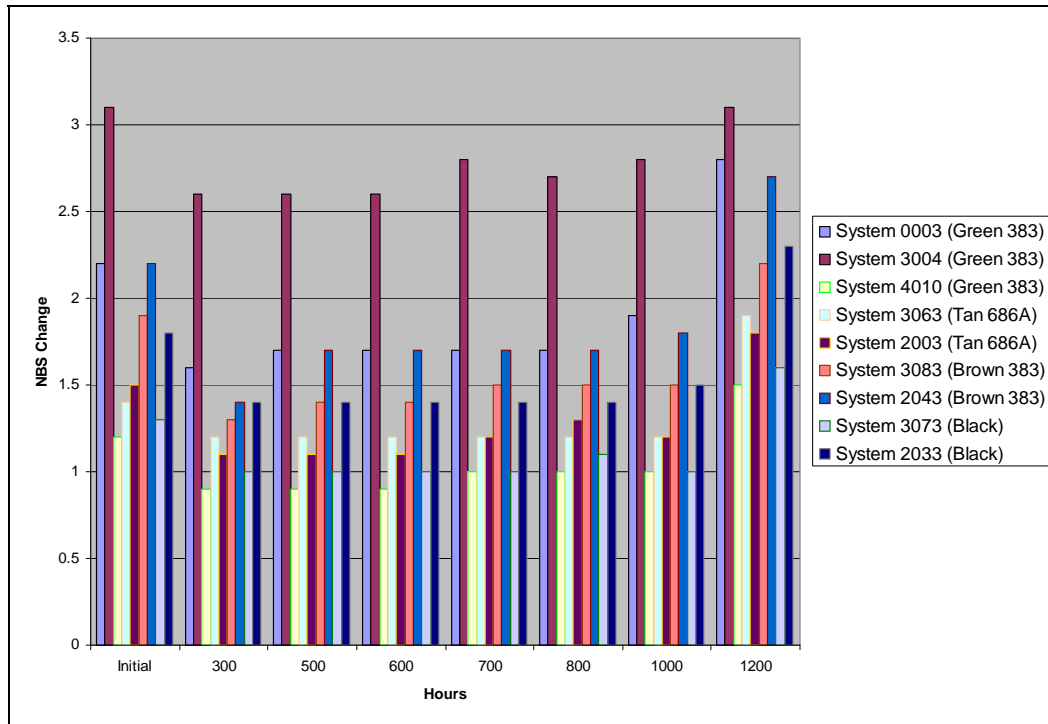


Figure 6. CARC topcoats, gloss at 85°.

4. Conclusions

None of the coatings that were tested sustained a catastrophic failure. QUV results demonstrated significant consistency for different colors from several manufacturers. Using the requirements that are specified in section 2.3 and in table 2, the performance of all of the tested topcoats is summarized in table 7.

Table 7. Performance of CARC topcoats subjected to UV irradiance.

Color	Manufacturer	Color Change		Specular Gloss	
		From Initial Value	From Center of Ellipse	60°	85°
Green 383	0003	P	P	P	P
	3004	P	P	P	P
	4010	P	P	P	P
Tan 686A	3063	P	P	P	P
	2003	P	P	P	P
Brown 383	3083	P	P	F	P
	2043	P	P	P	P
Black 37030	3073	F	F	P	P
	2033	P	P	P	P

Notes: P = Pass
F = Fail

Overall, all of the tested topcoats performed very well in their resistance to ultraviolet light; generally the camouflage properties of these topcoats were not significantly diminished. Of 36 performance results, only 8.3% did not meet the specified criteria. Only brown 383 from manufacturer 3083 did not pass the specular gloss requirement of 1.0 for 60°; it exceeded this value for the entire duration of the test. Two of the failures were for black 37030 from manufacturer 3073; between 500 and 600 hr of exposure, it was unacceptable for both of the color change requirements. It was acceptable for both categories of specular gloss through 1200 hr of exposure. All of the topcoats passed the 85° requirement for specular gloss.

This evaluation validated QUV testing as a screening test for CARC topcoats that must meet the requirements of MIL-DTL-53039B regarding color change and specular gloss. As indicated in section 2.1, QUV accelerated weathering should always be correlated with outdoor testing in geographical areas with strong irradiance such as Arizona and Florida.

5. References

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