

# Test Method Development for Improved Laboratory Accelerated Weathering of High Performance Coatings

Allen Zielnik

Presenter for Atlas Material Testing Technology LLC, 4114 N. Ravenswood Avenue, Chicago, IL 60613

## Abstract

The use of accelerated laboratory artificial weathering in coatings development is necessitated by the lengthy times required for natural outdoor weathering. Across a broad range of industries, weathering results from materials exposed in subtropical South Florida have become the benchmark to which accelerated test methods are compared. To date, there is substantial inconsistency in correlations between the Florida and laboratory accelerated exposures. An industry consortium of coating OEMs, material suppliers, users and test houses has collaborated on developing a new accelerated test protocol that has demonstrated greatly improved correlation. This new method focuses on both an improved spectral match to sunlight as well as a major improvement to moisture delivery. The new protocol is detailed as well as the validation of the method for high performance automotive and aerospace coatings. This improved method overcomes many of the known shortcomings of industry standard methods and may have major implications for the testing of other systems such as high performance exterior architectural coatings. More importantly, it serves as an example and overall framework for development improved test methods.

## 1. Acknowledgements

This paper includes substantial original research conducted by and more fully described in “**An Improved Accelerated Weathering Protocol to Anticipate Florida Exposure Behavior of Coatings**”, submitted for publication to the Journal of Coatings Technology and Research in June, 2011, authors: Mark Nichols, Tony Misovski, Cindy Peters (Ford Ford Research and Advanced Engineering, Dearborn, MI 48121); John Boisseau, Don Campbell, Lynn Pattison (BASF Coatings, Southfield, MI 48033); Don Smith, Karen Henderson (Bayer MaterialScience, Pittsburgh, PA 15205); Jill Seebergh, Douglas Berry (The Boeing Company, Seattle, WA 98124); Jeff Quill (Q-Lab, Cleveland, OH 44145); and Jacob Zhang (Atlas Material Testing Technology, Chicago IL 650613).

## 2. Introduction

One of the first documented references to formal paint weather durability testing dates back to the Fargo Agricultural College North Dakota Experiment Station ca.1906, with similar outdoor exposure tests subsequently soon begun in Atlantic City, NJ and Pittsburgh, PA<sup>i</sup>. Outdoor weathering exposures are common today, and many private and commercial test sites are available; most are located in the 15-35° latitude belts of both hemispheres.

Hot and wet conditions are recognized as usually being the most severe for coatings. Although these are located in many high solar radiation regions of the globe, subtropical South Florida near Miami has become established as the major benchmark location for coatings comparisons, and most coatings standards and specifications require outdoor exposures there.<sup>1</sup>

Real time testing (RTT) of long-lived coatings, however, simply takes too long to be useful in coatings development. The automotive industry, for example, has an expectation of five to ten year life for paint system for both performance and appearance. Even poor coatings will typically perform well for at least two or more years. Therefore, various accelerated weathering techniques have emerged to overcome this obstacle. One of the most widespread is laboratory accelerated artificial weathering which exposes test specimens to simulated solar radiation under controlled conditions of temperature and moisture delivery. The current best implementation utilizes xenon arc gas discharge lamps with special optical filters to spectrally match to sunlight in the UV and visible wavelengths<sup>ii</sup>.

The general requirements for these test apparatus, guidelines for their use and specific test method conditions are specified in various international standards<sup>iii,iv,v,vi</sup>. It is interesting to note, however, that the test conditions in these governing standards

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<sup>1</sup> AAMA 2603, 2604 and 2605 specifications require 1, 5 and 10 years South Florida weathering, respectively.

do not purport to represent any specific climate or locale, such as South Florida, nor do they claim that results will correlate with exposures in any outdoor location. In summary, they are designed as comparative tests under standardized conditions and are not tools for estimating either service life or performance.

The principal concept in accelerated testing is to apply the appropriate stress(es) at a higher level, and/or for a shorter period, and then extrapolate the data to normal use stress levels and time. In weathering testing this is difficult to achieve for several reasons. First, there are practical limits to the levels of overstress which can be applied. One research tool, for example, has been developed which can produce up to about 100X the intensity of the UV component of natural sunlight attempt shortening the test time<sup>vii,viii</sup>. Most experimental data, however, does not support increases over 10X and maintain proportional rates of degradation or the same degradation modes. This is especially true of polymer systems formulated with stabilizer additives<sup>ix,x,x</sup>.

Secondly, environmental stress factors are not independent variables and cannot be accelerated at the same rates, if at all, in laboratory testing. The implication is that different coating chemistries may react differently to a specific set of test conditions, or that specific stress levels may induce test artifacts.

Lastly, acceleration factors usually change during a test depending on the degree of specimen degradation; this complicates correlation of accelerated test times to actual outdoor aging.

Further complicating the process is that the external stresses may act on a material by three different mechanisms. First, overstress beyond the strength of a material to resist it can result in a non-reversible failure, such as “stone chipping” of an automotive coating. Secondly, cyclic fatigue such as from thermo- or hygro-mechanical stresses can result in failure. Third, chemical or physical degradation mechanisms may cause a gradual loss of requisite properties to some level considered a failure. If a test method is to reproduce the effects of natural weathering, all three failure modes must be considered.

The development of a new accelerated weathering protocol based on correlation with data from natural outdoor exposures in Florida is detailed here<sup>xii</sup>. The correlation of results from this new protocol with those from natural weathering exposures is presented for only a few of the automotive coating systems tested. Correlations are based on both chemical and physical bases.

## 2. Test Method Development

Successful accelerated weathering test method development generally involves several sequential and parallel steps:

1. Identify failure modes; a Failure Mode and Effects Analysis (FMEA) based approach often proves useful. Known or plausible failure modes are considered. This includes chemical and physical failure mechanisms of each coating component as well as system interfaces. A typical automotive paint system is illustrated in Figure 1.

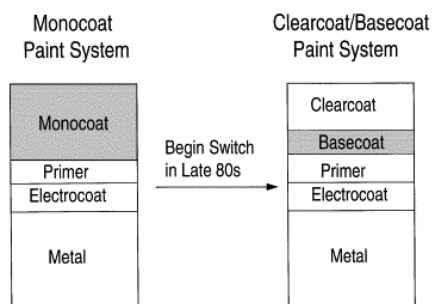


Figure 1. Typical automotive paint system.

2. Identify specific stress factors from (1) which may initiate the various failure modes. Determine which may need to be applied in the accelerated test (in which combinations, levels, cycles, etc., derived from climate data for the intended location). To be a useful method, these stresses must often be reconciled with the capabilities of commercial test equipment. In some cases separate tests or sequential exposures may be required if existing equipment cannot meet all of the requirements.

3. Identify failure criteria and evaluation methods. The test specimen requirements for analytical measurements (special form factors, replicates for statistical validity, measurement intervals, destructive vs. non-destructive tests, etc.) must be reconciled with the exposure specimen requirements in (2). Specimens must be representative of in-service use (substrates, processing, etc.).
4. Establish a design of experiment (DoE) if necessary and conduct screening if needed to test failure mode hypotheses, necessary stress combinations, levels and cycles to limit the number of factors and required specimens. Establish test plan
5. Implement (4).
6. Validate cause and effect and correlation to RTT; identify test condition bias.
7. Adjust and reiterate (1) through (6) as necessary.

### 3. Coating Degradation

Performance coatings failure may be mechanical or appearance based, such as adhesion loss or gloss loss. The inability to protect a substrate from the environment may also be considered failure. In coatings development, reliable performance evaluation and testing methods must be developed and useable on a reasonable timescale for exterior coatings chemical degradation of the binder is the primary failure mode. This degradation is mainly driven by photooxidation and hydrolysis<sup>xiii,xiv,xv,xvi</sup> and for many coating systems the former is the primary mechanism. As performance coatings may have a lifetime requirement of five to ten years or more, tests must provide reasonable acceleration, and evaluation methods sufficient resolution, to be useful. It must also faithfully reproduce the RTT results.

Coatings stabilized with ultraviolet absorbers (UVA) and hindered amine light stabilizer (HALS) free radical scavengers have been thoroughly investigated<sup>xvii,xviii,xix</sup> leading to models to predict the lifetime of coating systems<sup>xxi,xxii,xxiii</sup>. The presence of these stabilizers often affects the degradation kinetics and leads to a more complicated correlation of accelerated exposure to RTT as the relationship may be non-linear.

Most efforts to predict long term coating durability have focused on correlating performance to exposure in South Florida as this location has been shown to be harsher on paint systems than most populated terrestrial locations, and is easily accessible. In South Florida the combination of high solar load, high humidity, warm temperatures and high time of wetness drives rates of photooxidation, hydrolysis, and erosion to near maximal terrestrial rates. While year-to-year weather is a variable, South Florida exposure is the de-facto standard for coating weatherability, and results from any accelerated test must agree with those from South Florida exposure to be practical.

Water is known to play a key role in the weathering of many coatings. It is a plasticizer, decreasing both the  $T_g$  and tensile modulus of a coating<sup>xxiv</sup>, hydrolyzes coating binders and interferes with adhesion. Water will wash or ablate the coating surface and erode loosely bound material.

Previously, no accelerated weathering test has fully reproduced the behavior of paint systems exposed in sub-tropical climates. For example, the test cycle most commonly used for coatings with xenon arc weathering instruments has specimen water sprays for 18 out of every 120 minutes with continuous light exposure. South Florida averages 4200 hours per year or approximately 48% measurable surface "wet time" while only about 15% in the standard xenon methods. Furthermore, the short sprays on a hot specimen quickly dry out; the coating may not uptake water as completely as in outdoor exposures.

Lastly, the spectral power distribution (SPD) of the light source in laboratory weathering devices is critical to reproduce the same chemical changes in outdoor weathering. The recent development of properly filtered light sources which correctly reproduce sunlight, particularly in the UV region, improves the correlation between artificial accelerated testing and natural weathering as will be shown.

## 4. Experimental

A series of automotive basecoat (BC) / clearcoat (CC) systems of various chemistries and layering schemes was applied to standard 4 inch x 12 inch steel panels and baked under the appropriate conditions. The specific coating chemistries will not be described here, but some coating systems were included as controls which are known to demonstrate certain failure modes when exposed in South Florida, while other systems were formulated for long term durability.

One such control is a flexible polyester-urethane clearcoat, (identified herein as System #150), known to have a particular UV spectral sensitivity, was used for some of the experiments. This was applied to silicon discs and the cured film released to permit transmission infrared spectroscopy.

### 4.1 Natural weathering

Outdoor South Florida exposures were performed on standard commercial 5° inclined unbacked south facing exposure racks. Automotive specimens were exposed for a minimum of two years with specimen returns for evaluation every six months

### 4.2 Accelerated artificial weathering

Two types of apparatus were used: Atlas Ci4000 or Ci5000 Weather-Ometer® (Atlas Material Testing Technology LLC, Chicago, IL) with rotating rack and specimens mounted vertically, and Q-Lab (Q-Lab, Cleveland, OH) Q-Sun® flat array model with panels positioned near-horizontal. All instruments were equipped with xenon light sources fitted with the manufacturer's recommended daylight filters to best match the SPD of sunlight (Atlas RightLight™ inner and quartz outer filters, Q-Lab Daylight-F filters). A subset of test panels were also exposed in an Atlas Ci35 instrument fitted to the specifications of the SAE J2527 protocol<sup>2</sup> (Table 1). The majority of the test specimens were exposed in the xenon apparatus running a new test protocol.

Step#	Water Spray	Irradiance (W/m <sup>2</sup> @340 nm)	Humidity %	Air Temperature (°C)	Black Panel Temperature (°C)	Duration (minutes)
1	Off	0.55	50	47	70	40
2	On	0.55	95	47	70	20
3	Off	0.55	50	47	70	60
4	On	0	95	38	38	60

Table 1. SAE J2527 protocol 4.8 hour repeating cycle

SAE J2527 is often used in North America for testing automotive exterior components. However, as previously noted, other test method conditions, mostly using continuous light cycles with short intermittent water sprays, are also used by the global automotive community; some of these are listed in Table 2

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<sup>2</sup> Society of Automotive Engineers SAE J2527 Performance Based Standard for Accelerated Exposure of Automotive Exterior Materials Using a Controlled Irradiance Xenon-Arc Apparatus, daylight filters (Borosilicate Type S inner and outer or per the manufacturer's specification).

Standard	BST, in °C	BPT, in °C	CHT, in °C	Dark Phase	Filter System	E level, in W/m <sup>2</sup> (300–400 nm)	RH in %	Country
ISO 11341 Low T	55	50	38	No	Daylight	60–180	40–60	Germany
VDA 621-429 Option 8.1		55	36–41	No	Daylight	45	> 60	Germany
VDA 621-429 Option 8.2		55	36	No	Daylight	80	> 60	Germany
ISO 11341 normal	65	63	38	No	Daylight	60–180	40–60	Germany
VDA 621-429 Option 8.3	65		36	No	Daylight	55	55	Germany
JASO M351 Normal		63	Not spec.	Optional	Daylight	60–180	50	Japan
SAE J1960		70	47	Yes	Extended UV	0.55 W/(m <sup>2</sup> nm) at 340 nm	50	USA
SAE J2527		70	47	Yes	Extended UV or daylight	0.55 W/(m <sup>2</sup> nm) at 340 nm	50	USA
VDA 621-430 Option 3.1, 3.2		70	47	Yes	Extended UV	0.55 W/(m <sup>2</sup> nm) at 340 nm	50	USA
VDA 621-429 Option 8.4		70	47	Yes	Extended UV	0.55 W/(m <sup>2</sup> nm) at 340 nm	50	USA
VDA 621-430 Option 3.3	73–76	70	47	Yes	Extended UV	60	50	USA
JASO M351 High T		83	Not spec.	Optional	Daylight	60–180	50	Japan

Table 2. Common global automotive laboratory test methods.

As SAE J2527 comes closer to representing the diurnal temperature and moisture cycles of South Florida than these other methods, it was used as the starting point in this study. The newly developed test protocol differs from SAE J2527 by including two long water spray cycles at zero irradiance, one long cycle with higher irradiance without water spray, and a series of short wet/dry dark/light cycles (Table 3). It should be noted that many automotive and non-automotive paint and coating test methods use continuous light cycles with intermittent water sprays.

Step#	Water Spray	Irradiance (W/m <sup>2</sup> @340 nm)	Humidity %	Air Temperature (°C)	Black Panel Temperature (°C)	Duration (minutes)
1	On	0	95	40	40	300
2	Off	0.4	50	40	50	60
3	Off	0.8	35	48	70	780
4	Off	0	50	40	40	30
5	On	0	95	40	40	270
Repeat Below 8X						
6	On	0	95	40	40	30
7	Off	0.4	50	40	50	20
8	Off	0.8	55	48	70	120
9	Off	0	40	40	40	10
Return to Step 1						

Table 3. “New” protocol extended cycle.

Paint specimens were exposed for a minimum of 3000 kJ/m<sup>2</sup> @340nm, approximately the equivalent of one year’s of South Florida UV exposure, and for a minimum of twenty-one months in Florida. Exposed specimens were checked for adhesion using a razor to scribe an “X” in the coating with a tape adhesion pull after a 24 hour water soak.

Instrument to instrument variability was checked for a total of six different Atlas instruments at three locations, and four Q-Sun units at three locations.

To verify uniform water spray delivery, a piece of synthetic sponge was placed in several specific locations in the various apparatus, the spray cycle was run for five minutes, then the sponges were weighed for water mass uptake using standard techniques and adjusted to achieve a minimum of 7.0g of water at each location during a five minute spray.

#### 4.3 Analytical measurements (abbreviated summary)

Photoacoustic Fourier Transform Infrared (PAS-FTIR) spectra were obtained to provide a sampling of the top 8-12 μm of the coating and changes to the spectra were quantified using the method developed by Gerlock, *et al*, which tracks the growth of the [-OH,-NH] region of the IR spectrum versus exposure time. This is then normalized to the area of the [-CH] region. The

change has been shown to be representative of the amount of photooxidation and hydrolysis products accumulated during weathering<sup>xxv</sup>.

To compare the type of chemical changes that occur during weathering the IR spectra were compared using a previously developed comparison technique<sup>xxvi</sup>. Four peaks in the fingerprint region of the spectra were selected and peak heights were recorded as a function of the weathering time, then ratioed to each other (a:b and c:d). The ratios were then plotted against each other. Weathering tests which produce the same chemical composition changes show the same slope of the data using this comparison technique<sup>xxvii</sup>.

UV absorber distribution in some of the automotive paint systems was quantified via an ultraviolet micro-spectroscopy<sup>xxviii</sup> method where weathered coatings were released from a silicon substrate to obtain a film specimen. It was then adhered between two pieces of reference film using a solvent free adhesive to avoid UVA migration. The reference film was an acrylic/melamine clearcoat film with known UVA concentration and UV absorbance. The assembly was then microtomed into cross sections and analyzed in 5 $\mu$ m steps into the depth of the clearcoat.

Color and 20° gloss were measured. Visual evaluations were performed after each 6 month interval of South Florida weathering, or 1000 kJ/m<sup>2</sup> @340nm of accelerated weathering; photomicrographs were also taken and analyzed.

Water absorption was measured at intervals by a standard mass uptake methodology on specimens of each coating system, with measurements conducted during the dark exposure periods in the weathering apparatus. Some samples were also tested by soaking overnight in 23°C water to reach saturation.

## 5. Automotive Coating Results

### 5.1 Water absorption

The water absorption by paint system #25 exposed in a Ci4000 during an extended spray cycle is shown as a function of water exposure time (Figure 2). The initial absorption was linear ( $t^{0.5}$  scale) indicating standard Fickian diffusion into the paint system<sup>xxviii</sup>.

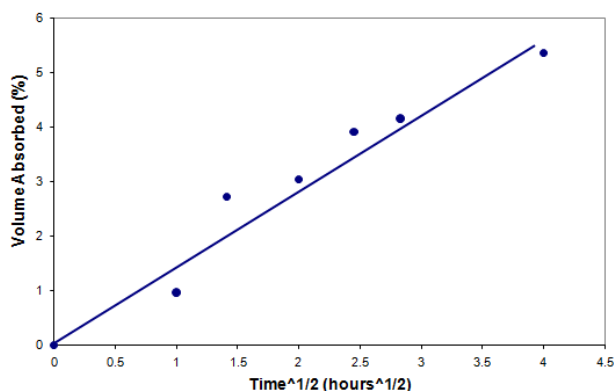


Figure 2. Coating system #25 water uptake in SAE J2527.

The water uptake volume of the same paint system after both a 16 hour condensing humidity (at 60°C) exposure and after overnight water soaking is shown (Figure 3).

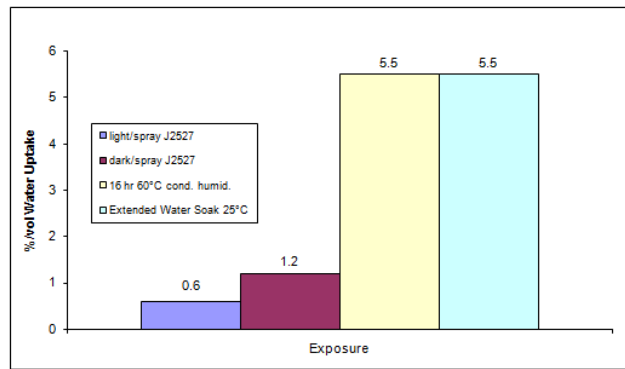


Figure 3. Coating system #25 water uptake.

Water saturation was reached after both of these exposures, but not during water sprays in SAE J2527 (Table 1, Steps #2 & 4).

### 5.2 Photochemistry

The UV portion of the SPD of the xenon arc with the new improved optical filters is shown (Figure 4) on a log scale where the “Boro/Boro” combination is the common SAE J2527 “daylight” implementation in the Atlas units.

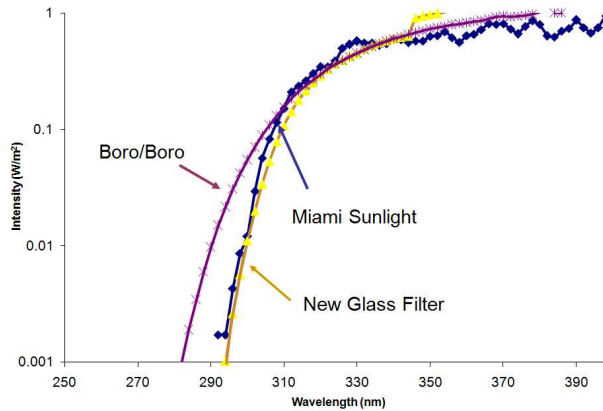


Figure 4. Sunlight, SAE J2527, “new” filter UV comparison.

The new filter sets correctly reproduce the sunlight UV cut-on radiation ca. 295nm, while the traditional daylight filters (Borosilicate-S types) contained some excess short wavelength UV not present in terrestrial solar radiation; this can distort the results obtained in accelerated testing.

The “fingerprint” region of the PAS-FTIR spectra of the polyester-urethane clearcoat is shown before and after accelerated weathering (Figure 5).

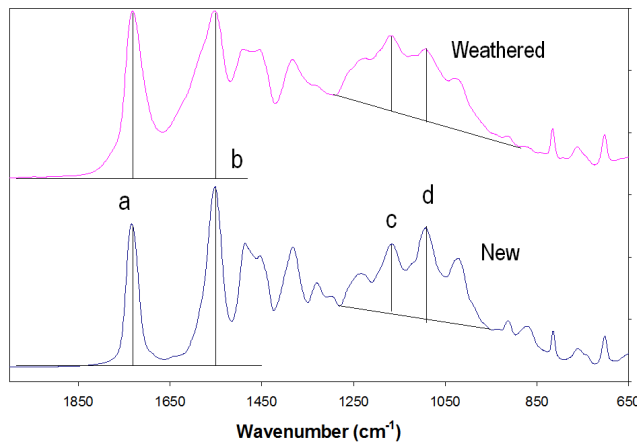


Figure 5. UV sensitive clearcoat weathering PAS-FTIR markers.

The ratio of the changes in the four peaks (a-d), described in Section 4.3, that occurred during weathering with the new protocol is shown in (Figure 6) for the new protocol, South Florida and Arizona outdoor, accelerated Fresnel concentrator exposure, and SAE J2527.

The slopes of the data obtained were very similar except for SAE J2527. The distance from the origin in this plot is indicative of the degree of degradation or time which has occurred while the slopes are indicative of the type of chemical changes that occurred during weathering. Data sets with equivalent slopes indicate that the type of chemistry that occurred during each exposure was equivalent. Differences in slopes indicate differences in the balance of the reactions that occur during the different exposures.

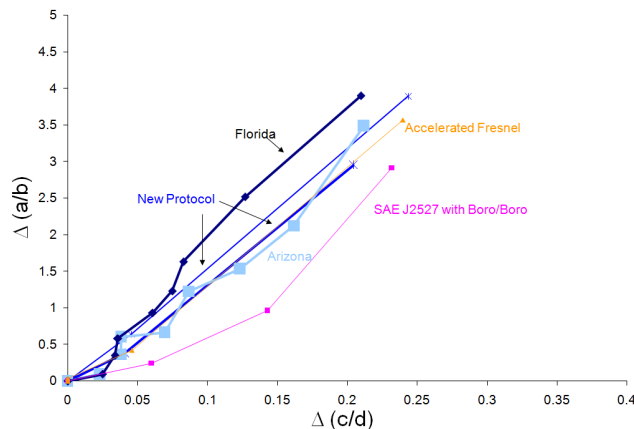


Figure 6. UV sensitive clearcoat weathering PAS-FTIR markers .

The [-OH, -NH] region of the spectrum has proven more applicable to quantify the overall amount of photooxidation. Changes in the [-OH, -NH] value as a function of accelerated weathering dose for four representative automotive coating systems is shown in Figures 7. Each graph contains data for the same coating systems run in multiple laboratories to demonstrate inherent lab-to-lab and instrument-to-instrument variability.

South Florida data was converted to dose rather than time by assuming an annual dose of  $3080 \text{ kJ/m}^2 @ 340\text{nm}$ .

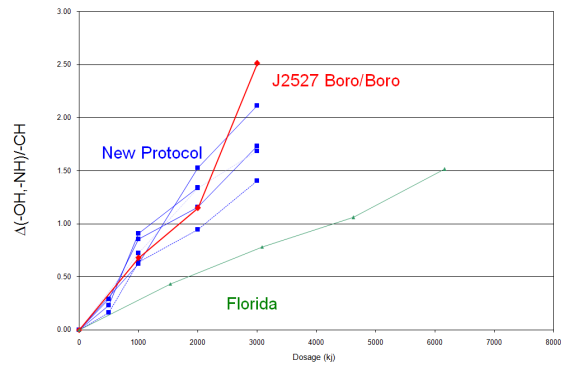
In general, the amount of degradation in a coating system is directly proportional to the [-OH, -NH]/[-CH] growth. Paint systems #13, 25 and 97 showed rapid photo-oxidation growth, a marker of poor long term durability. System 86 (Figure 7, bottom) exhibited much slower photooxidation growth and would be expected to have superior long term durability, as demonstrated in Figure 13.

The UV spectra as a function of coating depth is shown (Figure 8) for system 150 exposed to natural Florida weathering, accelerated weathering with the new protocol, and unweathered (the vertical axis is absorbance).

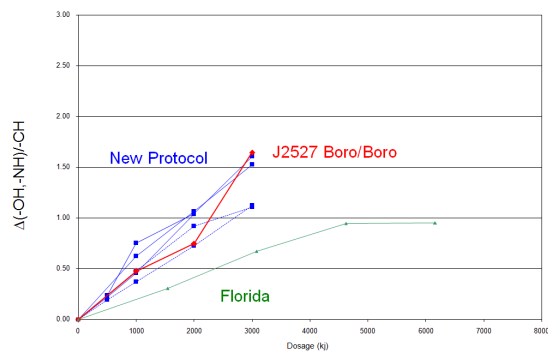


The absorption at a given wavelength is proportional to the amount of UV absorbed at that location. The unweathered specimen shows good uniform distribution in the paint system, but after weathering the UVA's form a concentration gradient with the surface being depleted relative to the bottom of the clearcoat.

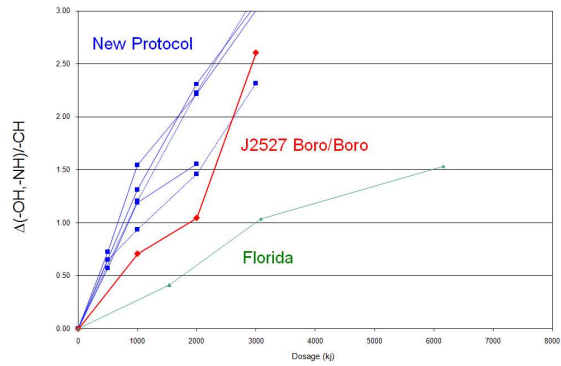
Sample 25



Sample 13



Sample 97



Sample 86

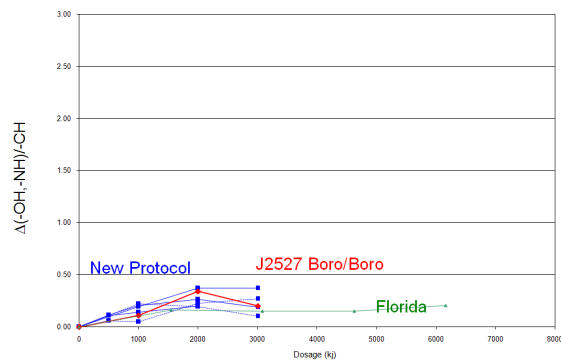
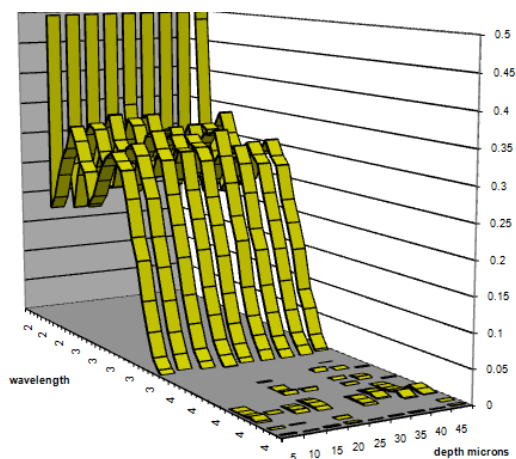
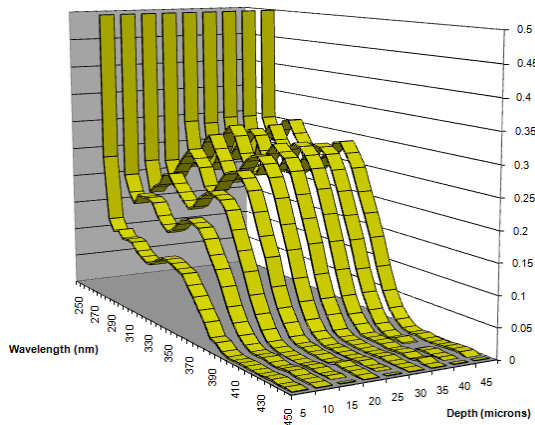


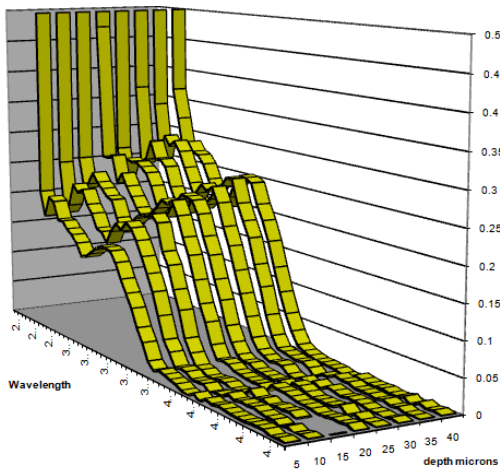
Figure 7. [-OH, -NH] growth as a function of weathering.



**Unexposed System 150**



**22 months Florida exposure System 150**



**4000 hours "new" protocol System 150**

Figure 8. UV absorbance profiles v. depth.

### 5.3 Physical failures

Paint system 13 failed the paint adhesion test (X-scribe after water soak) following two years Florida exposure (Figure 9) with some separation of the basecoat from the e-coat.

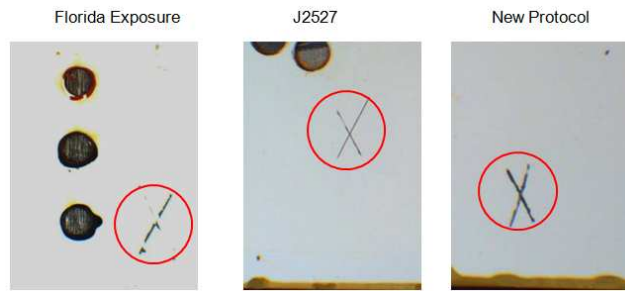


Figure 9. System 13 adhesion.

The same system similarly failed in the new protocol after 3000 kJ/m<sup>2</sup> @340nm but not in SAE J2527.

System 25 (Figure 10) failed by delamination of the basecoat from the e-coat after less than two years Florida exposure and the clearcoat contained numerous micro-blisters seen under optical microscopy (Figure 11).

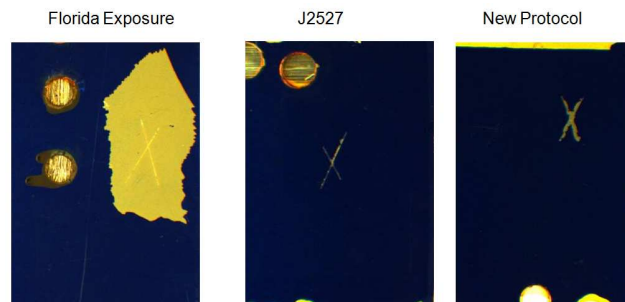


Figure 10. System 25 failure, new protocol.

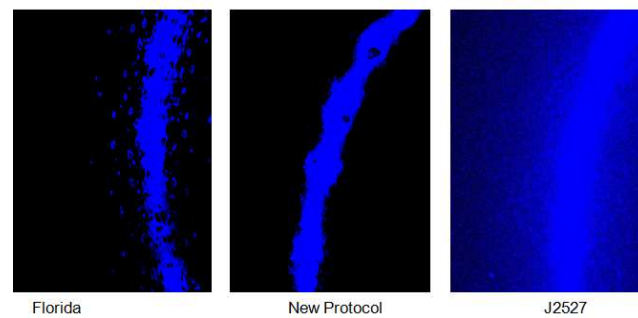


Figure 11. System 25 clearcoat micro-blisters.

The specimen tested in the new protocol also failed the adhesion test after 3000 kJ/m<sup>2</sup> @340nm and contained the Florida microblisters, while SAE J2527 showed less adhesion loss and did not contain microblisters.

System 97 (Figure 12) failed two years Florida with delamination and severe blistering of the clearcoat.



Figure 12. System 97 failure.

The same system in the new protocol also showed clearcoat delamination and blistering but SAE J2527 showed neither delamination failure nor blistering.

System 86 was a control sample which is known to perform well in Florida and also performed well in both accelerated weathering tests as shown in Figures 7 and 13.

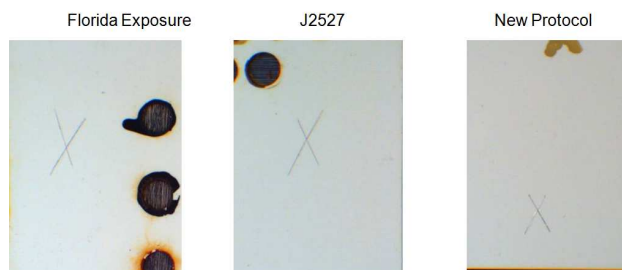


Figure 13. System 86 performed well in all tests.

System 103 (Figure 14) fails Florida and the new protocol with clearcoat delamination, blistering and gloss loss and the same in the new protocol, while SAE J2527 causes delamination and gloss loss but not blistering.

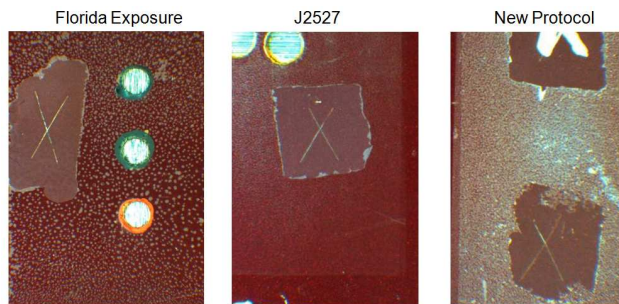


Figure 14. System 103 failure.

The inter-laboratory results showed excellent reproducibility in the results. Numerous other automotive coatings systems were tested similar to those detailed here. Those which performed well in Florida also performed well in the new protocol. Systems that failed by cracking in Florida also failed by cracking in the new protocol, but were not always correctly reproduced by SAE J2527. As automotive paint cracking failures do not photograph well they have not been included for illustration.

## 6. Test protocol discussion

To be of practical use an accelerated weathering test protocol must provide significant acceleration over the rate of natural weathering while still reproducing the chemical changes

If the accelerated test alters the degradation pathways or changes the chemistry, false positive or negative results may be obtained. This was a hard lesson learned with the introduction of the first automotive basecoat/clearcoat systems in which some of them, approved by accelerated testing, subsequently failed in the field with catastrophic delamination. This was a watershed event in accelerated testing showing that a fast test using conditions which didn't produce the same chemistry could prove misleading.

Most paint failures can be readily seen: gloss loss, color change, cracking and delamination can be visually detected. Therefore, an accelerated weathering test must not only produce the same chemical changes as the natural environment, but must also reproduce the appearance properties. Paint systems which crack during outdoor weathering should crack in the accelerated test and do so on a consistent time scale. Paint systems which perform well outdoors should perform similarly in the accelerated test at an equivalent exposure dose.

Unfortunately, no prior laboratory weathering tests have really achieved all of these goals, at least for high performance durable automotive coatings. Although the laboratory light sources used in artificial weathering have advanced from enclosed carbon arc (1915), to open flame "Sunshine" carbon arc (1933), through xenon arc (1954), the best accelerated weathering correlation was achieved using outdoor exposure with Fresnel type sunlight concentrators.

Until recently, none of the laboratory arc sources had the same SPD as sunlight, especially in the critical low-wavelength UV region which initiates most photochemical degradation. Most artificial accelerated weathering tests do not induce the same changes in natural weathering due to distortions in the degradation chemistry caused by an incorrect SPD of the light source.

However even the Fresnel exposure do not always reproduce the physical failures seen after natural exposure. This at least implies that there is more involved than only a good spectral match to sunlight. Prior work on automotive coatings and thermoplastic polymers has strongly suggested that this is due to the inadequate water absorption by the paint systems in the laboratory apparatus<sup>xxix</sup> compared to Florida exposure.

The newly developed test protocol seeks to address these two key issues of spectral match and water uptake. It should be noted that the conditions of the protocol described is likely not the only combination of radiation, temperature, moisture and time that will correctly reproduce the behavior of materials exposed in South Florida, and the method has been validated to date only for specific coatings systems. The test protocol described here is simply one reproducible and commercially implementable set of conditions that have been found to reproduce exposures in South Florida. However, small changes in the duration, frequency, and intensity of the water and temperature cycles will likely not significantly affect the test results.

### 6.1 Water absorption

Due to the high dew points in South Florida, coatings become covered with liquid water almost every night due to dew formation and are therefore regularly saturated with water. This contrasts with the water absorption which occurs during most standard accelerated weathering test methods. For example, the one hour water spray during the dark cycle of SAE J2527 only leads to approximately 22% of the saturation water content (Figure 2) in a typical paint system. The thermal-shock spray during the light cycle leads to only 11% of the saturation water content. Automotive paint failure mechanisms which depend strongly on water content include blistering and delamination and therefore may not be adequately reproduced without this saturation.

The newly developed protocol contains two relatively long water cycles to allow the test panels to approach saturation. The effects of the longer spray cycle in the new protocol compared to SAE J2527 are apparent in Figures 9, 10, 12 and 14. The water spray cycles of SAE J2527 (Table 1) and the new protocol (Table 2) can be visualized in Figures 15 and 16; graphs are compared on a ca. 50 hour time scale.

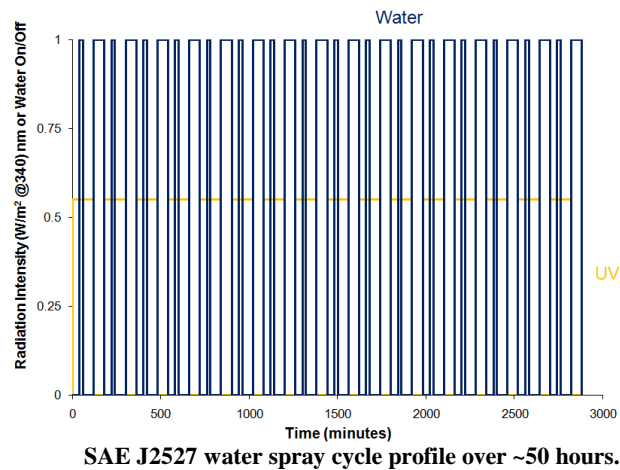


Figure 15. SAE J2527 water spray times during 50 hours.

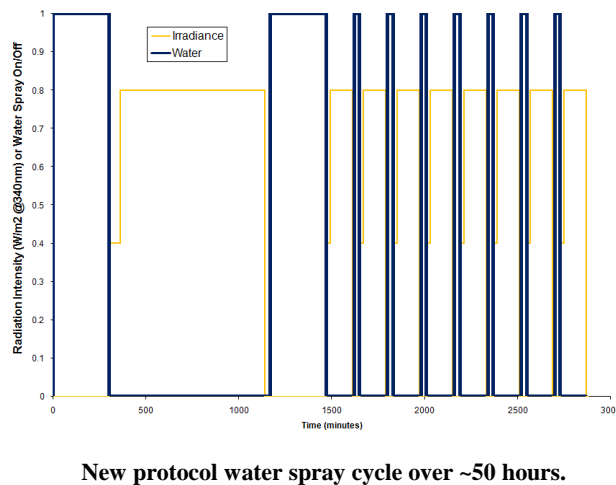


Figure 16. New protocol water spray times during 50 hours.

For System 25 (Figure 10), the expected failure mode was catastrophic delamination of the basecoat from the e-coat due to UV-induced degradation of the top of the e-coat (this scheme had no primer layer). However, the Florida samples also showed significant basecoat blistering prior to delamination. While both accelerated tests reproduced the delamination failure, only the new protocol correctly reproduced the micro-blisters seen in Florida (Figure 11). These blisters are thought to be the result of the interaction of water with a hydrophobic portion of the cured basecoat film.

System 97 (Figure 12) failed both Florida and the new protocol by clearcoat delamination and blistering but SAE J2527 did not show blistering and was inconsistent in delamination failure. Clearly, significant water penetration and absorption are required to disrupt the bonding between the clearcoat and the basecoat. The lower water absorption in SAE J2527 is insufficient to reproduce the Florida failures in this paint system.

System 103 (Figure 14) fails by clearcoat delamination of with massive blistering, as seen only in both the Florida and new protocol results. These several examples demonstrate the improved predictive capability of the protocol as compared to SAE J2527 and the importance that water plays.

## 6.2 Spectral match to sunlight

As described, the accelerated weathering light source should closely match the SPD of sunlight to avoid changing the degradation chemistry, especially in the low-UV region. Most durable coatings intrinsically absorb very little UV, however even small amounts of absorption, including by impurities, can affect durability due to the free radical nature of degradation

in most coatings (Figure 17). The formation of free radical species by low wavelength UV not present in sunlight can result in changed chemistry.

If the coating absorbs where both the light source and sunlight spectra are the same, the differences in photochemical degradation will be minimal. But, when the SPD match to sunlight is poor, significant alterations to the photochemical mechanisms can occur. This can be seen with the polyester-urethane automotive clearcoat (Figure 6). The absorption tail of this coating overlaps with the UV cut-on wavelength for the SAE J2527 “daylight” (Figure 4, Borosilicate-S type filters) which is below that of sunlight. This produces significant degradation in SAE J2527 and other test methods where the UV cut-on occurs at an unnaturally low wavelength. This is why, for example, the ISO and ASTM standards caution against the use of light sources which are not a good spectral match to sunlight.

When the solar cut-on is correctly reproduced, as with Fresnel-type sunlight concentrators or the new xenon lamp filters used in the new protocol, the degradation is correctly reproduced. This is shown in Figure 6 where the slopes of the curves are very close for the polyester-urethane (control) clearcoat exposed in outdoors in Florida and Arizona, Fresnel concentrator and with the new protocol. This clearcoat system exhibits excellent Florida weatherability but will crack prematurely due to significant photooxidation when accelerated laboratory tested in apparatus with traditional “daylight” filters (e.g., Borosilicate-S type) as in SAE J2527.

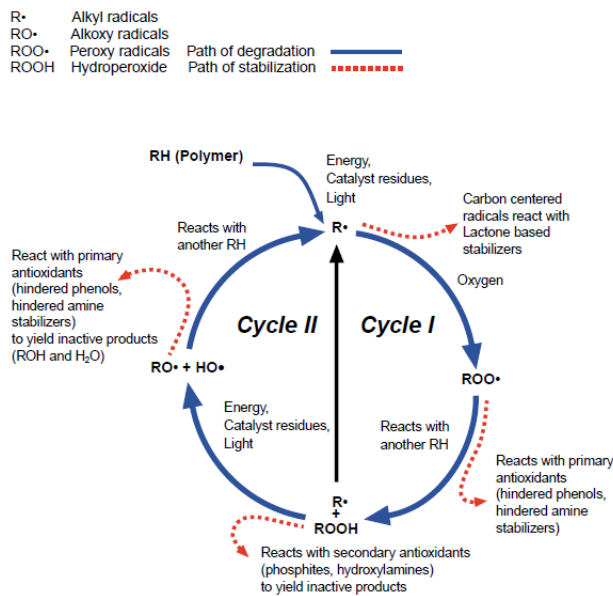


Figure 17. Typical free radical autooxidation cycle pathways.

The alternative to using a light source with an accurate spectral match to sunlight is to measure the absorption or action spectrum of a coating or system (Figure 18) and then expose the coating to only that wavelength of light to drive the correct photochemistry. However this is very impractical as the absorbing species are usually present in very low concentrations making their measurement difficult. This would also require individual spectral conditions for each specimen chemistry type, which makes it impractical as a general test method in commercial apparatus.

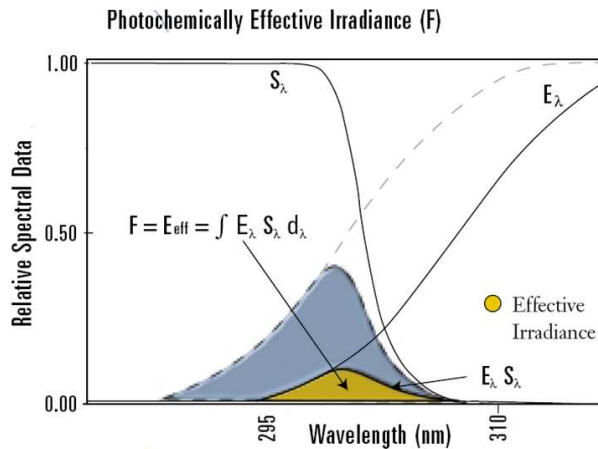


Figure 18. Relationship between spectral irradiance and spectral sensitivity. The area under both curves is the “effective” irradiance ( $E_{\text{eff}}$ ),  $E_{\lambda}$  is the spectral irradiance and  $S_{\lambda}$  is the spectral sensitivity of the material.

System 13 (Figure 9) is a paint system whose failure is strongly governed by UV absorption. The underlying electrocoat has a strong and broad absorption peak up through 400nm so the exact UV cut-on of the light source will not as strongly influence its degradation. Rather, its lifetime is mostly a function of the UV transmissivity of the basecoat/clearcoat layers where small differences in film thickness can lead to significant differences in failure time. This can be seen in System 13 (Figure 9) where a small amount of adhesion loss is seen in the Florida and new protocol exposures but surprisingly not seen in the SAE J2527 exposure. However, with the SAE J2527 specimen the film thicknesses of the basecoat and clearcoat are slightly higher (as measured) leading to less UV dose to the electrocoat and a lower photodegradation rate. Therefore, one must guard against broad conclusions without ensuring that equivalent specimens have been used for all tests.

### 6.3 Cyclic conditions

The water spray and irradiation cycles in the new protocol are the result of an extensive iterative approach to design a new accelerated weathering protocol. The many incremental iterative steps to the final protocol are not detailed and were guided by the expected versus obtained failure modes for a variety of paint systems, only a few of which are described here.

As previously described, deep water penetration is required to reproduce the adhesion and blistering failures. Unless the coating system approaches saturation it may not display the proper adhesion loss or blistering as Florida exposure. Other researchers conducting proprietary work on various organic coatings, polymeric films, and other organic materials have reported significantly improved correlation to South Florida weathering by substantially increasing water delivery in accelerated weathering tests, including Fresnel concentrator exposures.

To produce the necessary water uptake in the accelerated test it would seem obvious to reproduce the long Florida overnight wetting with very long spray cycles, but this is problematic. First, the protocol would require large quantities of relatively expensive deionized water. Secondly, with long dark spray times test acceleration would be diminished since the light cycle photooxidative degradation would be retarded.

Initial test protocol experimentation began with long alternating twelve hour dark spray and light only cycles, using the new xenon lamp filters with the correct SPD (at a higher irradiance of  $0.75 \text{ W/m}^2$  @340nm than SAE J2527). However, this did not produce the correct physical failures in some paint systems. Systems which failed by blistering and delamination in Florida also failed by the same mechanisms with this cycle, but those that failed by cracking, either stress induced or weathering induced, did not appropriately fail. This cycle did not sufficiently fatigue specimens to cause cracking failures.

Using an extensive set of paint systems which failed via different modes in South Florida testing, the protocol cycles were adjusted after each round of testing. Insufficient adhesion or blistering failures led to longer dark spray cycles while insufficient cracking led to more frequent short water cycles. After successive iterations the balance between long and short water cycles and long and short light cycles was developed. This produced a high quality match to the behavior of multiple paint systems exposed in South Florida. The resulting protocol is described in Table 3 and Figure 16.



Importantly, the frequency of the temperature and wet/dry cycles also scales approximately with Florida exposures. On an annualized average, panels exposed in Florida (5° south facing, unbacked) receive 8.4 kJ/m<sup>2</sup> @340nm solar radiation per day. Florida panels go through one wet/dry cold/hot daily cycle which produces cyclic fatigue stresses into the paint system due to mismatches in moisture absorption and thermal expansion coefficient between the coating and the substrate. SAE J2527 exposure only produces ca. 3.9 kJ/m<sup>2</sup> @340nm per 3 hour cycle due to the short, frequent steps used (Table 1 and Figure 15). By contrast, the new protocol results in 8.8 kJ/m<sup>2</sup> @340nm per cycle, very near the Florida value. This scaling also improves the correlation between Florida and the new protocol for paint systems prone to cracking.

#### 6.4. New protocol test acceleration

The rate at which degradation is accelerated is one of the main factors to assess accelerated weathering test, provided, of course, that correlation with natural weathering is preserved. A fast test that produces unreliable results is of no value.

The FTIR [-OH, -NH] ratio method previously described has proven a sensitive means of quantifying a coating's degradation. Concentrating on this region of the IR spectrum avoids complications with other analytical techniques such as carbonyl index, which can change in a complex manner in urethane and other coatings<sup>xxx</sup>. The use of a failure-based metric to quantify the degradation rate is also difficult, as some failures occur suddenly with little warning or are difficult to monitor over time. For systems without a clearcoat, gloss loss provides a reasonably reliable and convenient method for assessing durability and degradation rate.

The degradation rate for some of the coatings is shown in Figure 7 in which the [-OH, -NH] region of the IR spectrum is plotted as a function of radiant energy dose (@ 340nm). In System 13, for example the rate of degradation for both SAE J2527 and the new protocol is approximately the same on a *dose* basis as indicated by the slopes. The Δ[-OH, -NH] value of the coating is approximately 1.0 after about 1700 kJ/m<sup>2</sup>@ 340nm exposure. The rate of degradation in Florida is less than one-half of either accelerated test with Δ[-OH, -NH] = 1.0 after 4300 kJ/m<sup>2</sup>@ 340nm. However, as both the irradiance and proportion of time spent in the light cycle is higher for the new protocol, the rate of degradation on a *time* basis is substantially faster than with SAE J2527.

Averaging all of the paint systems examined, the new protocol reaches the same level of chemical degradation approximately 40% faster than SAE J2527 (Borosilicate-S type "daylight" filters), leading to a chemical degradation acceleration factor of approximately 10X over South Florida exposure.

#### 6.5 Positive controls

Paints systems which fail South Florida must exhibit the same mechanisms in the accelerated test. Conversely, systems that perform well in natural Florida exposure with little chemical degradation must also perform similarly in the accelerated test to avoid false negative results. Tests must correlate without false positive or false negative results.

Paint System 86 (Figure 12) was a control sample which performs well in Florida and undergoes little chemical change in both the outdoor test and accelerated weathering (Figure 6). This system also shows no failure in the new protocol and numerous other control paint systems have performed as expected in the new protocol.

#### 6.6 UVA longevity

Both hindered amine light stabilizers (HALS) and ultraviolet light absorbers (UVA) are added to all modern automotive paint systems to improve long term weatherability. During aging both of these additives are consumed or lost due to various photochemical and physical processes. This can be seen in Figure 7 for System 150 where the UV absorber is depleted near the surface following natural and new protocol weathering. The post-weathering concentration gradients were similar, the main difference being the somewhat shallower gradient and higher overall UVA loss in the new protocol at 4000 kJ/m<sup>2</sup> @340nm compared to the Florida specimen at 22 months. The UVA was consumed at the coating's surface and a gradient was formed from the top surface down into the bulk. A coating's surface typically experiences a higher loss rate, not from exudation or evaporation of the UVA but rather due to the higher rate of photooxidation there. The higher photooxidation rate is due to the UVA's inability to protect the absolute surface of the coating as a consequence of the Beer-Lambert Law when the path length goes to zero.

The attack on the UVA by free radicals is thought to be the primary mechanism for this UVA depletion. The gradient is generated and then maintained, as most UVAs do not possess sufficient mobility in weathered coatings to diffuse any appreciable distance. The loss rate of these additives under accelerated weathering does not typically scale by the same factor as the chemical degradation; the reasons for this are not clear.

For example, the UVA concentration data shown for System 150 (Figure 8) is approximately 2X as degraded, as measured by [-OH, -NH] growth, after 4000 kJ/m<sup>2</sup> @340nm as the 22 month Florida sample. The rate of a coating's degradation is a sum of all the photochemical, hydrolytic and thermal oxidative degradations. As the latter two do not significantly affect the stabilizer additives their effects are not as easily accelerated as those from photooxidation. Other reasons for the inability to completely accelerate UVA consumption to the same extent as chemical degradation or physical failures have not been determined.

The inconsistent correlation of accelerated weathering results with that of South Florida has been problematic. Coatings that perform well in accelerated testing have failed in service prematurely while others, whose

## 7. Conclusions

A new accelerated weathering test protocol has been developed that correctly anticipates almost all failure modes observed in South Florida exposed coating systems. Further, the new protocol is about 40% faster than the current state-of-the-art accelerated weathering testing for automotive coatings system, SAE J2527. This protocol was developed and validated using an established test method development process. Prior studies were conducted (prescreening) to establish the lack of spectral sunlight match and moisture delivery with the existing test methods to be source of test bias.

The new protocol's improved correlation is based on using a light source with an excellent match to terrestrial sunlight, particularly in the short wavelength UV region of the spectrum. This drives the correct photochemistry in automotive paint systems, which enables the use of higher irradiance to increase test acceleration. This improved spectral match has also been validated with improved correlation to South Florida for a variety of engineering thermoplastics<sup>xxx1</sup>.

The correct physical failures are induced by ensuring that the paint systems are subjected to high amounts of liquid water, thus enabling water absorption near saturation levels. This has been shown to be crucial to reproducing adhesion and blistering failures in paint systems that experience those failure modes in South Florida.

The failure of paint systems by cracking in Florida exposure is also correctly reproduced by the new protocol with the inclusion of several short hot/cold, dry/wet stress cycles. This correctly scales the stress cycle to the UV dose during a diurnal cycle in Florida. Systems that demonstrate no failures after Florida exposure also perform well in the new test protocol. This new test protocol offers improved accuracy and reduced testing time that will be beneficial to paint formulators and coating users to reduce product development time and reduce the risk of premature failures of paint systems.

Although the protocol has been validated only for a variety of automotive coatings systems, the frequent inconsistency of chemical and physical degradation in accelerated test methods when compared to South Florida has been seen with other coatings systems and the new test protocol may provide substantial improvement in test correlation for these coatings as well. At a minimum, the test development and validation methodology described may serve as a blueprint for developing other accelerated test methods to predict coating and other material performance in climate zones other than subtropical South Florida.

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