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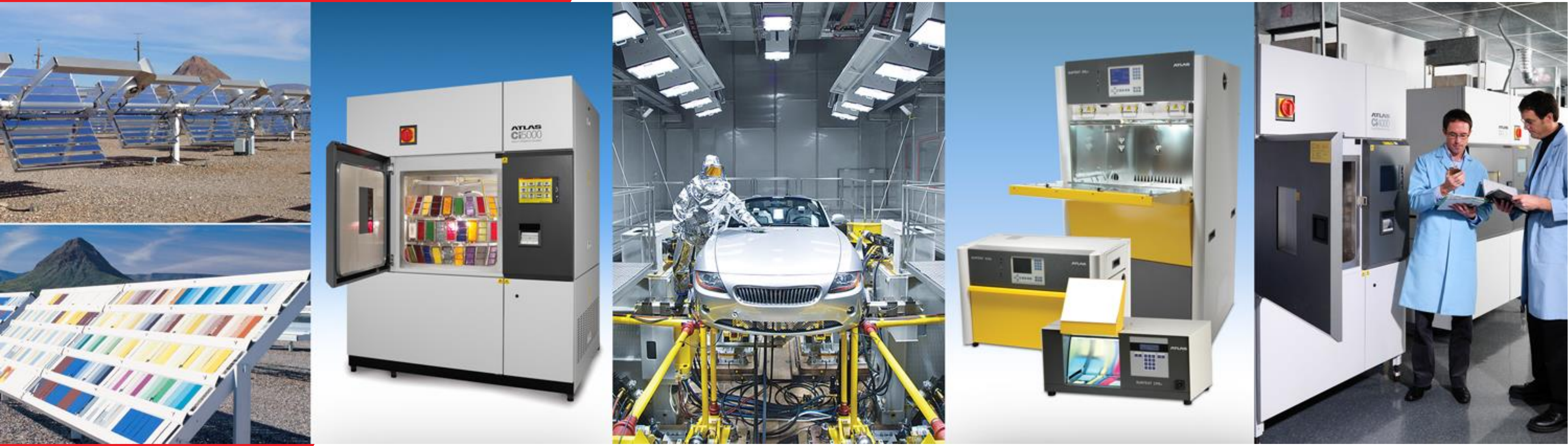

Thermal Cycling/Water Spray, ASTM D7869 A Better Laboratory Approach to Climate Simulation

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Thermal Cycling/Water Spray, ASTM D7869 A Better Laboratory Approach to Climate Simulation

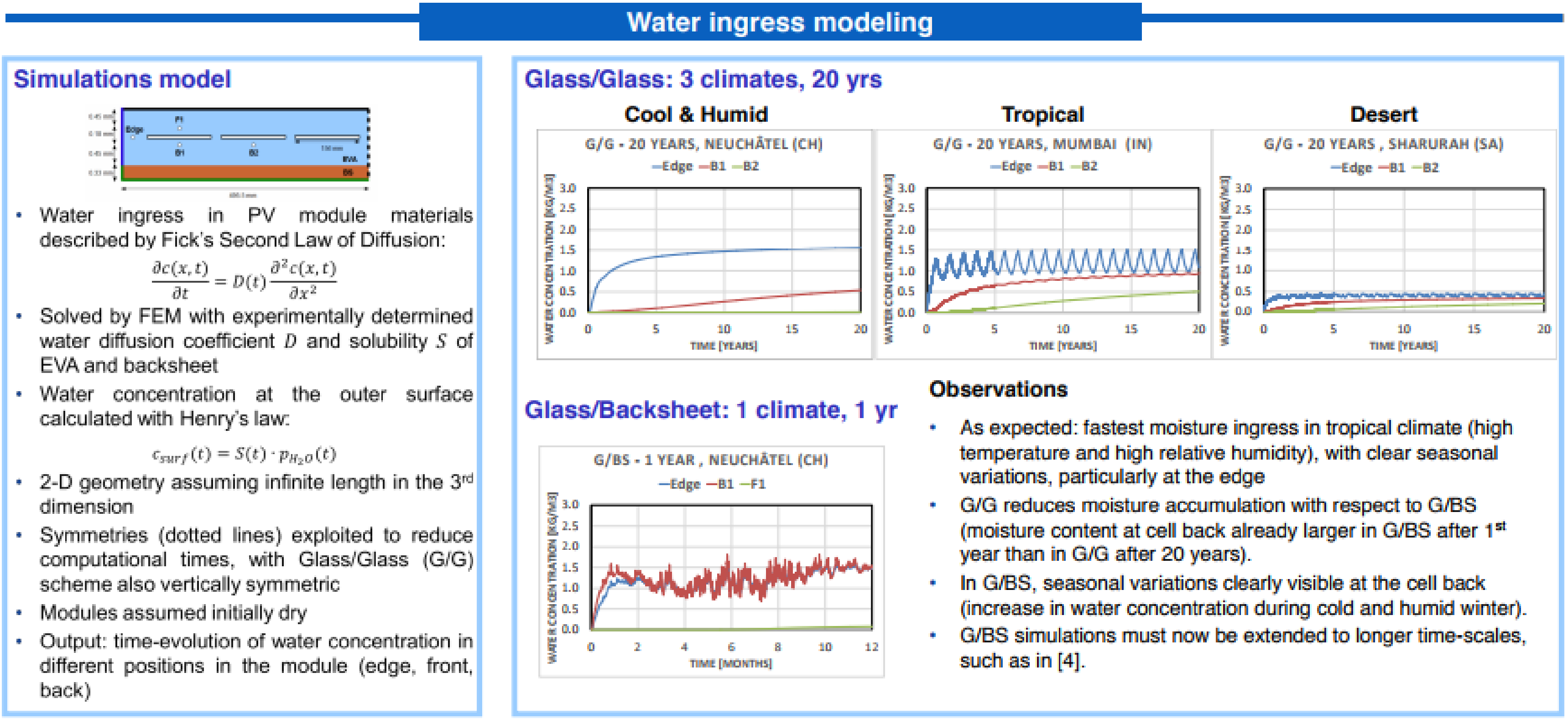
4th Atlas-NIST Workshop on PV Materials Durability
NIST, Gaithersburg, MD USA. 5-6 December, 2017

Allen Zielnik
Global Applications Manager

Moisture ingress in modules

"Water concentration inside PV modules was simulated for different climates and encapsulation schemes:

- As expected, tropical climate induces fastest water ingress, however cool & humid climate also features high water content after 20 years
- G/BS after 1 year already shows higher water content than G/G after 20 years"



Water ingress modeling

Simulations model

- Water ingress in PV module materials described by Fick's Second Law of Diffusion:

$$\frac{\partial c(x,t)}{\partial t} = D(t)\frac{\partial^2 c(x,t)}{\partial x^2}$$

- Solved by FEM with experimentally determined water diffusion coefficient D and solubility S of EVA and backsheet
- Water concentration at the outer surface calculated with Henry's law:

$$c_{surf}(t) = S(t) \cdot p_{H_2O}(t)$$

- 2-D geometry assuming infinite length in the 3rd dimension
- Symmetries (dotted lines) exploited to reduce computational times, with Glass/Glass (G/G) scheme also vertically symmetric
- Modules assumed initially dry
- Output: time-evolution of water concentration in different positions in the module (edge, front, back)

Glass/Glass: 3 climates, 20 yrs

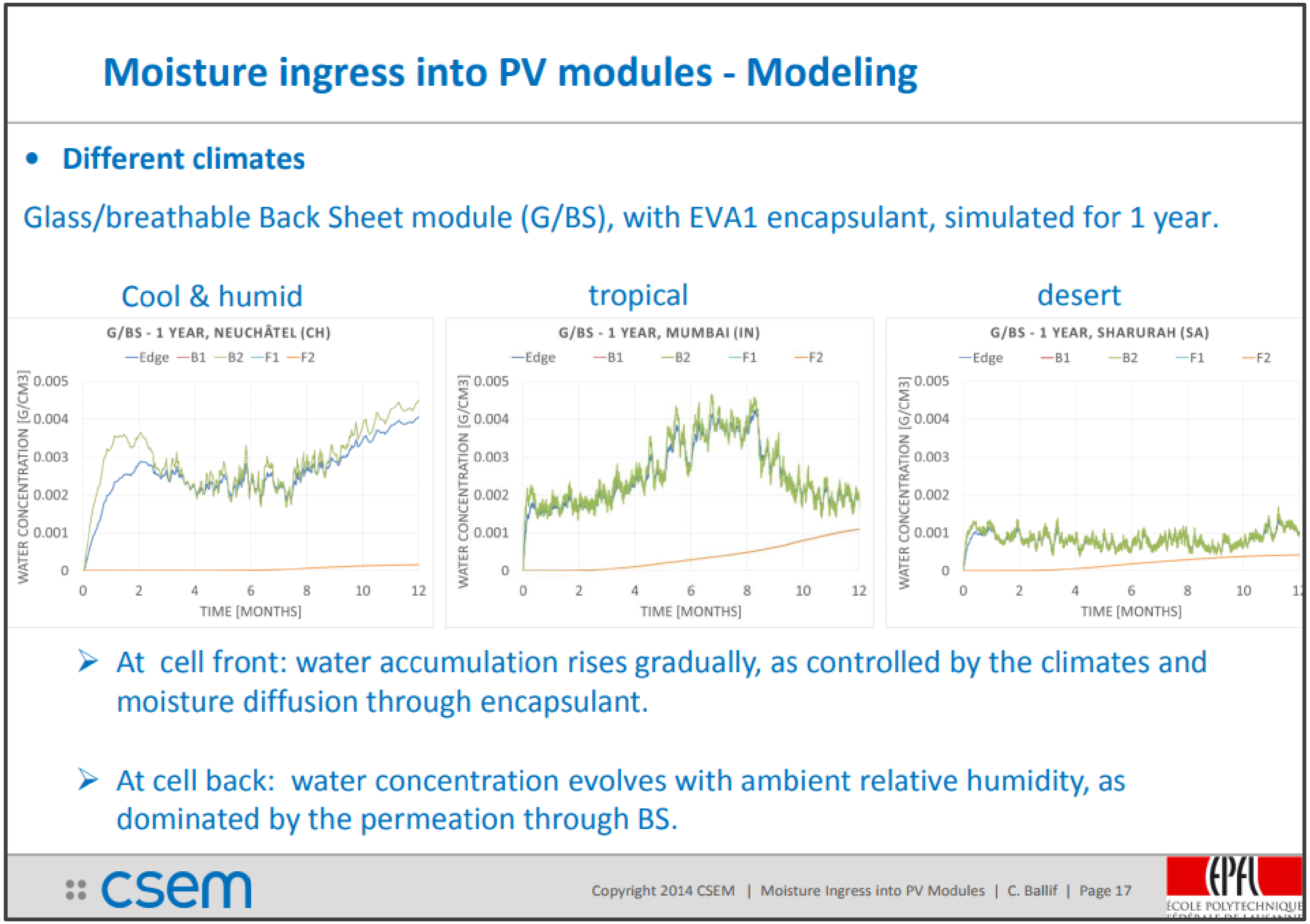
Glass/Backsheet: 1 climate, 1 yr

Observations

- As expected: fastest moisture ingress in tropical climate (high temperature and high relative humidity), with clear seasonal variations, particularly at the edge
- G/G reduces moisture accumulation with respect to G/BS (moisture content at cell back already larger in G/BS after 1st year than in G/G after 20 years).
- In G/BS, seasonal variations clearly visible at the cell back (increase in water concentration during cold and humid winter).
- G/BS simulations must now be extended to longer time-scales, such as in [4].

Eleonora Annigoni, Federico Galliano, Marko Jankovec, Heng Yu Li , Laure-Emmanuelle Perret-Aebi, Christophe Ballif , Fanny Sculati-Meillaud, **Moisture ingress into PV modules: long-term simulations and a new monitoring technique;** 2015_pvmrw_27_annigoni.pdf

Moisture ingress in modules



Moisture ingress into PV modules - Modeling

- **Different climates**

Glass/breathable Back Sheet module (G/BS), with EVA1 encapsulant, simulated for 1 year.

Cool & humid | tropical | desert

- At cell front: water accumulation rises gradually, as controlled by the climates and moisture diffusion through encapsulant.
- At cell back: water concentration evolves with ambient relative humidity, as dominated by the permeation through BS.

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Copyright 2014 CSEM | Moisture Ingress into PV Modules | C. Ballif | Page 17

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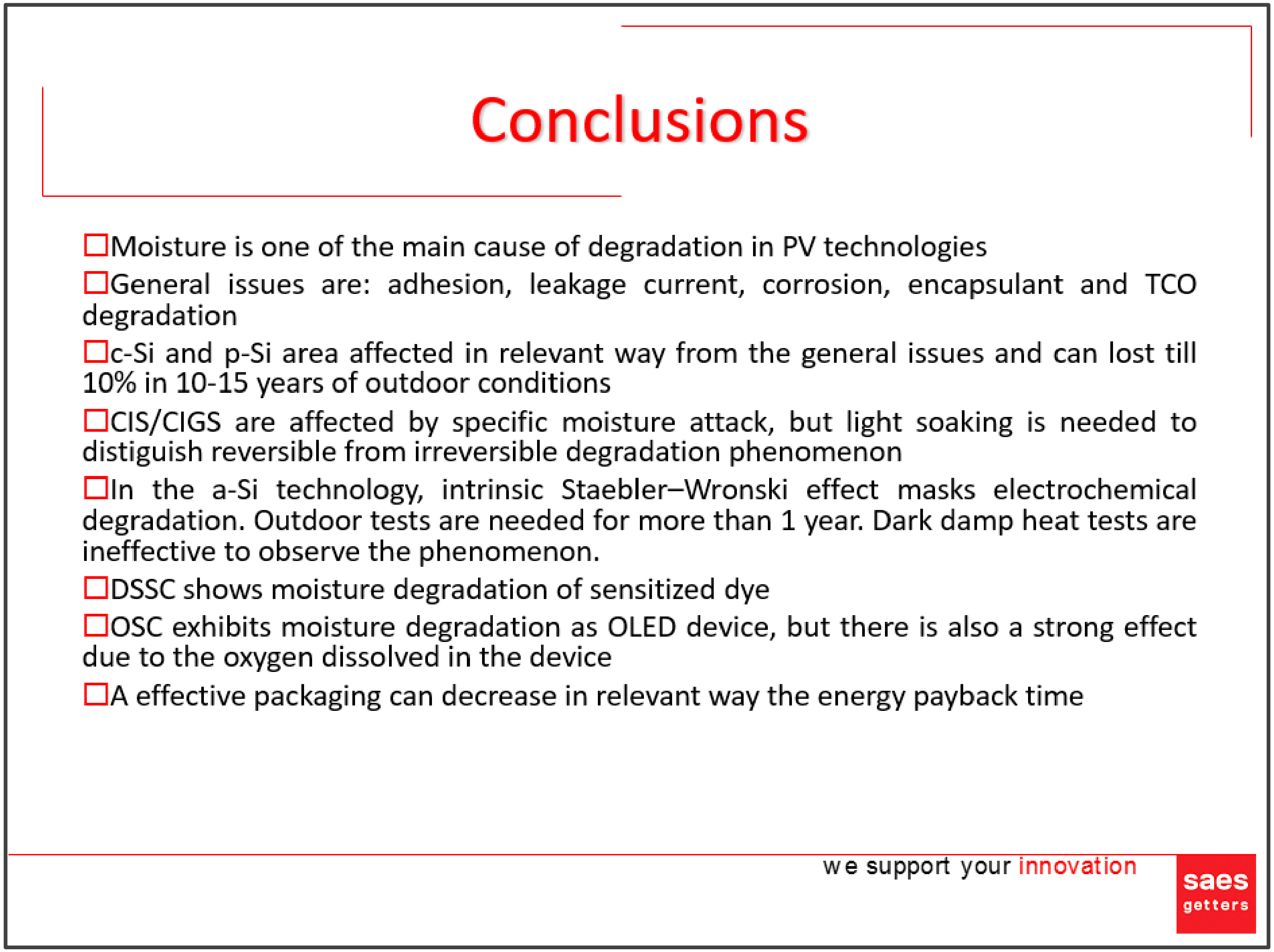
- C. Ballif, H.-Y. Li, E. Annigoni, F. Galliano, J. Escarré, F. Meillaud, L.-E. Perret, **Impact of moisture ingress in PV modules on long-term performance: the role of EVA formulation, module design and climate,** pv_modulworkshop/pv_modulworkshop_2014/23_Ballif_Impact_of_Moisture_Ingress_in_PV_Modules.pdf

Moisture effects in modules



Conclusions

- ☐Moisture is one of the main cause of degradation in PV technologies
- ☐General issues are: adhesion, leakage current, corrosion, encapsulant and TCO degradation
- ☐c-Si and p-Si area affected in relevant way from the general issues and can lost till 10% in 10-15 years of outdoor conditions
- ☐CIS/CIGS are affected by specific moisture attack, but light soaking is needed to distiguish reversible from irreversible degradation phenomenon
- ☐In the a-Si technology, intrinsic Staebler–Wronski effect masks electrochemical degradation. Outdoor tests are needed for more than 1 year. Dark damp heat tests are ineffective to observe the phenomenon.
- ☐DSSC shows moisture degradation of sensitized dye
- ☐OSC exhibits moisture degradation as OLED device, but there is also a strong effect due to the oxygen dissolved in the device
- ☐A effective packaging can decrease in relevant way the energy payback time

we support your innovation

saes getters

A. Bonucci, S. Rondena, G.Longoni, **Moisture as main degradation cause in photovoltaic technology;** Bonucci_AIV_09_Moisture as main degradation factor in PV.pdf

Moisture effects in modules

- “Moisture can diffuse into photovoltaic (PV) modules through their breathable back sheets or their ethylene vinyl acetate (EVA) sheets. When in service in hot and humid climates, PV modules experience changes in the moisture content, the overall history of which is correlated with the degradation of the module performance. If moisture begins to penetrate the polymer and reaches the solar cell, it can **weaken the interfacial adhesive bonds**, resulting in **delamination** and increased numbers of ingress paths, **loss of passivation**, and **corrosion of solder joints.**
- Of these possibilities, the occurrence of corrosion has one of the highest frequencies in outdoor-exposed PV modules. Significant losses in PV module performance are caused by the **corrosion of the cell**, that is, the SiNx **antireflection coating**, or the **corrosion of metallic materials**, that is, **solder bonds and Ag fingers.** Corrosion is defined as the destructive chemical or electrochemical reaction of a metal with its environment. The moisture from the environment may lead to electrochemical reactions that can result in corrosion.
- As mentioned above, **PV modules are degraded by ambient temperature and humidity**; moreover, these factors can accelerate the degradation. This degradation is mainly caused by corrosion. It can be assumed that the temperature of a PV module is uniform; **however, moisture concentration in a PV module is not uniform. Therefore, it is difficult to predict moisture-induced degradation**

N.C. Park, W.W. Oh, D.H.Kim, **Effect of Temperature and Humidity on the Degradation Rate of Multicrystalline Silicon Photovoltaic Module**, International Journal of Photoenergy, Volume 2013, Article ID 925280

Climate relationship to moduledegradation

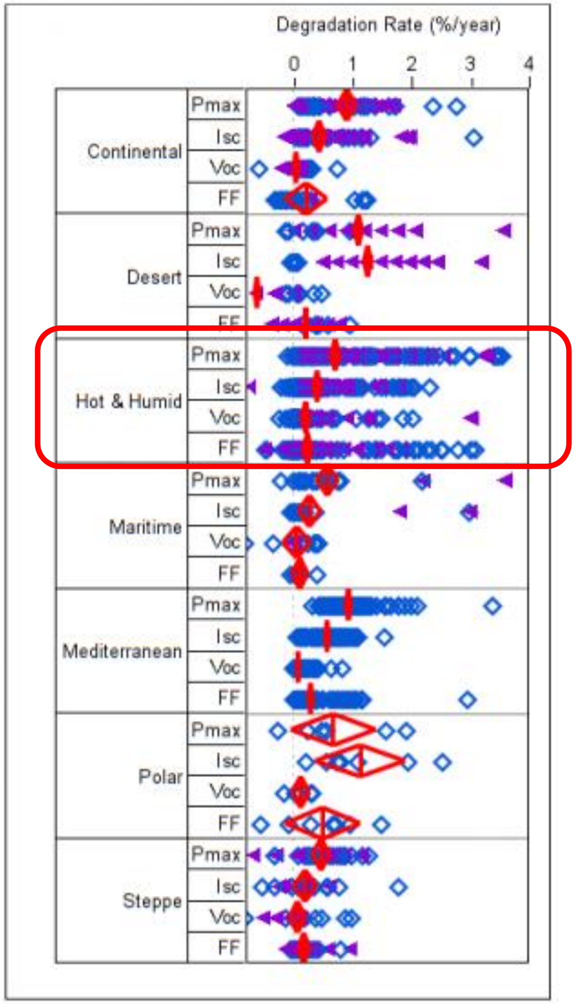
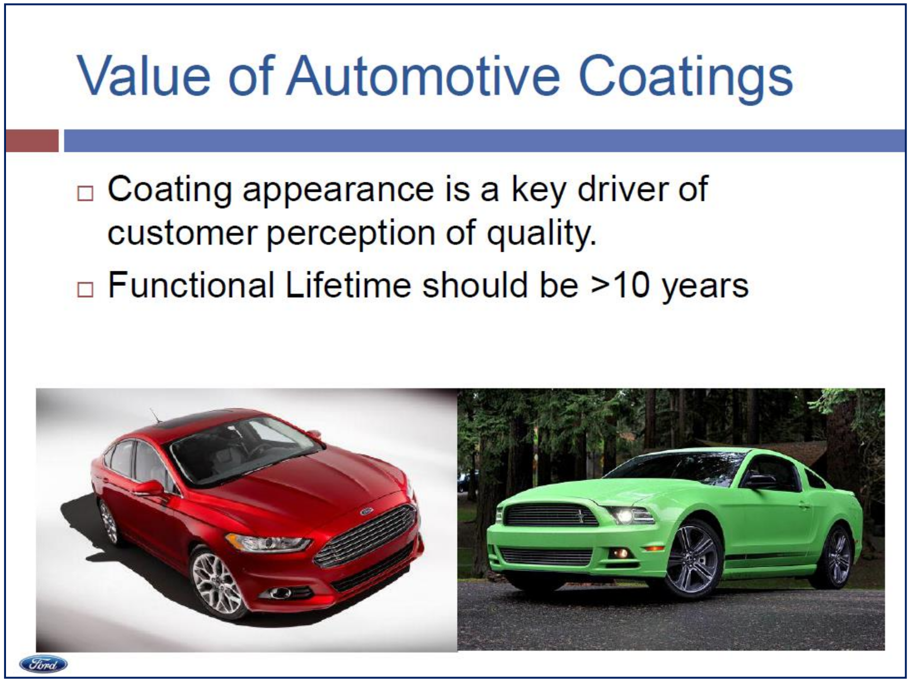


Figure 6: IV parameter degradation for mono-Si (open diamonds) and multi-Si (filled triangles) by climate zones based on Köppen-Geiger classification. The 95% confidence interval is denoted by the diamonds with the mean as the crossbar.

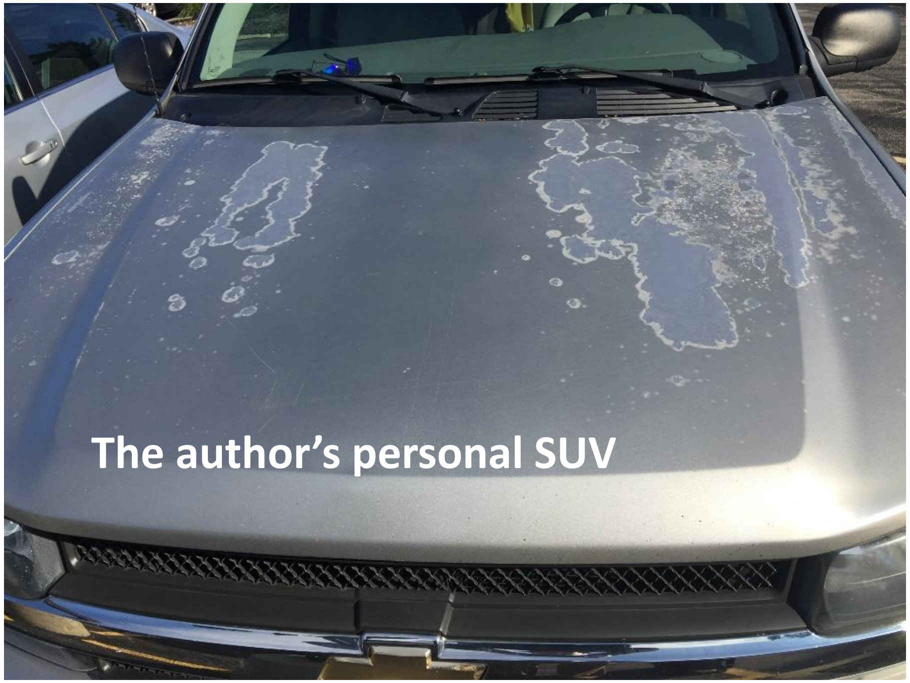
D.C. Jordan, J.H. Wohlgemuth, S.R. Kurtz, **Technology and Climate Trends in PV Module Degradation (Preprint),** 27th European Photovoltaic Solar Energy Conference an Exhibition, September 2012, Conference Paper NREL/CP-5200-56485 October 2012

Paint Sells Cars. . . or Not!



Value of Automotive Coatings

- Coating appearance is a key driver of customer perception of quality.
- Functional Lifetime should be >10 years



The author's personal SUV

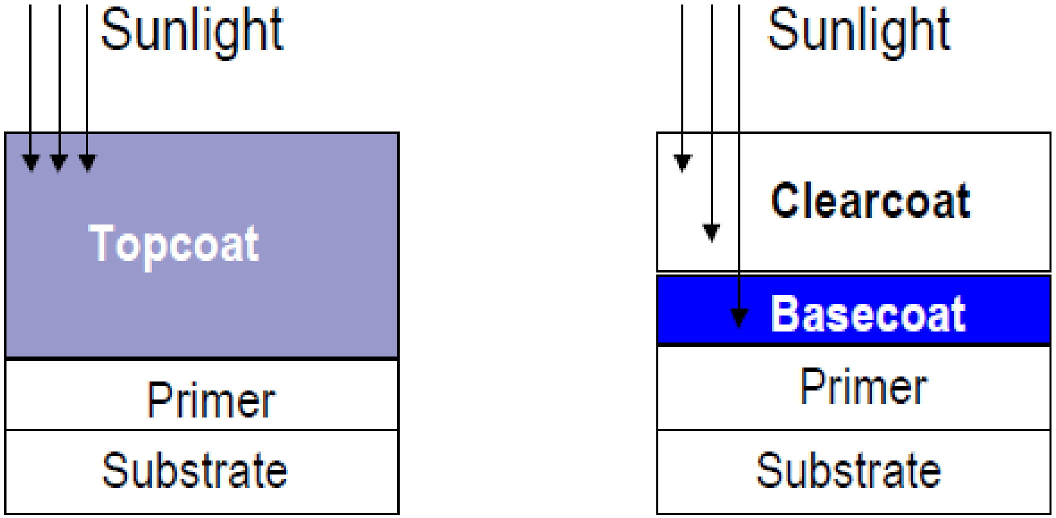
M.Nichols, *et al*, **Accelerated Weathering of Automotive Coatings: Exposure Conditions and Analysis Methods**, Atlas Technical Conference on Ageing in the Environment, Oxford, UK, September, 2008.

Must Reduce the Risk to an Acceptable Level

Even a poor performing paint system will last 2 years or more; that can mean production of 520,000 – 940,000 vehicles from a single plant before you even realize there is a problem.

Transportation Coatings

Monocoat and Clearcoat/Basecoat paint systems are fundamentally different.



Pigment restricts photo-degradation to surface.

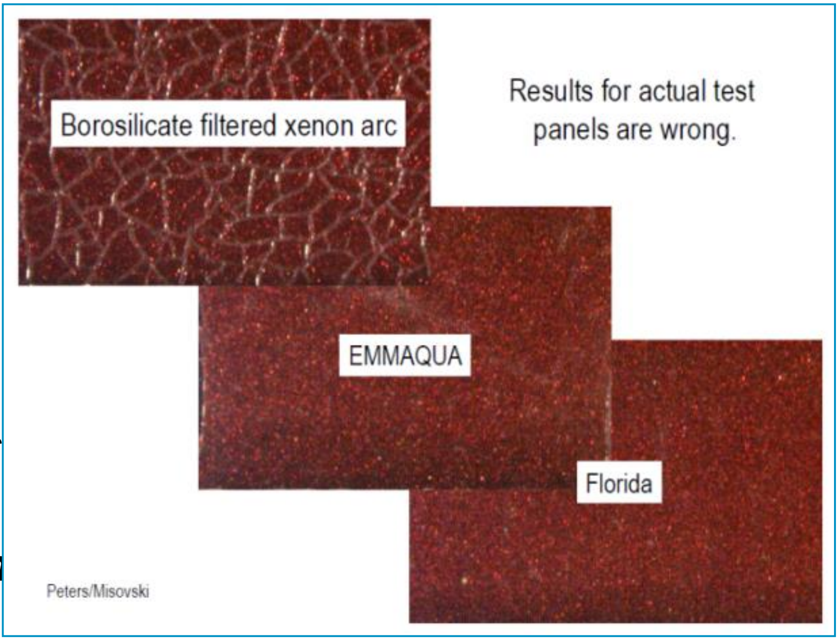
Gloss reveals much about the weathering performance.

Photo-degradation need not be restricted to surface.

Gloss need not reveal weathering performance.

15 Years of basic automotive paint research

- Following **catastrophic failures** of early basecoat/clearcoat (BC/CC) paint systems, Ford led a decade of scientific research into paint weathering failures and why lab tests didn't predict them.
- Key findings:
  - *EMMAQUA caused the <u>same chemical changes</u> as 5-year outdoor weathering, but lab light source tests did not;* ***spectral*** *differences suspected, particularly UV cut-on λ*
  - *All lab tests and cycles did not mimic outdoor* ***diurnal (daily) cycle in moisture or temperature, nor reach outdoor levels***
  - *Lab tests provided* ***inadequate moisture*** *wet time as compared to South Florida, including short water sprays onto* ***hot*** *samples while at full irradiance*
- **This led to the formation of a multi-participant consortium plus *another* 5 years of research and empirical method development (trial and error approach) and validation, resulting in ASTM D7869.**

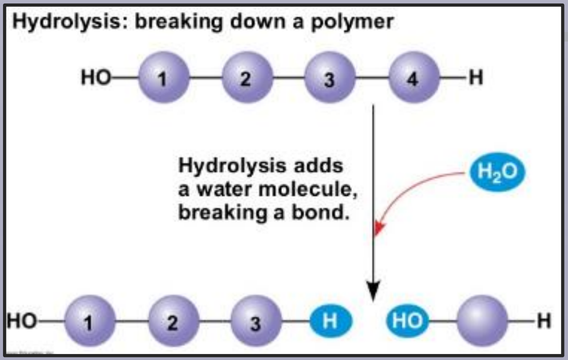


Peters/Misovski

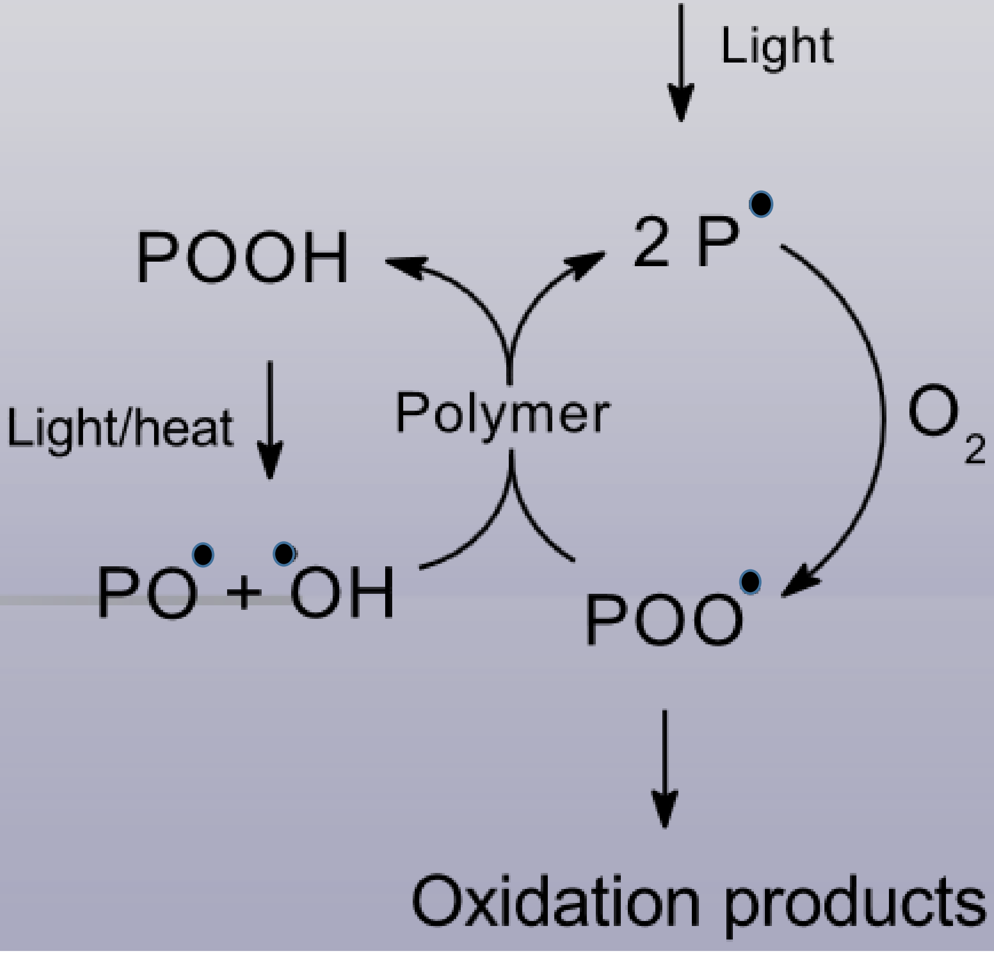
Autocatalytic Photooxidation Pathway

Light (UV) initiates process, subsequent free radical chemistry is driven by heat

This chemistry drives changes in physical properties. Environmental stresses placed upon the paint system then cause the systems to eventually fail.

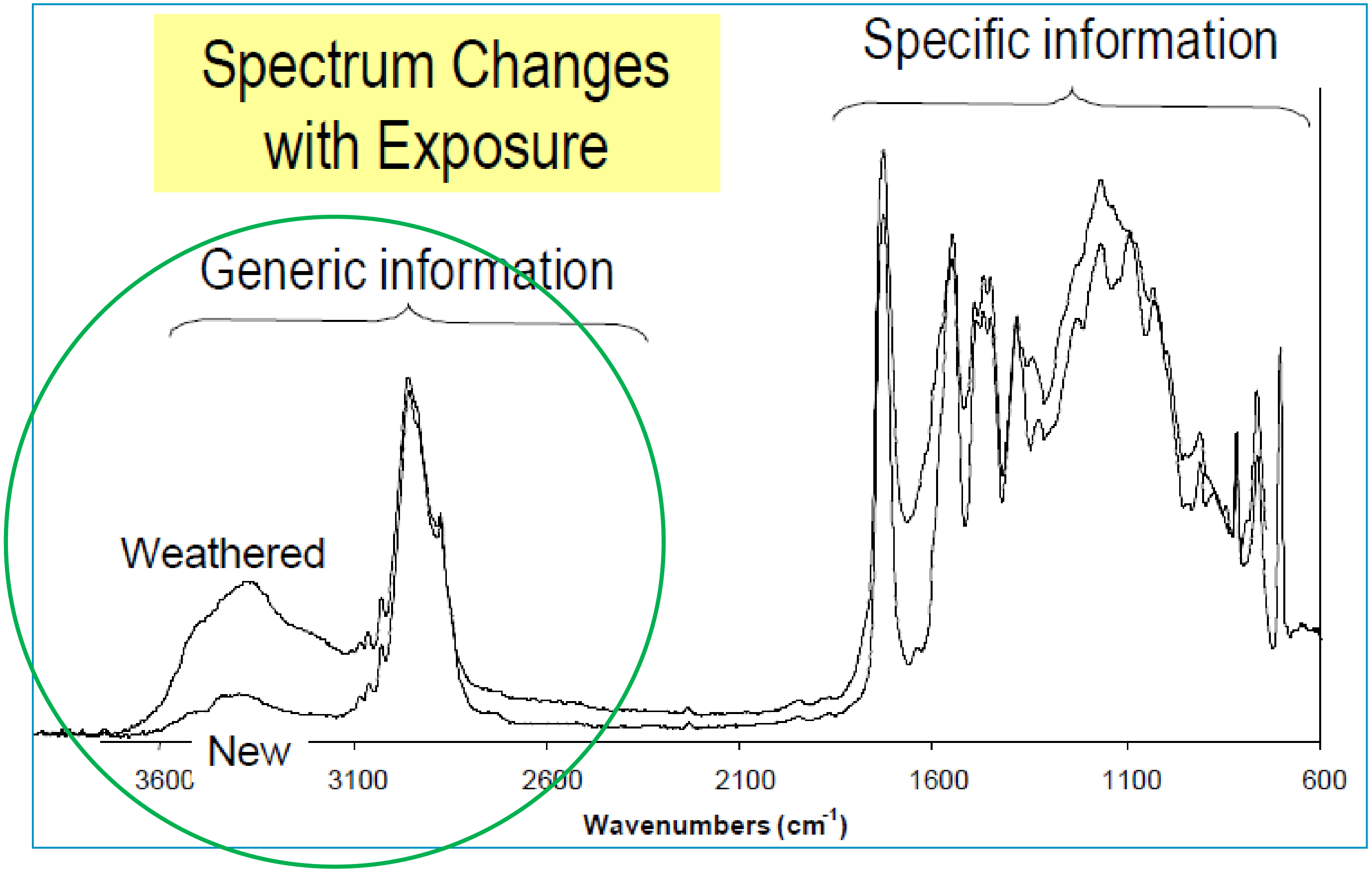


Hydrolysis: breaking down a polymer



Hydrolysis reactions often occur in exposed coatings in addition to photooxidation.

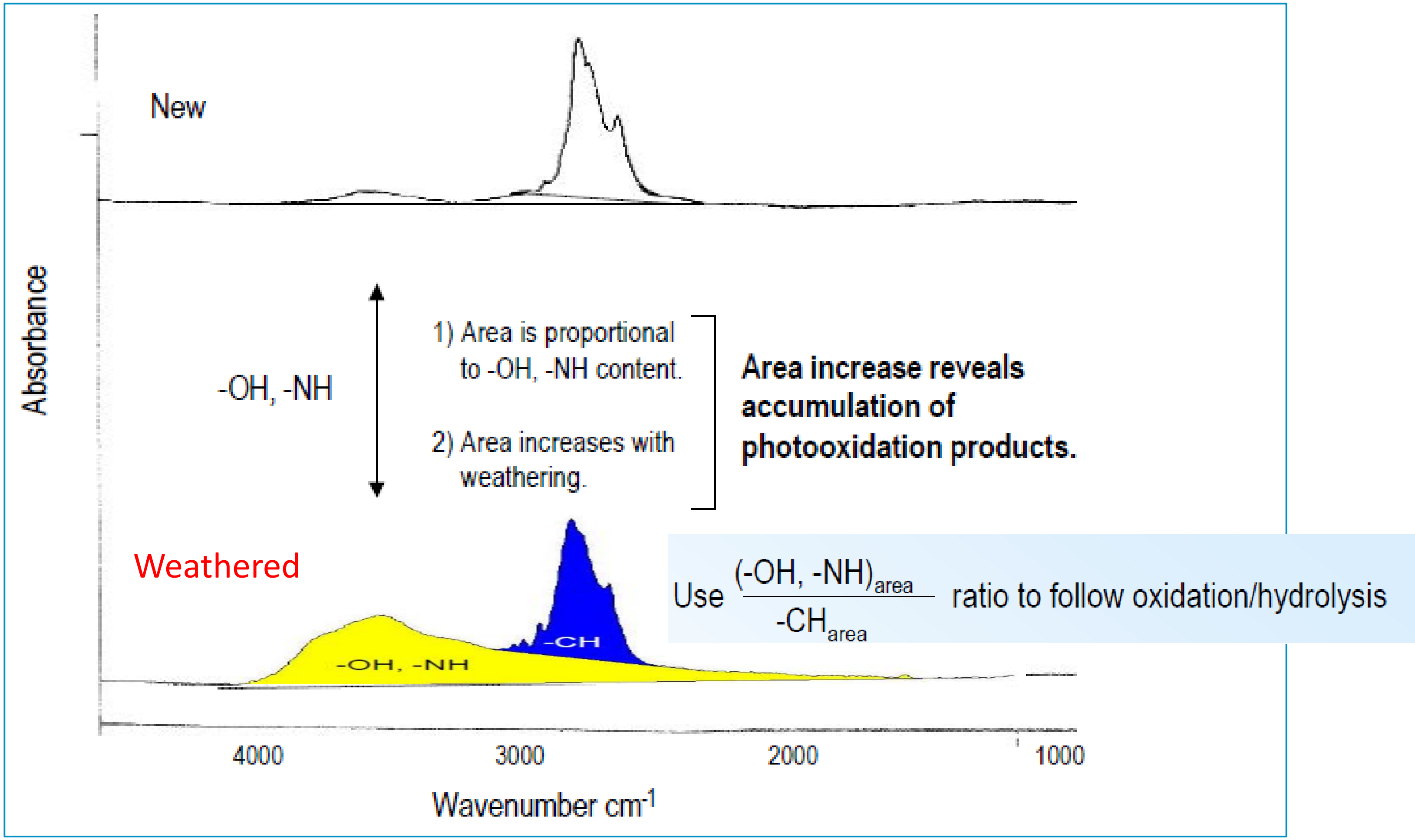
Detecting Chemical Changes via FTIR



To compare the weathering behavior of coatings from different chemical families (acrylic-melamine, acrylic-urethane, etc.) – compare changes in the generic region of the FTIR spectra (2600cm^{-1} – 3800 cm^{-1}).

Source: M.Nichols, *et al*, "Test Methods to Determine the Long Term Weathering Performance of Coatings Systems – Chemical and Mechanical Testing of Paint Systems, October 6, 2005,

Detecting Chemical Changes via FTIR



1) Area is proportional to -OH, -NH content.

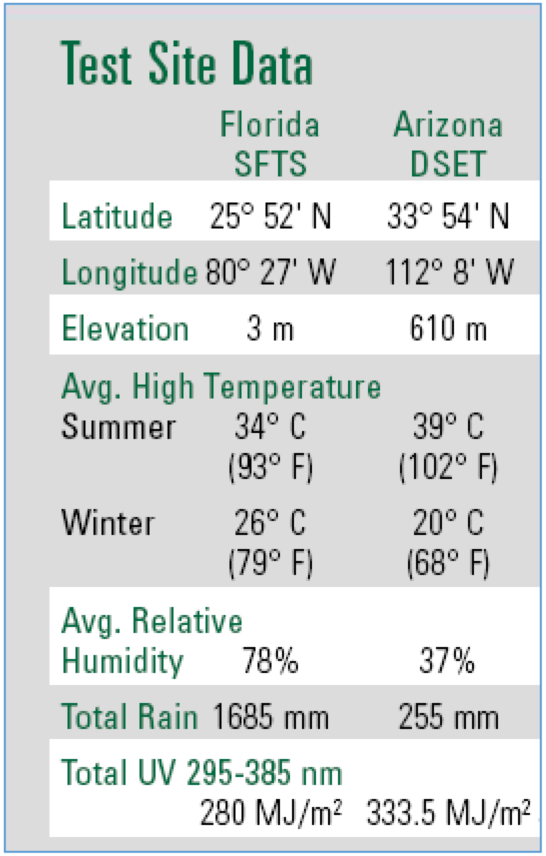
2) Area increases with weathering.

Area increase reveals accumulation of photooxidation products.

Use $\frac{(\text{-OH, -NH})_{area}}{\text{-CH}_{area}}$ ratio to follow oxidation/hydrolysis

Plot the changes in the (-OH, -NH) / -CH area v. time to follow photooxidation

Time of wetness in xenon arc weathering tests



Test Site Data

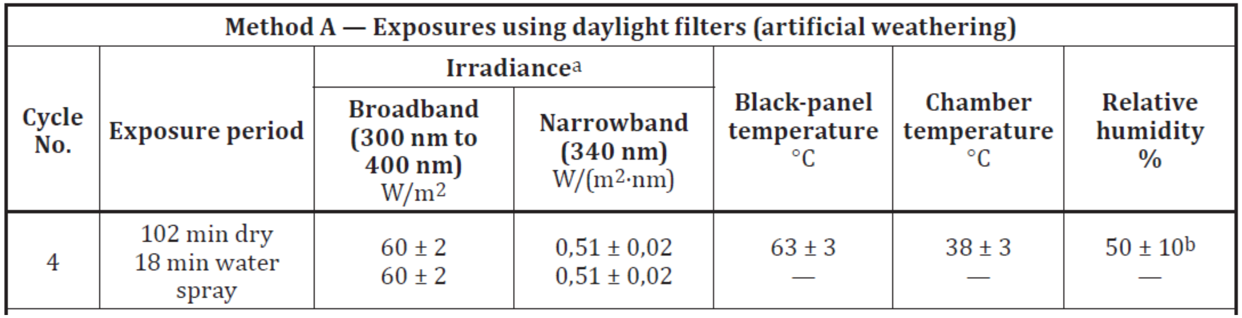
	Florida SFTS	Arizona DSET
Latitude	25° 52' N	33° 54' N
Longitude	80° 27' W	112° 8' W
Elevation	3 m	610 m
Avg. High Temperature		
Summer	34° C (93° F)	39° C (102° F)
Winter	26° C (79° F)	20° C (68° F)
Avg. Relative Humidity	78%	37%
Total Rain	1685 mm	255 mm
Total UV 295-385 nm	280 MJ/m²	333.5 MJ/m²

Average Time of Wetness

	4200 h	***372 h***

South Florida averages measureable surface wetness 48% of the time.

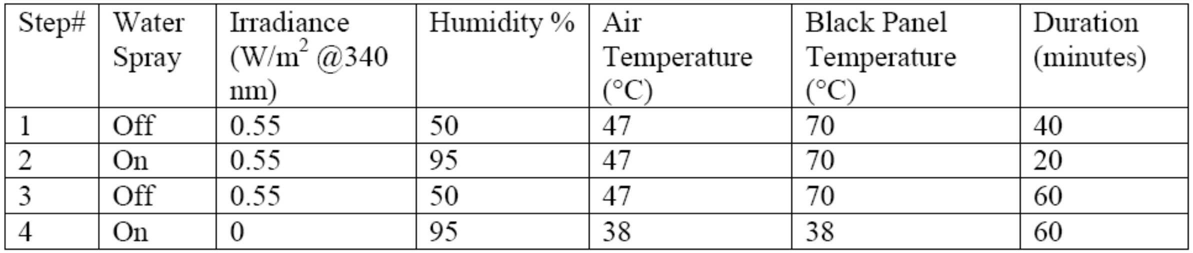
ISO 4892-2 / ASTM G155



Method A — Exposures using daylight filters (artificial weathering)

Cycle No.	**Exposure period**	**Irradiance[a]**		**Black-panel temperature** °C	**Chamber temperature** °C	**Relative humidity** %
		Broadband (300 nm to 400 nm) W/m²	**Narrowband (340 nm)** W/(m²·nm)			
4	102 min dry 18 min water spray	60 ± 2 60 ± 2	0,51 ± 0,02 0,51 ± 0,02	63 ± 3 —	38 ± 3 —	50 ± 10[b] —

SAE J2527

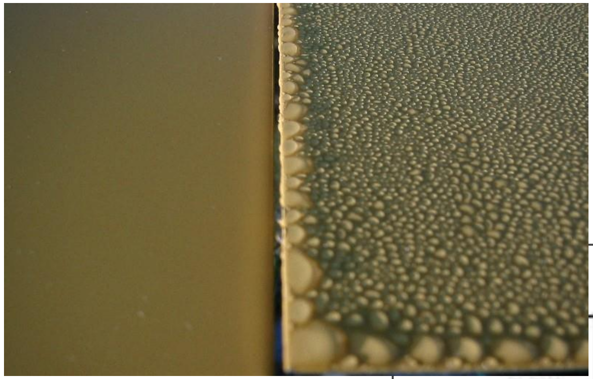


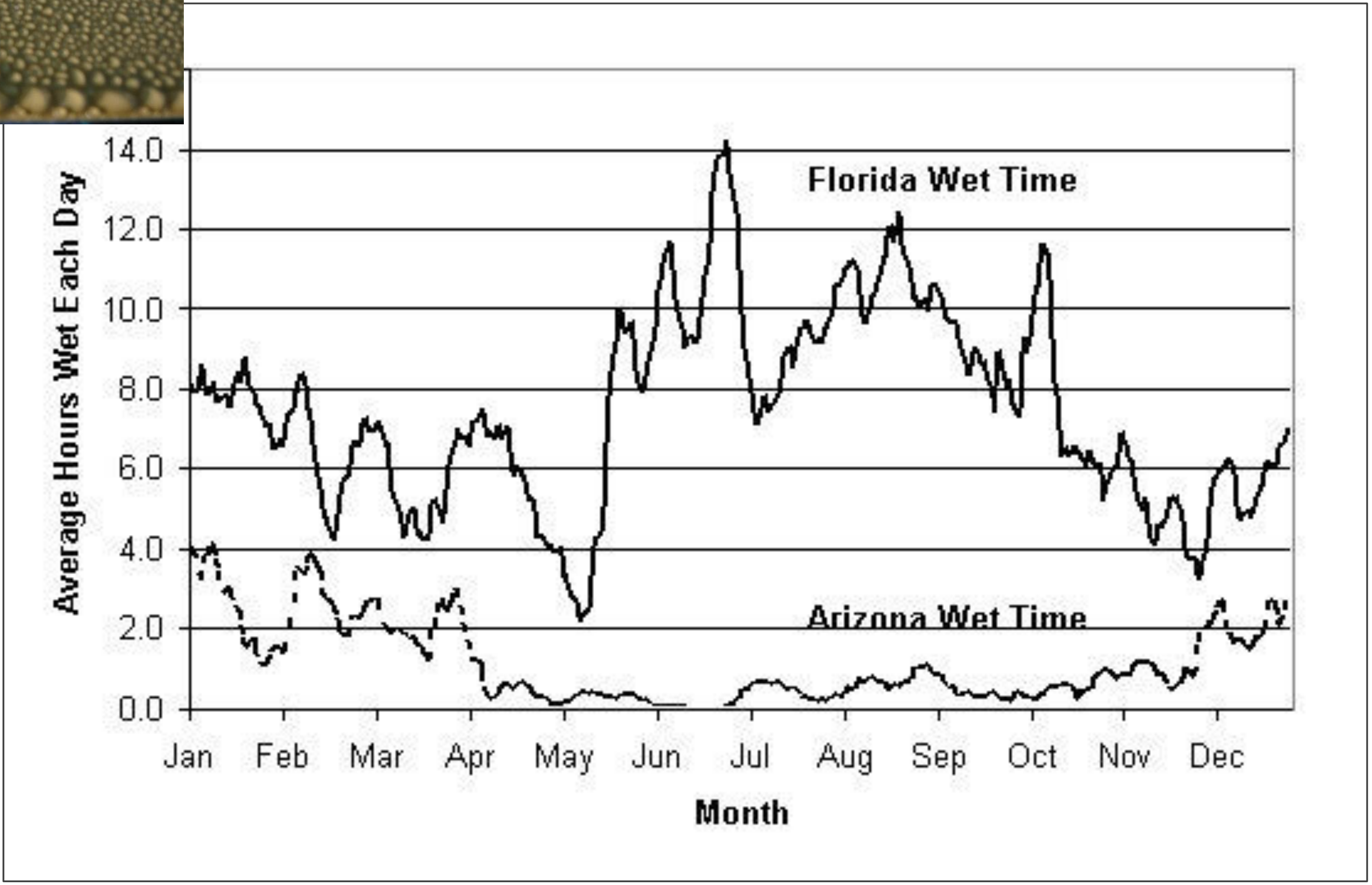
Step#	Water Spray	Irradiance (W/m² @340 nm)	Humidity %	Air Temperature (°C)	Black Panel Temperature (°C)	Duration (minutes)
1	Off	0.55	50	47	70	40
2	On	0.55	95	47	70	20
3	Off	0.55	50	47	70	60
4	On	0	95	38	38	60

ISO 4892-2 102/18 cycles spray water 15%
And SAE J2527 3-hr cycle water sprays 33% the time . . .

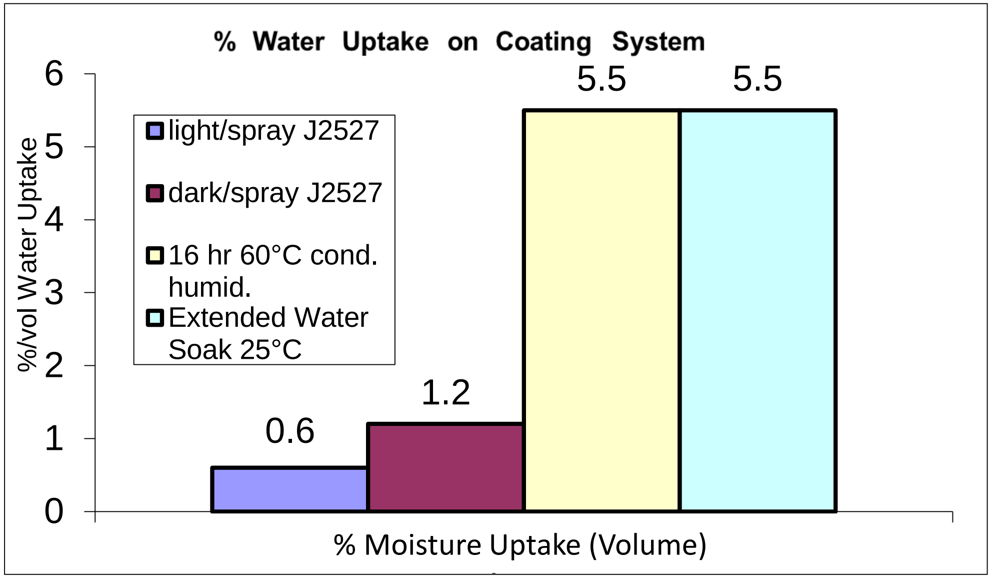
. . . but spray times are too short to reach coating water saturation as in Florida and dry out much too quickly.

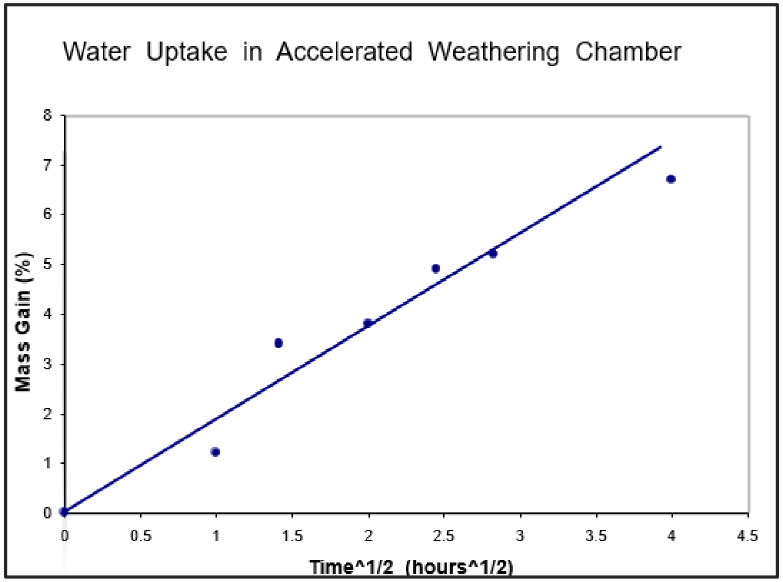
South Florida v. Arizona Wet Time





Moisture cycle in SAE J2527

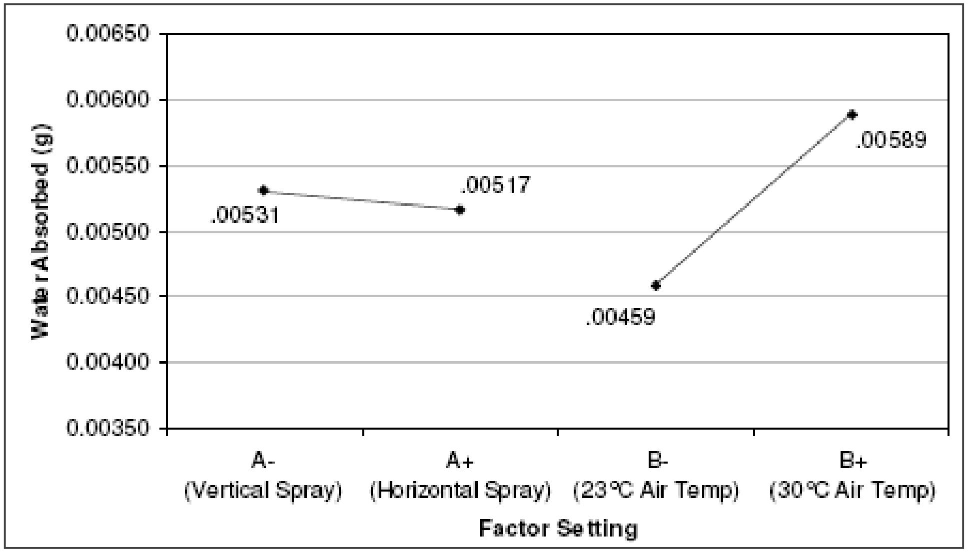




Graphs courtesy of Nichols et al.

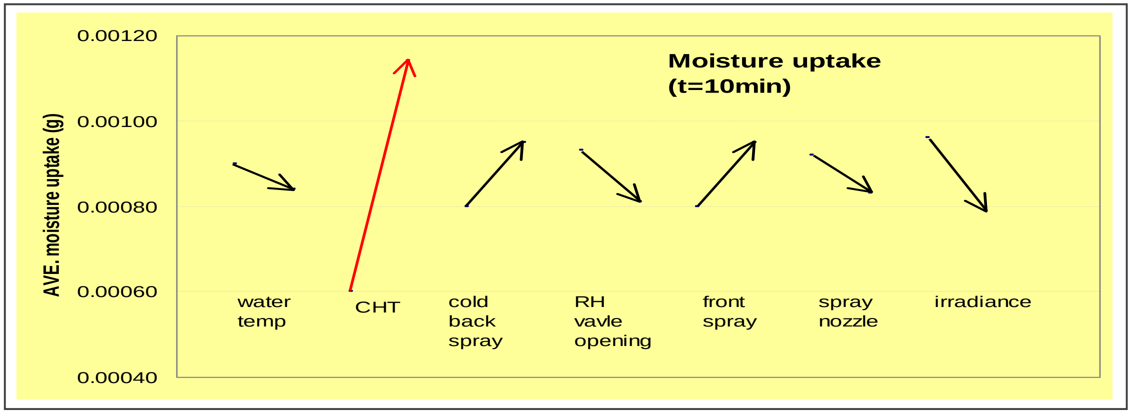
Baseline test method evaluation showed SAE J2527 spray cycles not effective in providing moisture uptake seen in natural South Florida exposures

Factors influencing moisture uptake



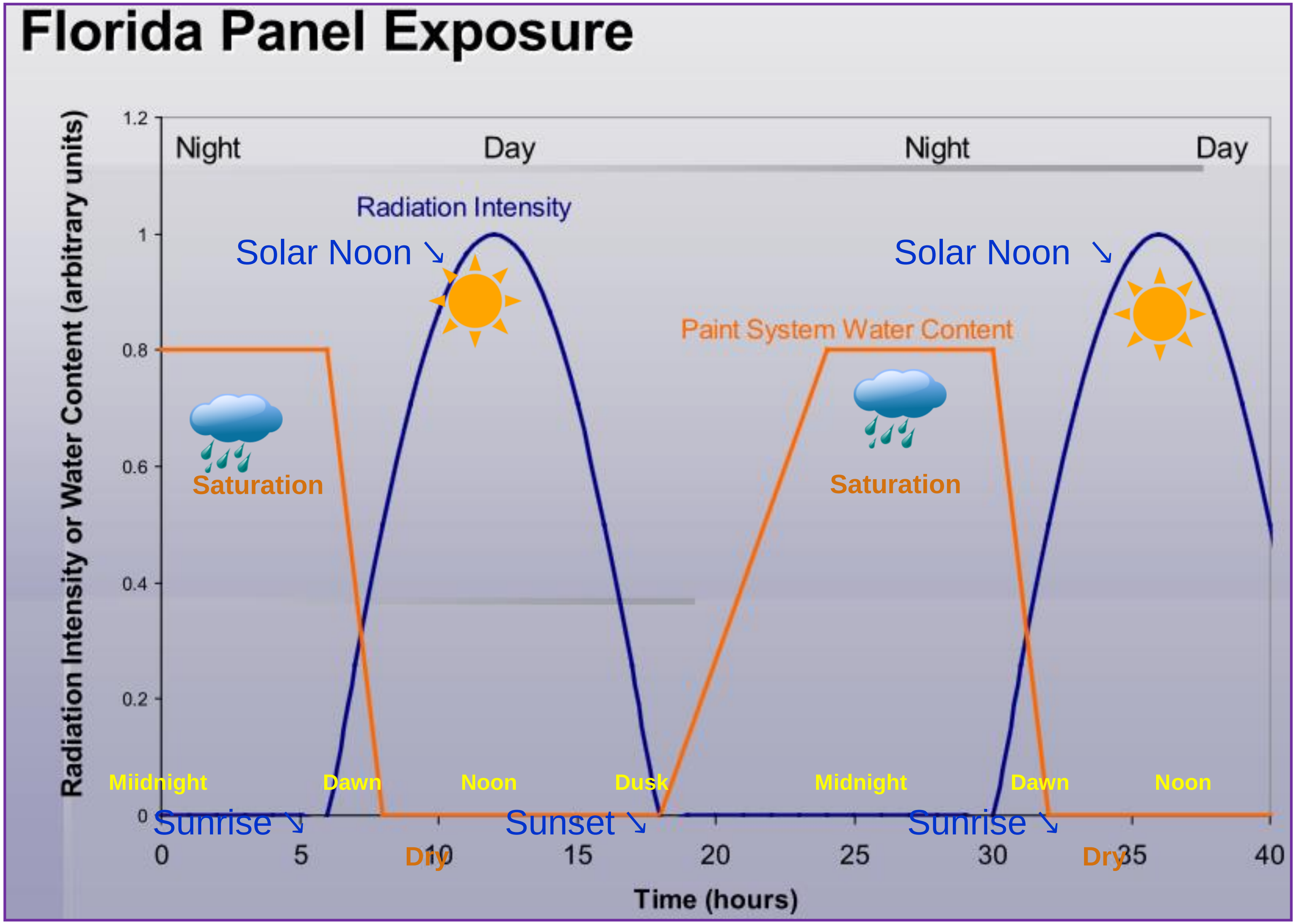
DOE studies have shown exposure angle is not a significant factor in automotive coating moisture uptake rate

Chamber air & specimen temperature has the greatest influence on moisture uptake



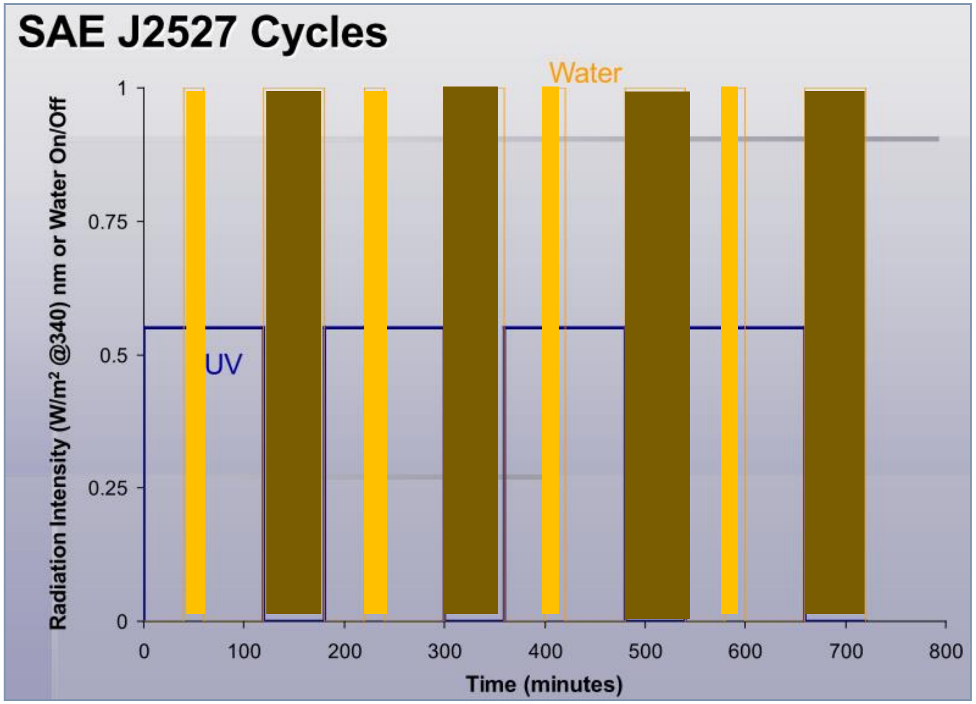
H.K. Hardcastle, W.L.Meeks, **Considerations for characterizing moisture effects in coatings weathering studies,** J Coat Technol Res (2008) 5: 181. https://doi.org/10.1007/s11998-007-9078-0

South Florida diurnal cycle



M.Nichols, *et al*, **Accelerated Weathering Testing: A New Approach to Anticipating Florida Exposure Results,** 2011 Coatings Science International, Noordwijk, Netherlands, June 30, 2011

SAE J2527 test cycle



Note spray temperature & irradiance combinations

M.Nichols, *et al*, "Accelerated Weathering of Automotive Coatings: Exposure Conditions and Analysis Methods", Atlas Technical Conference on Ageing in the Environment, Oxford, UK, September, 2008.

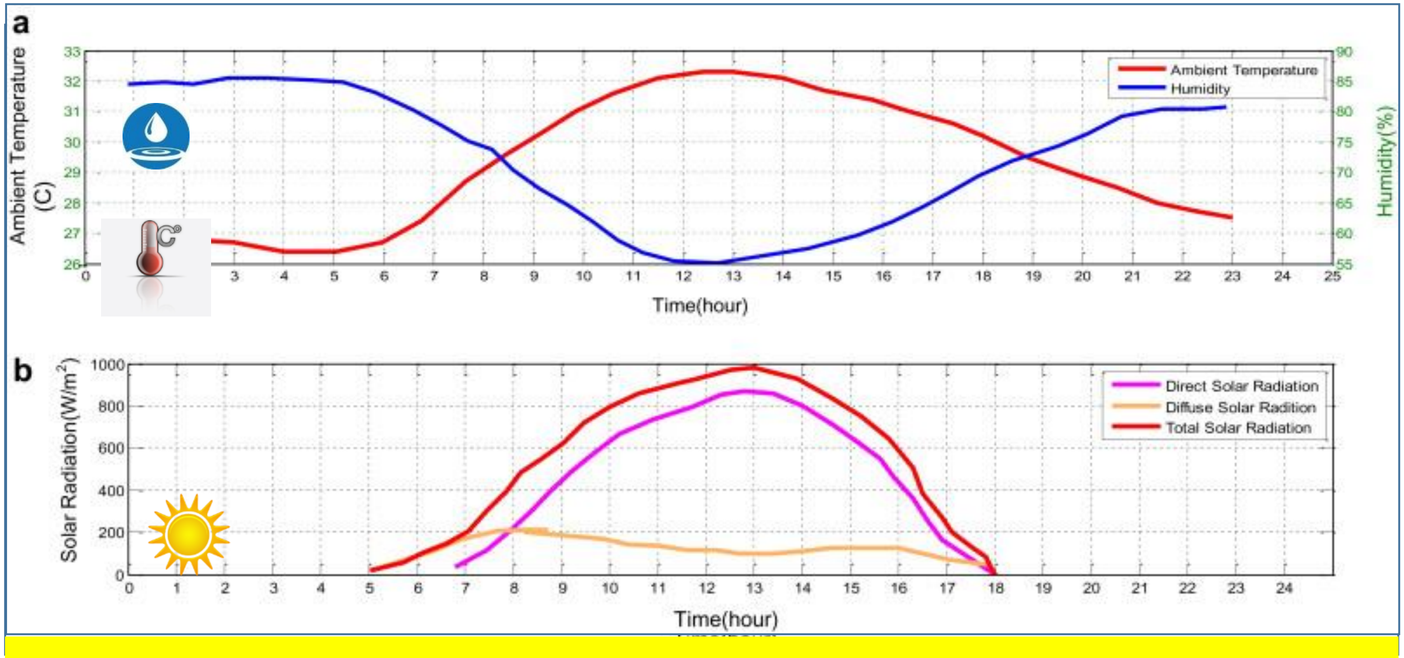
Step#	Water Spray	Irradiance (W/m^2 @340 nm)	Humidity %	Chamber Temperature (˚C)	Black Panel Temperature (˚C)	Duration (minutes)
1	Off	0.55	50	47	70	40
2	Front Spray	0.55	50	47	70	20
3	Off	0.55	50	47	70	60
4	Back Spray	0	95	38	38	60

Xenon arc device weather stresses

Solar spectrum, daily intensity & cycles

Solar IR load, heating and cycles

RH%. Dew, rain, cycles



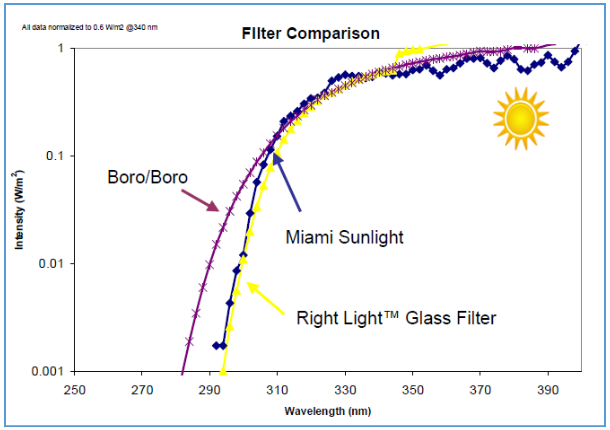
Current test methods have very limited, if any, cycling.

Xenon arc devices accelerate weather stresses

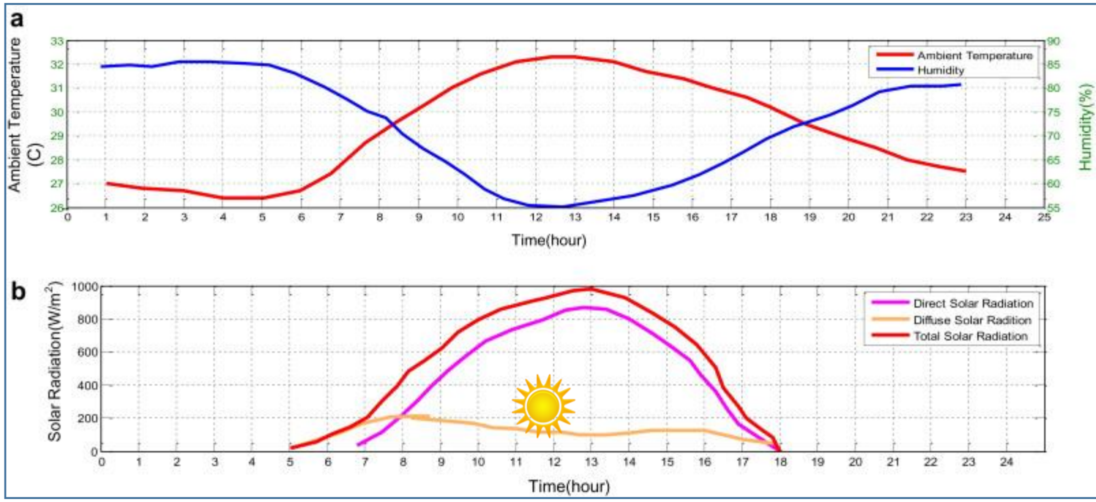
Solar spectrum, daily intensity & cycles

Solar load, heating and cycles

RH%. Dew, rain, cycles



Source: M.Nichols, *et al*, "Accelerated Weathering of Automotive Coatings: Exposure Conditions and Analysis Methods", Atlas Technical Conference on Ageing in the Environment, Oxford, UK, September, 2008.



However, current test methods have very limited, if any, cycling.

The seeds of a better, predictive test

15+ years of experimental research findings:

- Much of the failure was traced to a **spectral misma**tch between the lab light source and outdoors. Fluorescent UV abandoned for qualification tests.
- Ford & GM add automotive glazing UV filtering to cabin interior xenon test methods
- Various tests with ozone-filtered xenon led Ford *et al* to use Boro-S-Boro-S daylight xenon filters rather than SAE J1960 Quartz/Boro "extended UV".
- FTIR spectroscopy showed only EMMAQUA produced the same photodegradation chemical marker changes as real time outdoor testing.
- Clearcoat UV Absorbers depleted from the top down (microtomy and ATR spectroscopy)
- Search to "Get the light right" led to iterations of improved spectral match filters, especially in UV cut on wavelength and IR heat reduction.
- **Extended water soak and EMMAQUA spray cycles revealed inadequate water uptake of coatings with current methods. And it doesn't rain when the sun is brightly shining!**

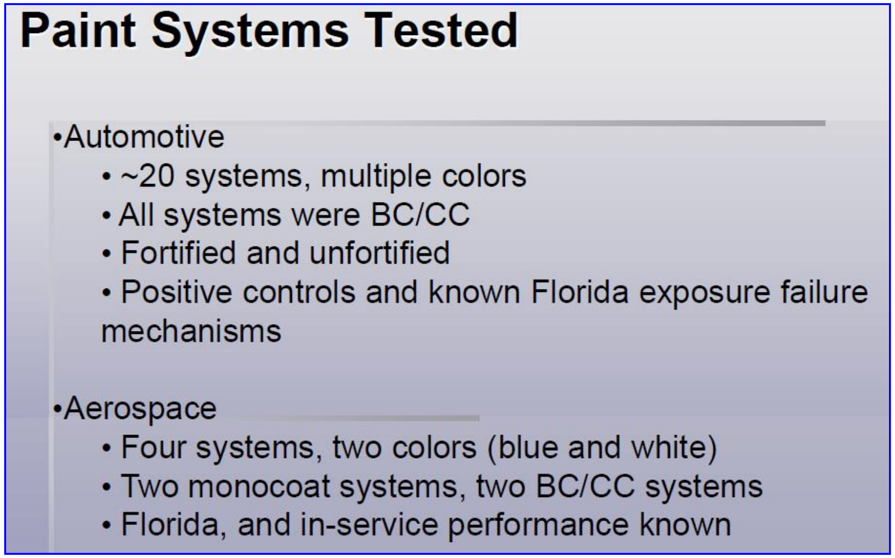
Collaborators

Volvo, Mazda, BASF, DuPont, PPG, Akzo, RedSpot, **Visteon**, **Ciba**, Cytec, **General Electric**, **Sabic**, **Momentive**, **Henkel**, **Atlas, Q-Panel**, Suga, Bruker, 3M, **Exatec**, **Bayer,** AOC, Ashland, Dow, **Fusion UV, NIST**, U. of Michigan, Eastern Michigan U., U. Blaise Pascal, U. Mulhouse France, **NDSU**, Swedish National Testing Institute, **GM, Chrysler**.

The seeds of a better, predictive test

Followed by 10 years of consortium effort leading to ASTM D7869:

- The methodology described is the result of a multi-year collaborative effort between researchers at the following companies:
  - *Ford Motor R&D*
  - *Boeing Commercial Aircraft*
  - *BASF, Bayer MaterialScience*
  - *Atlas Material Testing Technology,*
  - *Q-Lab*
  - *and later, Honda R&D Americas*



Paint Systems Tested

- Automotive
  - ~20 systems, multiple colors
  - All systems were BC/CC
  - Fortified and unfortified
  - Positive controls and known Florida exposure failure mechanisms
- Aerospace
  - Four systems, two colors (blue and white)
  - Two monocoat systems, two BC/CC systems
  - Florida, and in-service performance known

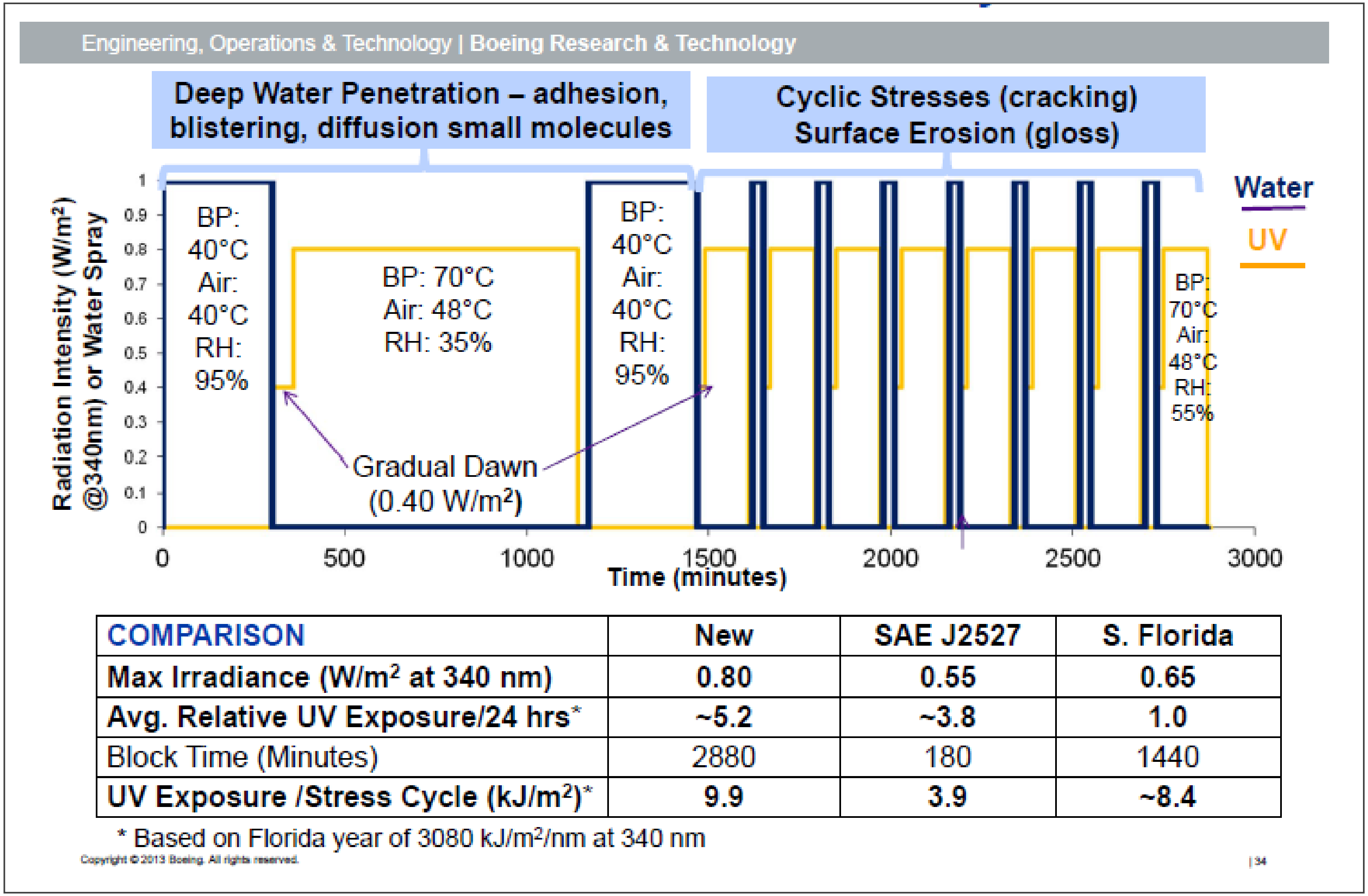
M.Nichols, *et al*, "Accelerated Weathering Testing: A New Approach to Anticipating Florida Exposure Results:, 2011 Coatings Science International, Noordwijk, Netherlands, June 30, 2011

A New ASTM Test Method D7869

ASTM D7869 Test Cycle Sequence

Step Number	Step Minutes	Function	Irradiance Set Point[1] @340nm (W/m²/nm)	Black Panel Temperature Set Point[1]	Chamber Air Temperature Set Point[1]	Relative Humidity Set Point[1]
1	240	dark + spray	-	40°C	40°C	95%
2	30	light	0.40	50°C	42°C	50%
3	270	light	0.80	70°C	50°C	50%
4	30	light	0.40	50°C	42°C	50%
5	150	dark + spray	-	40°C	40°C	95%
6	30	dark + spray	-	40°C	40°C	95%
7	20	light	0.40	50°C	42°C	50%
8	120	light	0.80	70°C	50°C	50%
9	10	dark	-	40°C	40°C	50%
10	Repeat steps 6-9 an additional 3 times (for a total of 24 hours = 1 cycle)					

ASTM D7869 Test Cycle
Comparison to SAE J2527 and S. Florida



Engineering, Operations & Technology | Boeing Research & Technology

Deep Water Penetration – adhesion, blistering, diffusion small molecules

Cyclic Stresses (cracking) Surface Erosion (gloss)

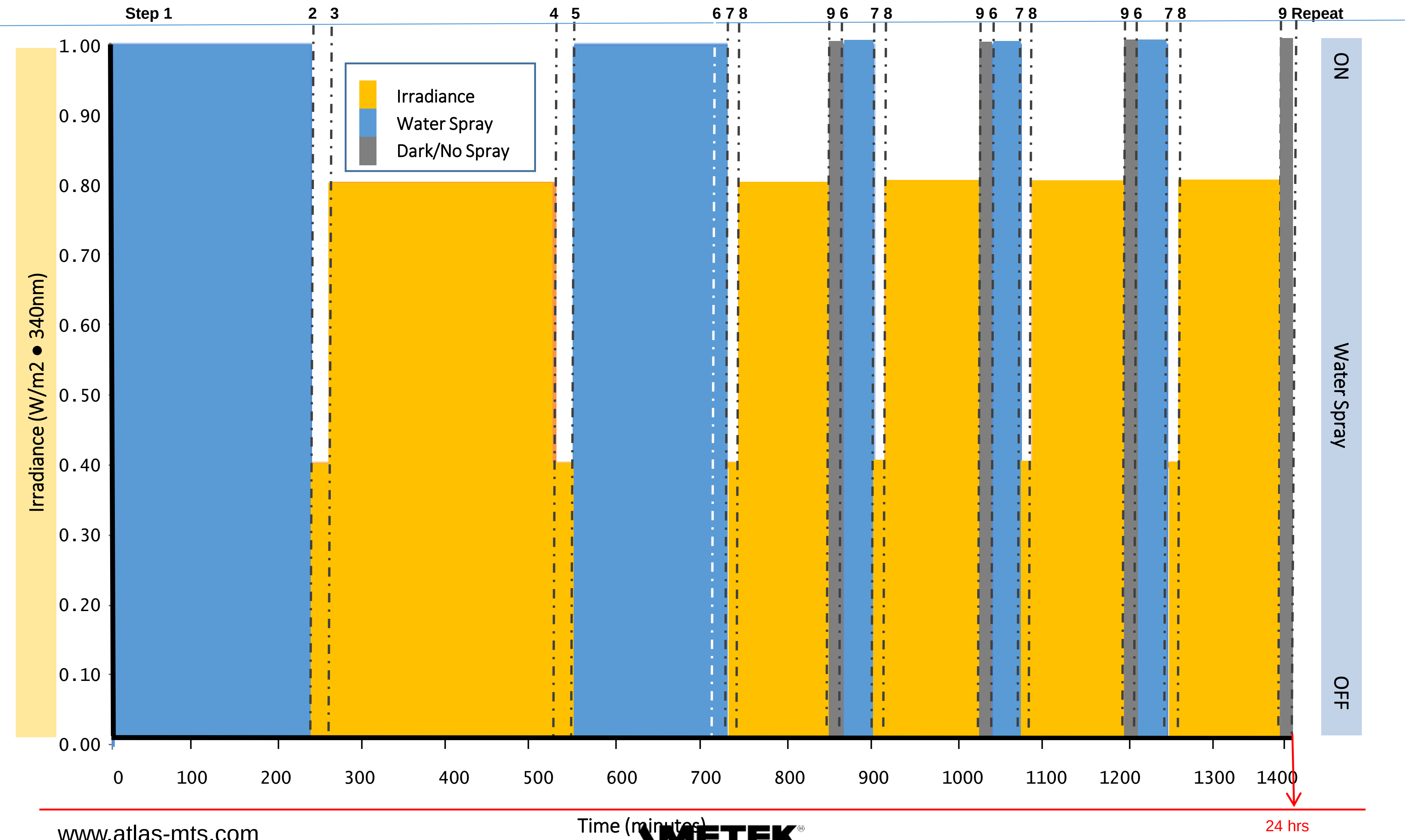
COMPARISON	New	SAE J2527	S. Florida
Max Irradiance (W/m² at 340 nm)	0.80	0.55	0.65
Avg. Relative UV Exposure/24 hrs*	~5.2	~3.8	1.0
Block Time (Minutes)	2880	180	1440
UV Exposure /Stress Cycle (kJ/m²)*	9.9	3.9	~8.4

* Based on Florida year of 3080 kJ/m²/nm at 340 nm

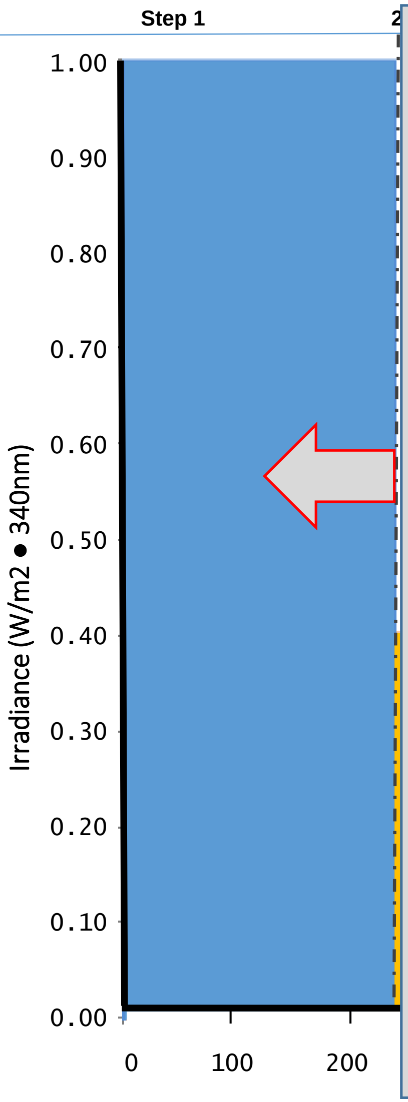
| 34

D. Berry, **An Investigation of Weathering Test Protocol Development and Durability of Exterior Aerospace Coatings**, International Symposium on Weathering and Service Life Prediction, Japan May 2013.

Final Iteration ASTM D7869 Test Cycle



Step 1 – Deep Moisture Saturation



240 min, Dark + Spray, BPT 40^{o}C, CHT 40^{o}C, 95% RH

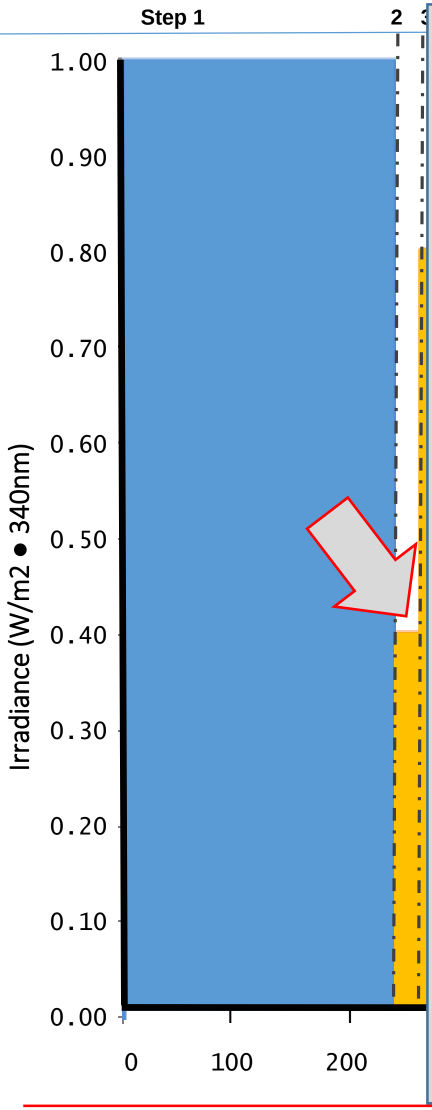
- **Purpose** - to produce water uptake within the coating that is similar to the maximum uptake in a normal day outdoors in south Florida

- Water uptake *more than* what is achieved in Step 1 did not produce significant changes in test results. However, water uptake *less* than what Step One achieves did fail to produce degradation of the types found in Florida

- Dark cycle, because almost all wetness in Florida occurs when there is no sunshine. The vast majority of wet time is caused by nighttime dew.

- Outdoor data show that natural specimen wet temperature is lower in Florida, typically 20^{o}C to 25^{o}C. But outdoor wet periods were also much longer, ranging from 8h to 16h. ***So 4h at 40^{o}C produces similar water uptake to the much longer, but cooler, Florida wet periods***

Step 2 – Removing the water



30 min, Light, 0.40 W/m^2 @ 340nm *with new filter*, BPT 50^{o}C, CHT 42^{o}C, RH 50%

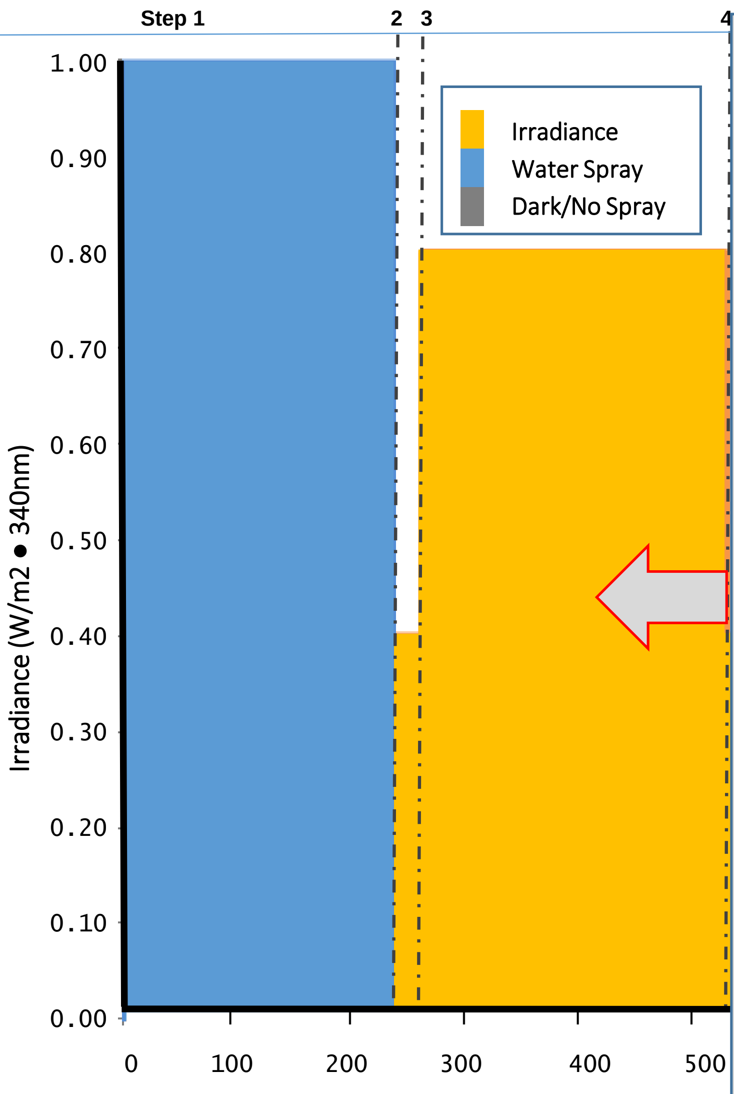
- **Purpose** - to remove all of the water from within the coating layers

- The irradiance is set at a relatively low level, 0.40 W/m2/nm, **because Florida data has shown that all the water was driven out from the coating before the sun ever got high** enough in the sky to produce higher irradiances

- The Black Panel Temperature is set at 50^{o}C, because Florida data has shown that by the time the sun heats the specimen to 50^{o}C, almost all of the water has been removed from the coating

- A time of 30 minutes was chosen because data has shown that ***30 minutes at 50^{o}C is the time required to take the water content to near zero.***

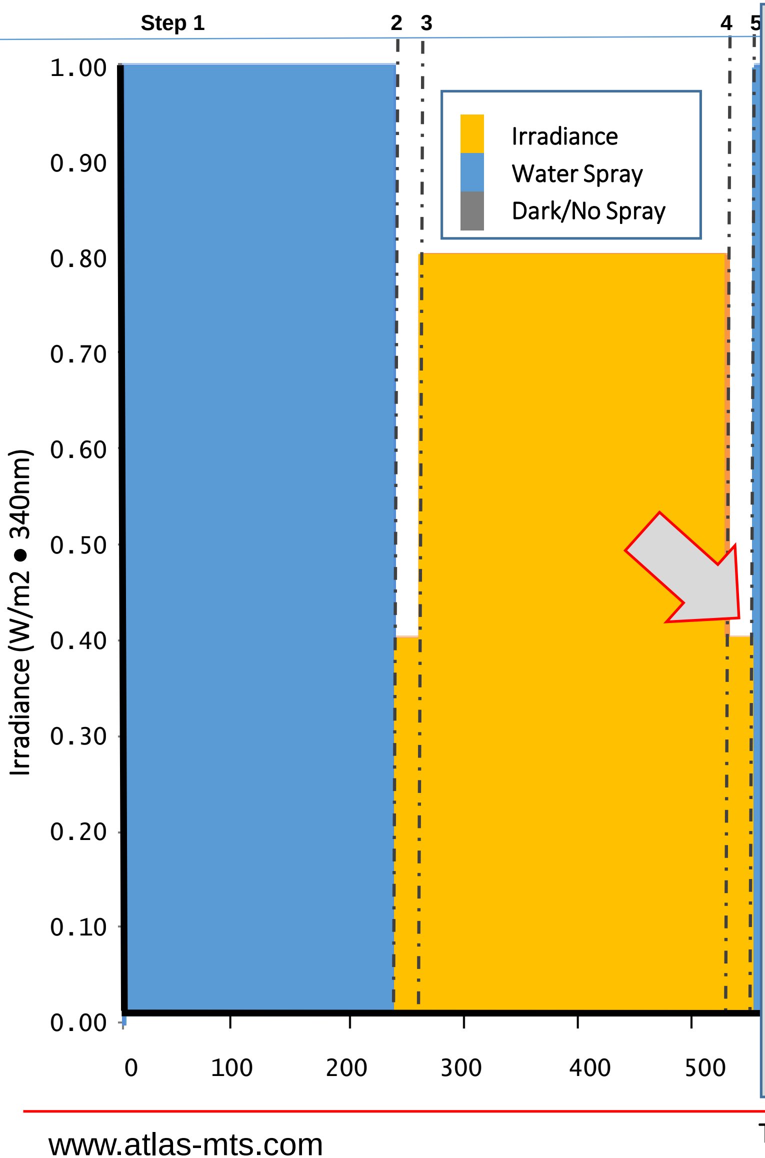
Step 3 – Exposure to the Right Light



270 min, Light, 0.80 W/m² @340nm, BPT 70°C, CHT 50°C, RH 50%

- **Purpose** – to simulate the effects of bright sunlight on the coatings.
- Most Florida sunlight exposure occurs at much lower irradiances than noon midsummer sunlight. So this irradiance can be expected to produce significant acceleration.
- **The irradiance is set at somewhat higher than the maximum irradiance seen in Florida with noon midsummer sunlight.**
- **The Black Panel Temperature is set at 70°C, because this approximates the maximum specimen temperature averaged across the color palette.**

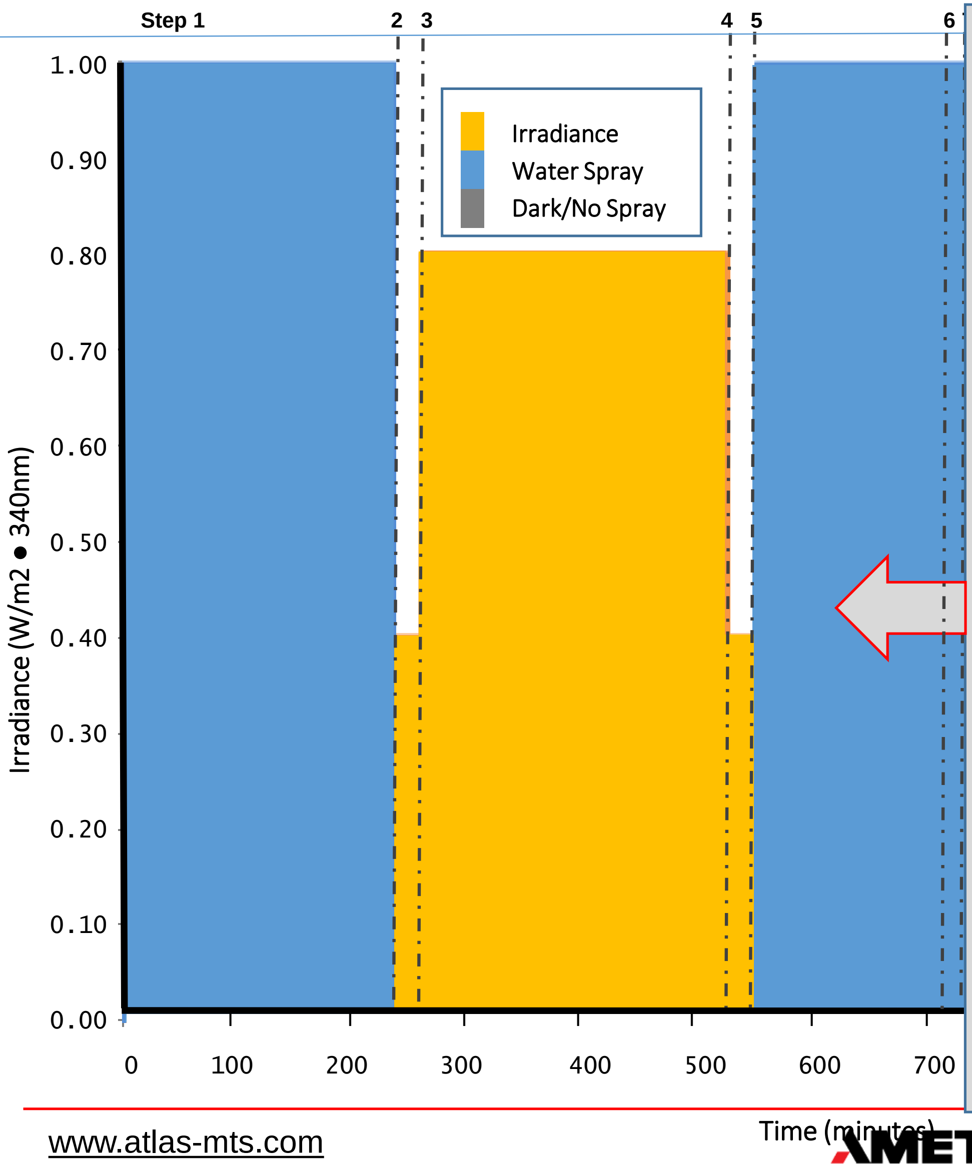
Step 4 – "Relaxation"



30 min, Light, 0.40 W/m² @ 340nm, BPT 50°C, CHT 42°C, RH 50%

- **Purpose** - to **transition** between the hot, high-irradiance "daytime" step and the dark, cool, wet "night time" step.
- This step gradually **reduces thermal stresses** within the coating, similar to what occurs as the sun gets lower in the sky during the evening.
- Unnatural effects can be produced if the test does not cool down the specimens before water is introduced. For instance, excessive cracking and micro cracking can be produced if cold water is sprayed onto a hot specimen.
- **The relatively low set points for irradiance and temperature are typical of what has been measured in FL late afternoon and early evening.**

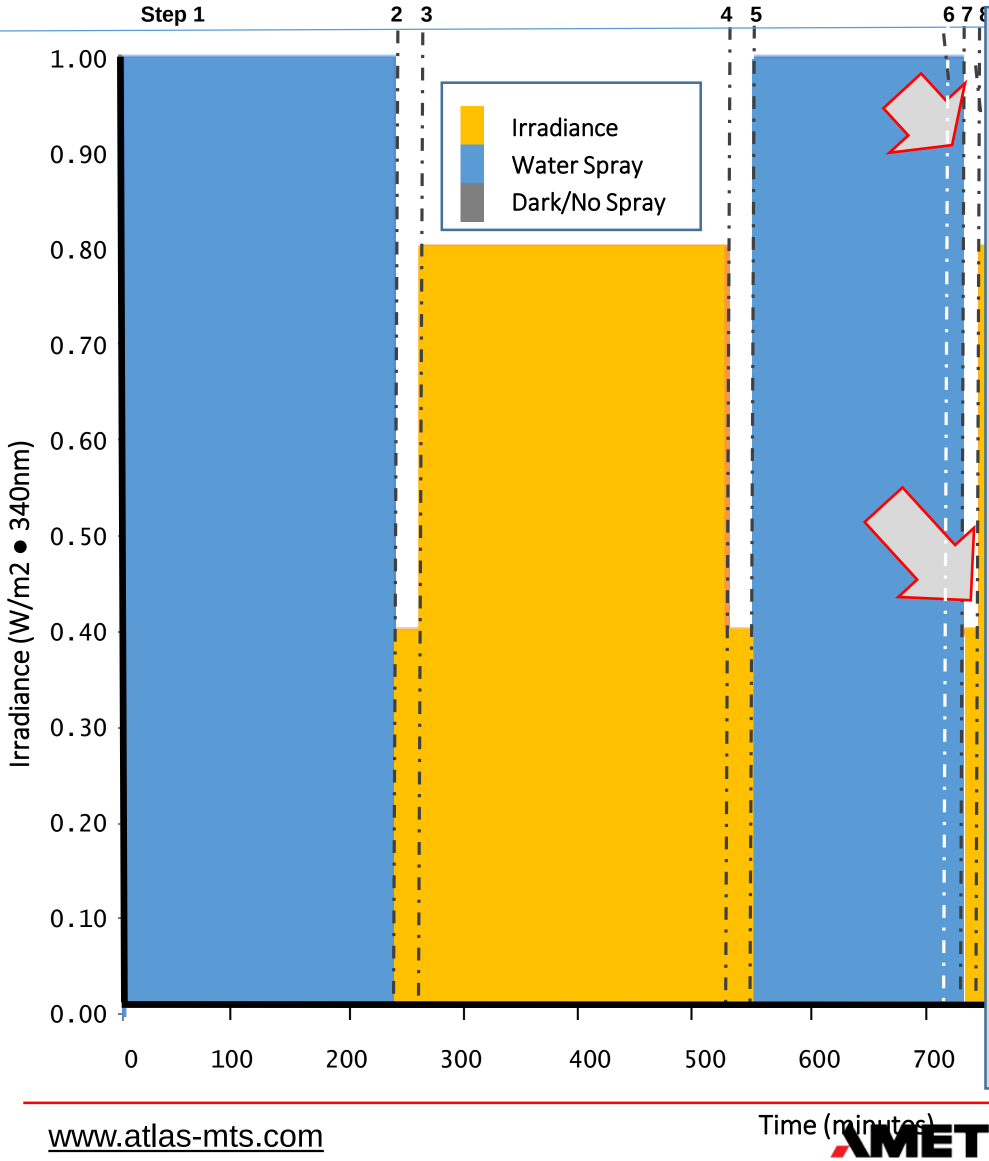
Step 5 – Water (Again)



150 min, Dark + Spray, BPT 40ºC, CHT 40ºC, 95% RH

- **Purpose** - to produce significant water uptake within the coating, but at somewhat less than the maximum uptake observed
- The temperatures and humidities in Step 5 are the same as in Step 1, for the same reasons.
- **The data has shown that the maximum water uptake does not occur every day in Florida. This step is intended to simulate those days of less than maximum uptake.**

Steps 6 & 7 Rain Event and Controlled Dry Out



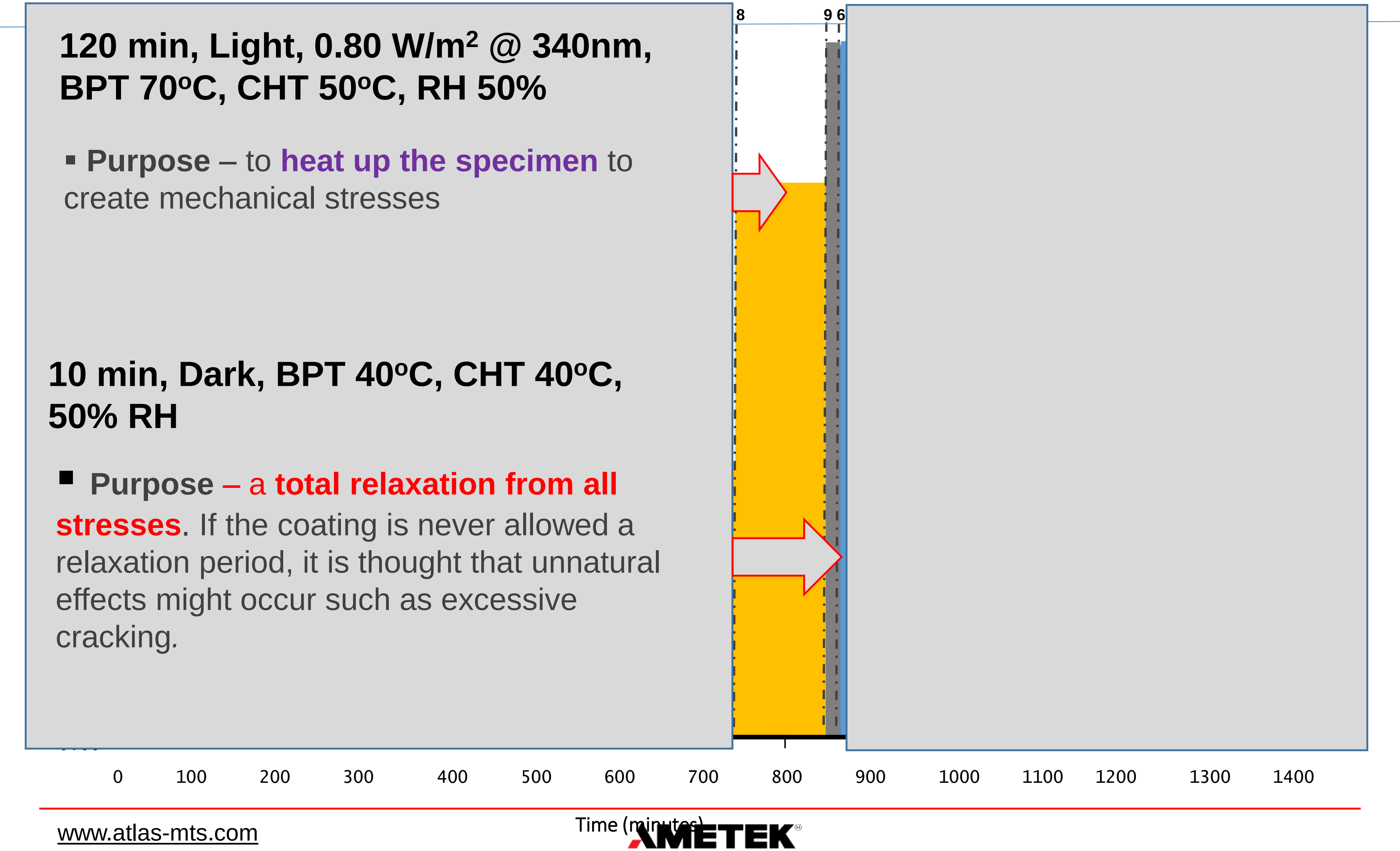
30 min, Dark + Spray, BPT 40ºC, CHT 40ºC, 95% RH

- **Purpose** – to simulate a very short time water event, such as a night where little condensation occurs, **or a very short rain event**

20 min, Light, 0.40 W/m^2 @340nm, BPT 50ºC, CHT 42ºC, RH 50%

- **Purpose** – to **remove the water** from the coating at a controlled rate

Steps 8 & 9 – Heat/Mechanical Stress & Relaxation



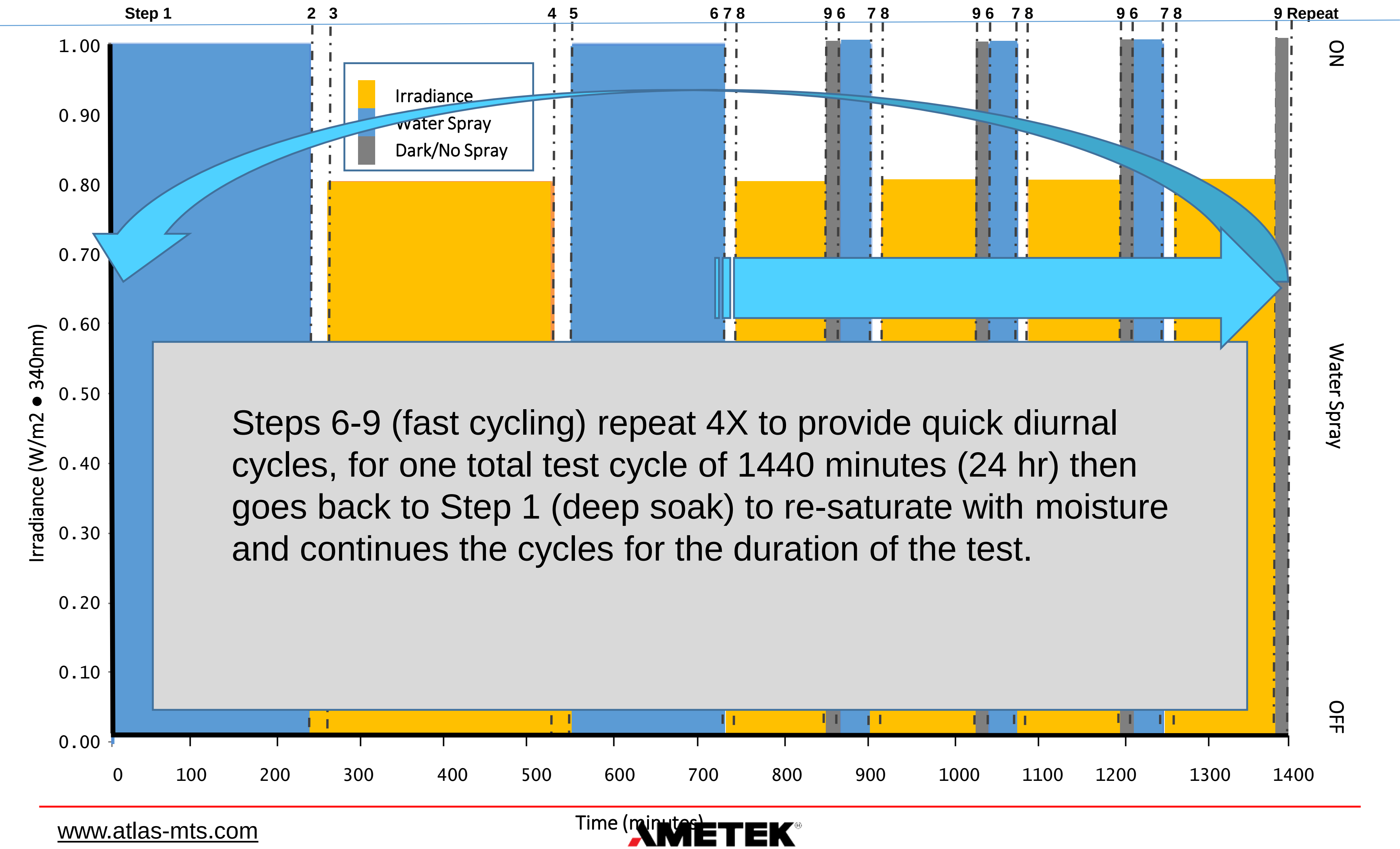
120 min, Light, 0.80 W/m^2 @ 340nm, BPT 70ºC, CHT 50ºC, RH 50%

- **Purpose** – to **heat up the specimen** to create mechanical stresses

10 min, Dark, BPT 40ºC, CHT 40ºC, 50% RH

- **Purpose** – a **total relaxation from all stresses**. If the coating is never allowed a relaxation period, it is thought that unnatural effects might occur such as excessive cracking.

Repeat fast cycling – 5 diurnal cycles/test day



Steps 6-9 (fast cycling) repeat 4X to provide quick diurnal cycles, for one total test cycle of 1440 minutes (24 hr) then goes back to Step 1 (deep soak) to re-saturate with moisture and continues the cycles for the duration of the test.

Implications for PV

Key takeaways for PV:

Serves as a model for science-based test method development

- Weathering can be complex: both both chemical and physical cyclic stresses
- Can't ignore material-specific degradation mechanisms
- Physical – Solar load thermal heating
- Chemical – Must reproduce the same chemical changes from in-service exposure
- Time of wetness is important for hydrolysis reactions (e.g., PET); WVTR for PA backsheets, PVB encapsulants, etc.
- Cycling is important - steady state isn't natural
  - *Material to material interfaces (adhesion)*
  - *Promotes cracking, delamination, corrosion as seen in nature*
  - *Transitions are where much of the stress occurs*
  - *Thermo-mechanical stress*
- Need to match service environment climate conditions and cycles for the test to be predictive – *implications for climate-based module durability ratings and suitability for use of specific materials*

Thank you!

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