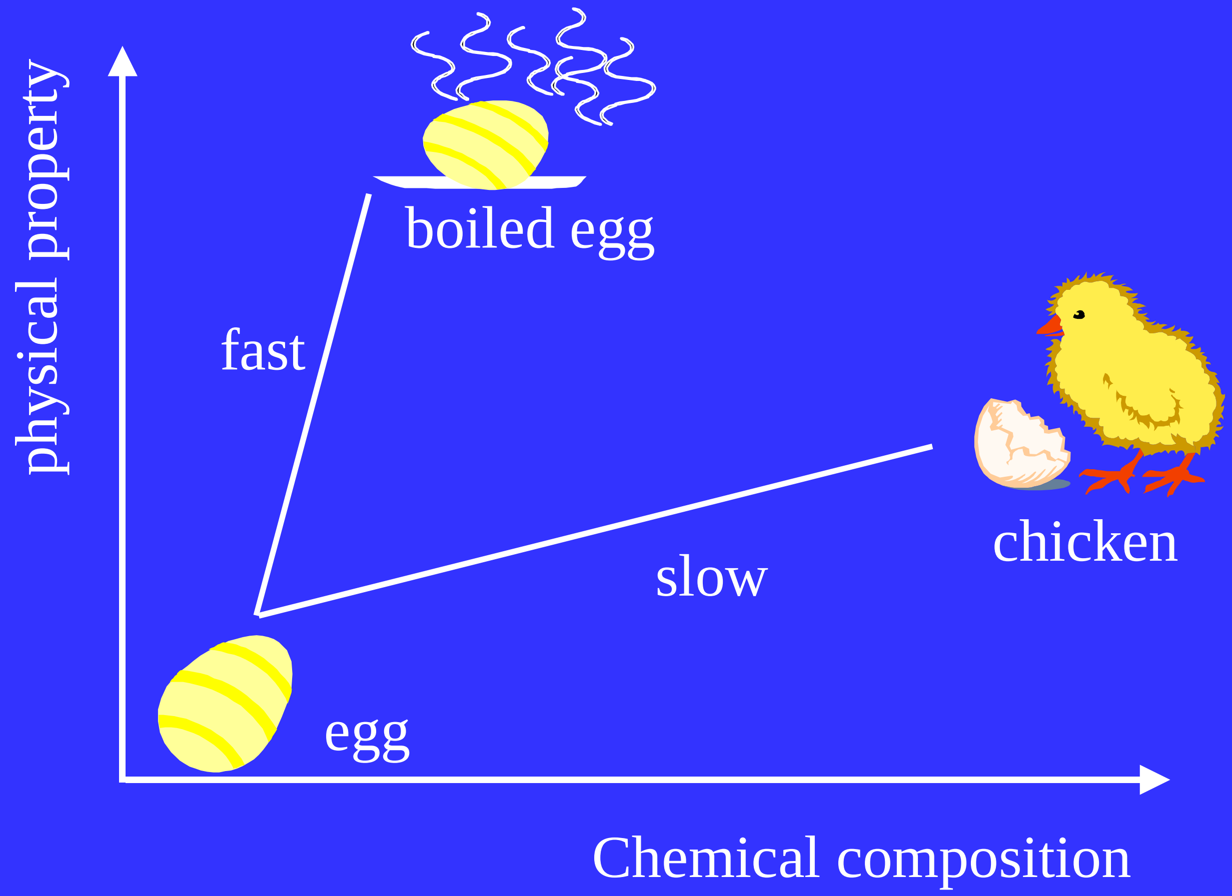
HOW CAN WE EFFECTIVELY USE ACCELERATED METHODS TO PREDICT THE DECORATIVE PROPERTIES OF PVDF-BASED COATINGS?

A “practical approach”

Dr. Kurt A. Wood
Arkema, Inc.
900 1st Avenue
King of Prussia PA 19406 USA
+1 610 878 6914
Kurt.Wood@arkema.com

The famous egg diagram



physical property

boiled egg

fast

chicken

slow

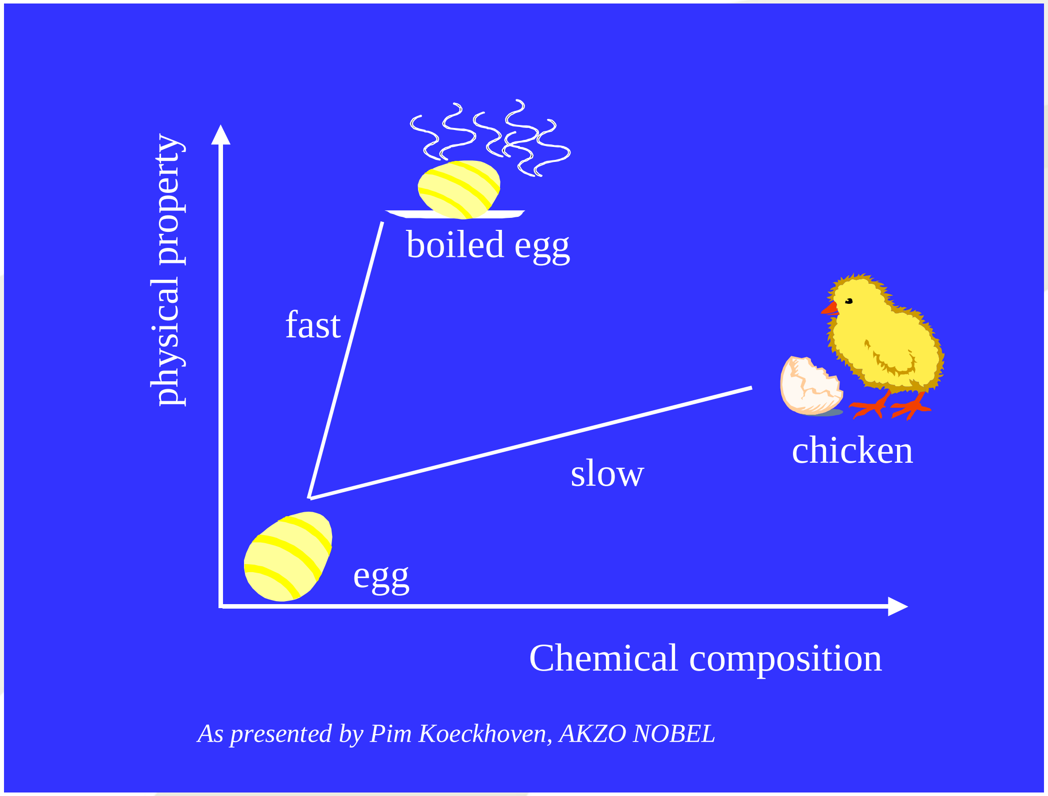
egg

Chemical composition

As presented by Pim Koeckhoven, AKZO NOBEL

Our business

- We’ve looked at thousands of chicken eggs under all kinds of conditions
- And now, we have some duck eggs too which we want to sell!

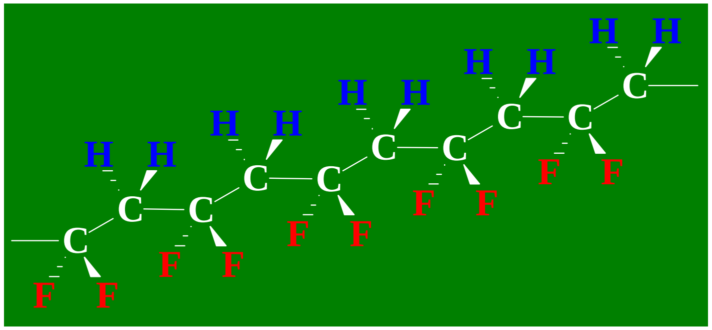


As presented by Pim Koeckhoven, AKZO NOBEL

Outline

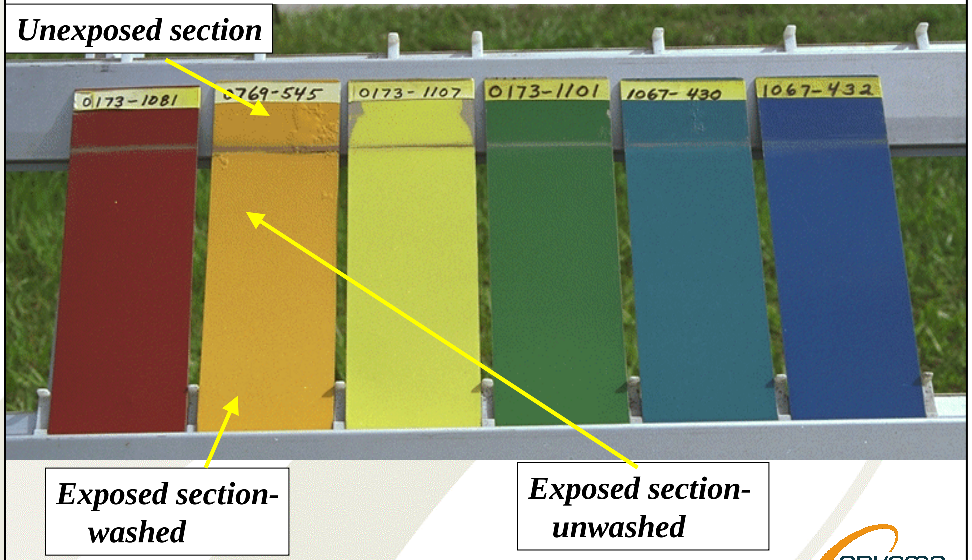
- Overview of PVDF-based coatings
- Quantitative Model for the Prediction of Gloss Retention, Color Change, and Chalking for Poly(Vinylidene Fluoride)/Acrylic Blends
- Accelerated weathering of PVDF/acrylic blends: opportunities and limitations

Commercial coatings based on blends of 70-80 wt% PVDF/ 20-30% acrylic show outstanding color retention and chalk resistance over decades

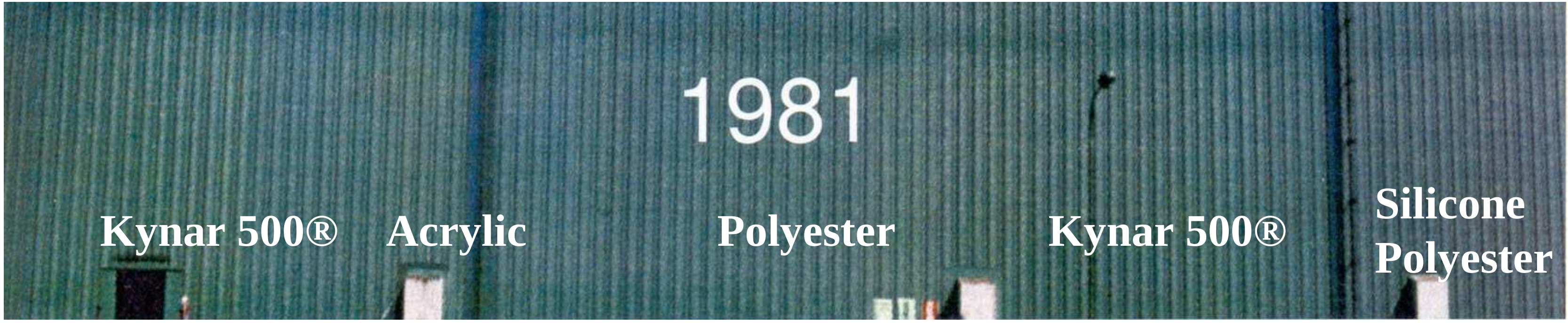


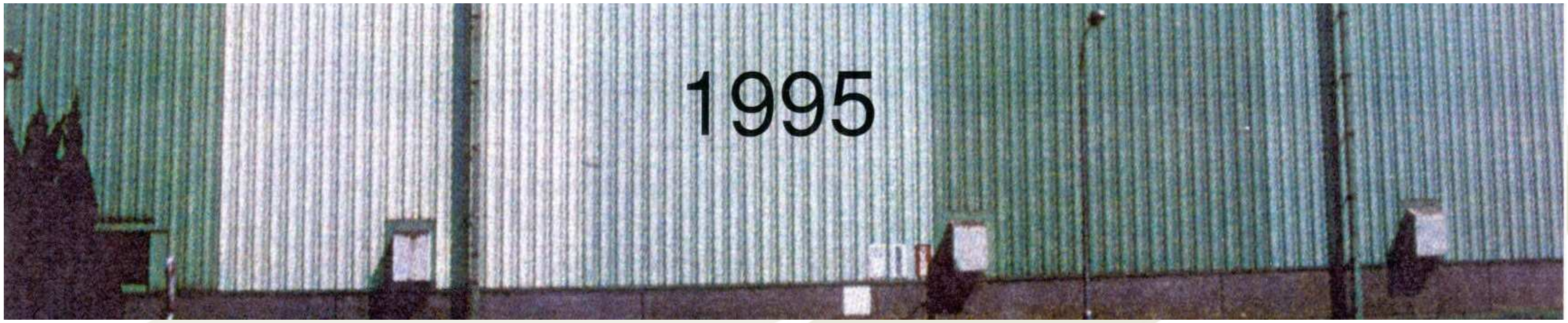
PVDF ($–[CH_2\text{-}CF_2]_n–$) does not absorb solar UV and is very resistant to photochemical and free radical attack

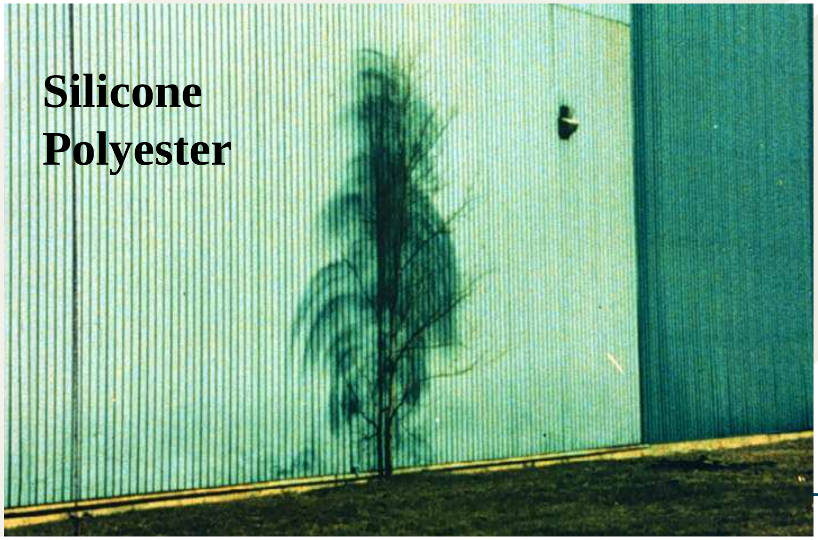
25-30 year South Florida exposures–
KYNAR 500® PVDF coatings with metal oxide pigments



Why architects specify “KYNAR” coatings







When very stable pigments are used, the color fade of coatings in the sunlight is generally due to degradation of the polymeric matrix (the “binder”)- a process commonly called “chalking”

The big (commercial) opportunity: New products based on newer waterborne PVDF hybrid dispersion technology

PRIX PIERRE POTIER 2010
L'innovation en chimie en faveur du développement durable

- Environmentally friendly coatings which (unlike traditional solvent PVDF finishes for metal) don't require a high temperature factory bake
- But how can our customers for these products rapidly get them into the marketplace? (warranty expectations, other marketing tools, qualifications, etc.)
- The commercial reality: If we can't generate sales fast enough, the product won't survive

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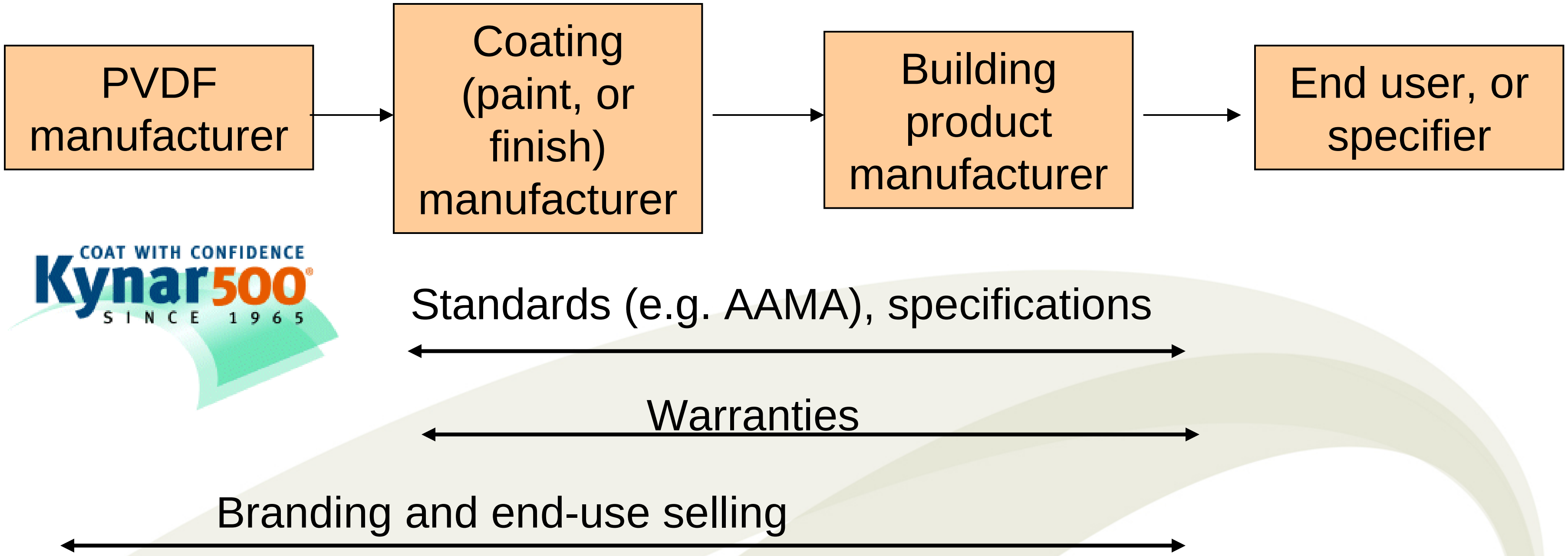
Value chain for PVDF-based coatings



PVDF manufacturer

Coating (paint, or finish) manufacturer

Building product manufacturer

End user, or specifier

COAT WITH CONFIDENCE
Kynar500®
SINCE 1965

Standards (e.g. AAMA), specifications

Warranties

Branding and end-use selling

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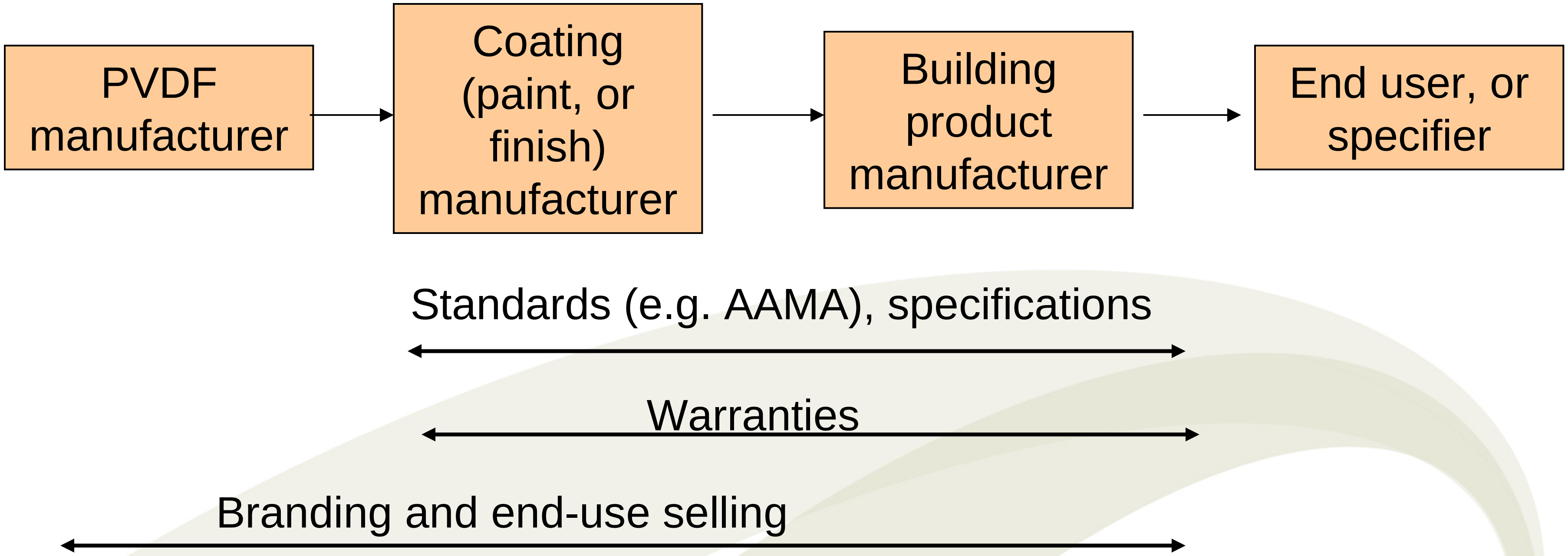
The SLP challenge



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Typical composition of dry coating, by weight	
PVDF resin	44%
Acrylic co-resin	19%
Inorganic pigment	35%
Additives	2%

Each coating company’s formulations may include 10-20 additives in dozens or hundreds of combinations

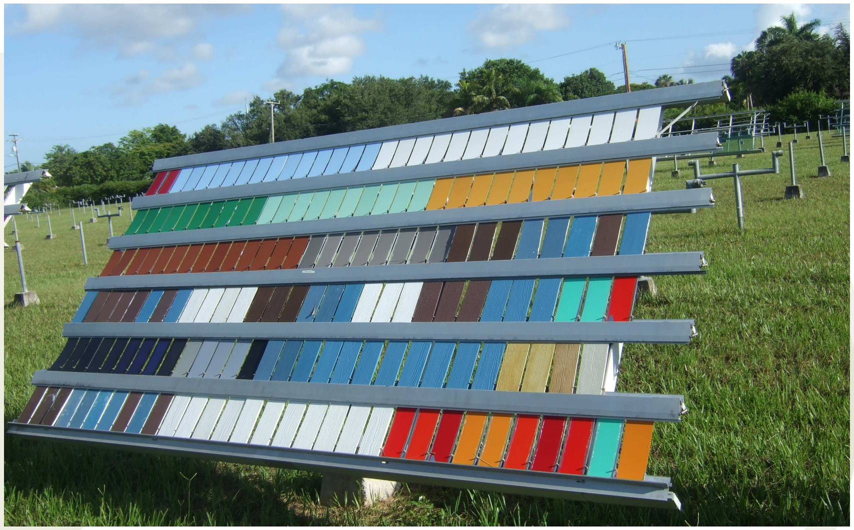
We have *extensive* Florida test fence data . .

Traditional solvent (baked) PVDF finishes

Several thousand panels, up to 45 years old

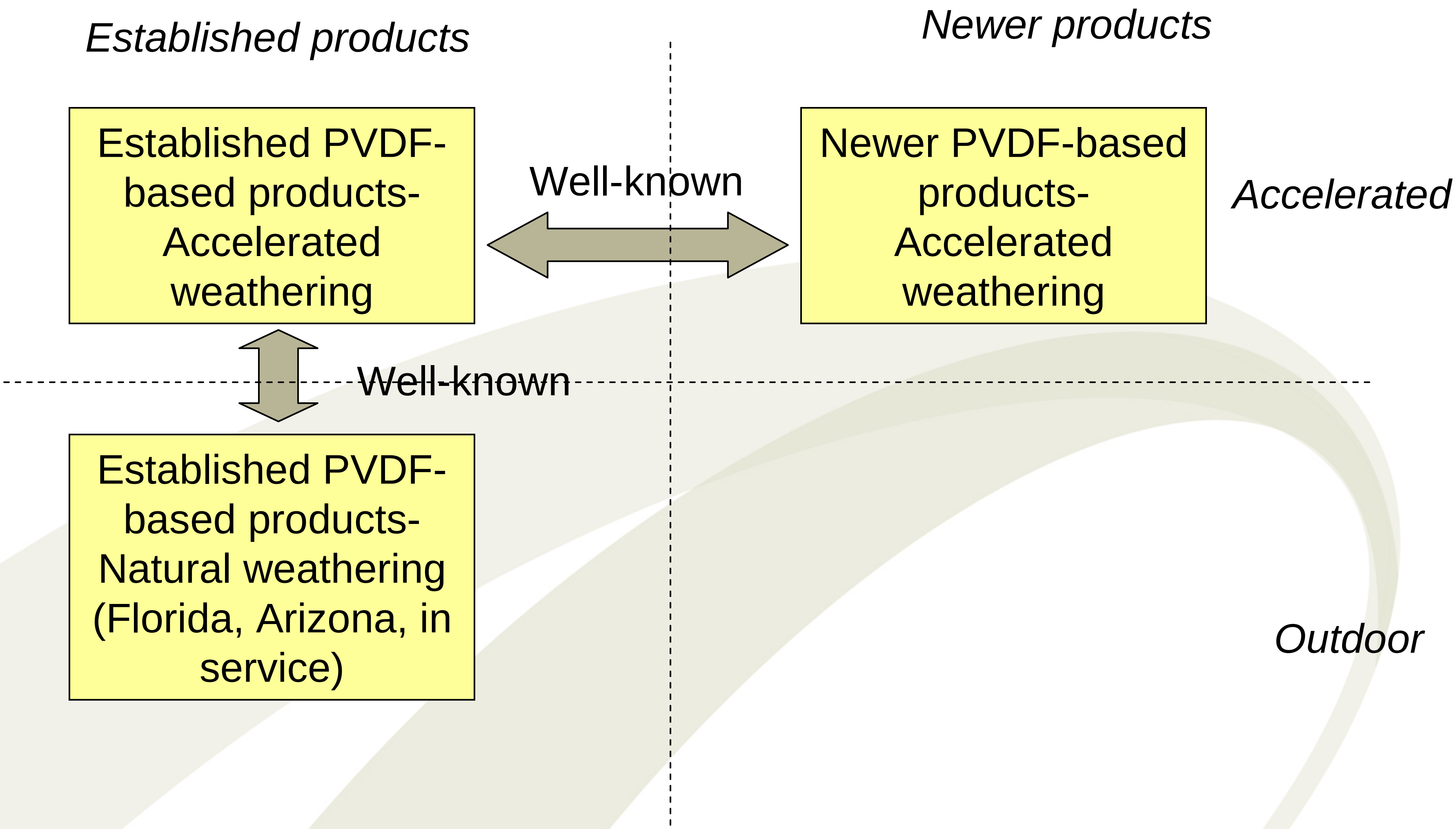
Waterborne PVDF hybrid systems,

About 1000 panels, up to 15 years old



- *As well as accelerated data (often using several different accelerated test methods) for most of our test panels ; also selected data for exposures in other outdoor test sites*

Extensive data we have:



Established products

Newer products

Established PVDF-based products- Accelerated weathering

Well-known

Newer PVDF-based products- Accelerated weathering

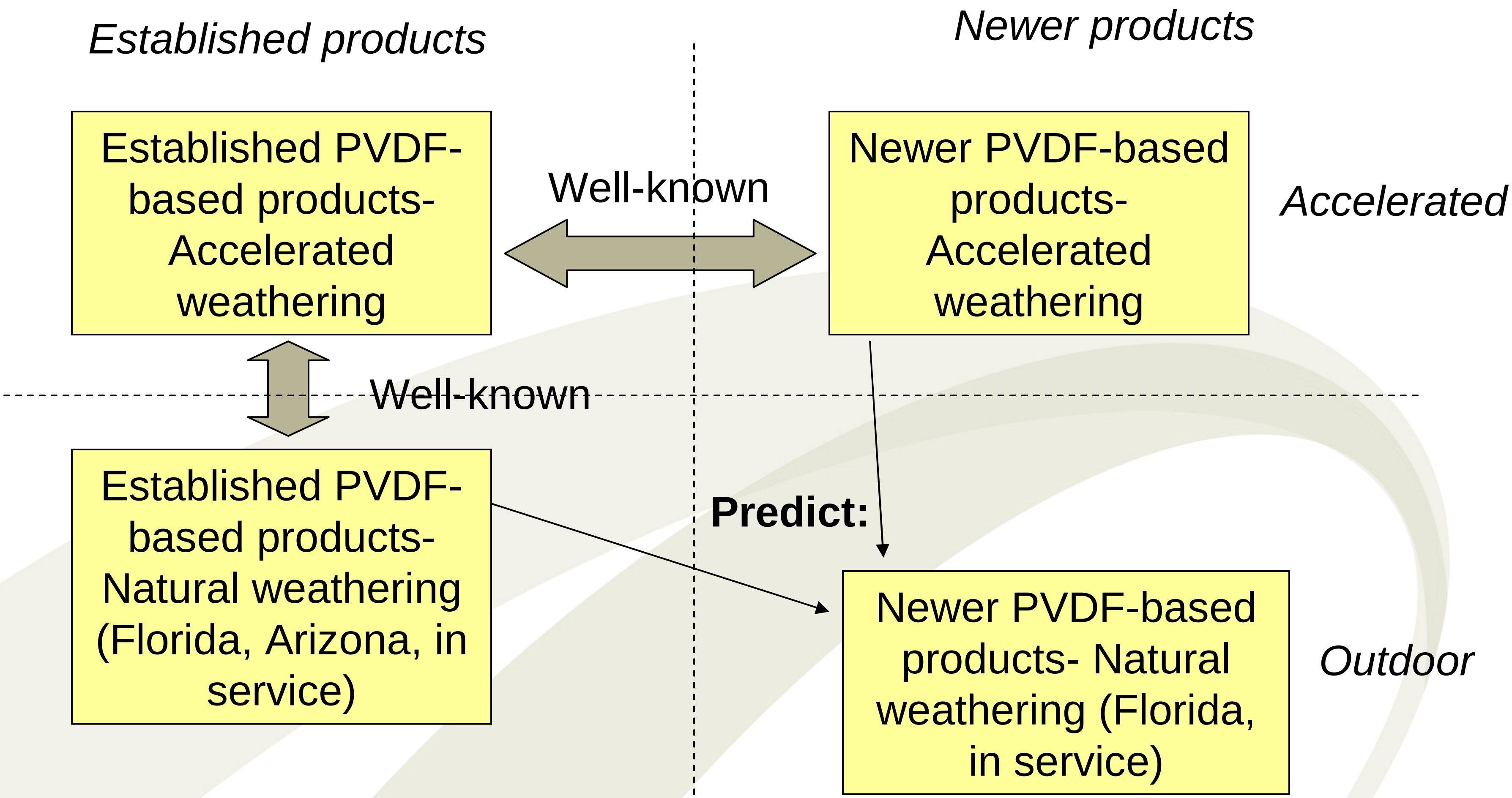
Accelerated

Well-known

Established PVDF-based products- Natural weathering (Florida, Arizona, in service)

Outdoor

Our general practical approach



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Established PVDF-based products- Natural weathering (Florida, Arizona, in service)

Predict:

Newer PVDF-based products- Natural weathering (Florida, in service)

Outdoor

- *The predictions rely on a general model for weathering of PVDF-acrylic blends*

Outline

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- **Quantitative Model for the Prediction of Gloss Retention, Color Change, and Chalking for Poly(Vinylidene Fluoride)/Acrylic Blends**
- Accelerated weathering of PVDF/acrylic blends: opportunities and limitations

“Contraction” model for paint gloss loss and chalking

51

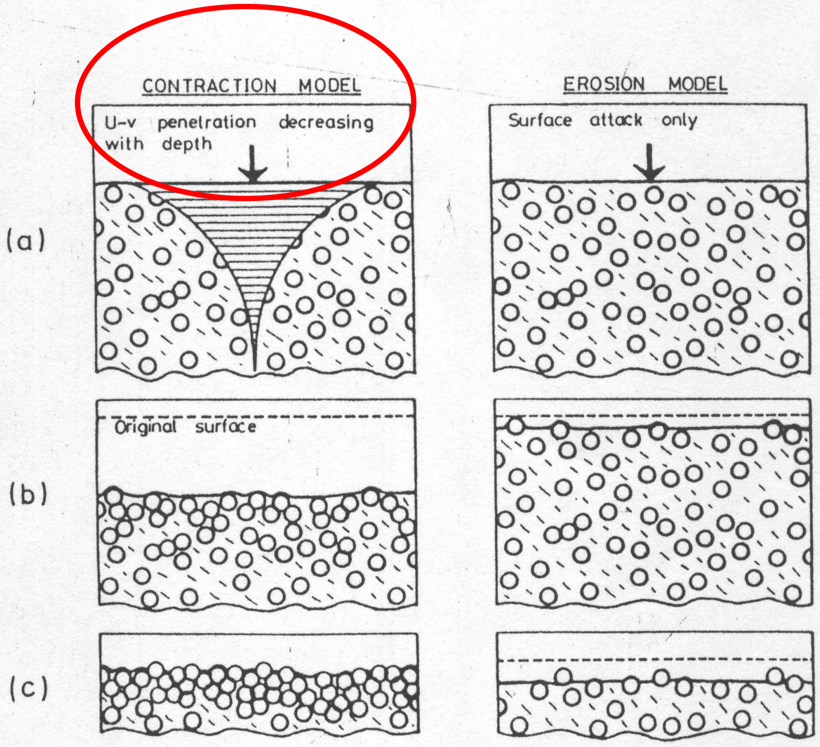
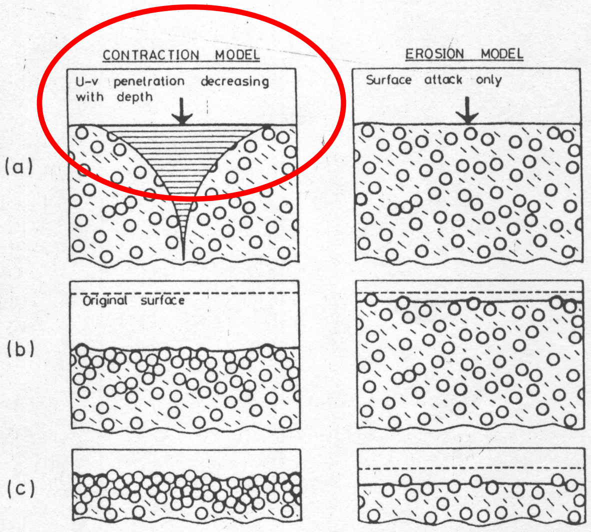


Fig. 1. Comparison of basic contraction and erosion models (diagrammatic). (a) Unweathered. Initial PVC ~ 12.5%. (b) After some degradation, but no loss of pigment. (c) After further degradation; pigment loss is beginning.

From J. H. Colling and J. Dunderdale, *Prog.Org. Coat.* **9** (1981) 47-84.

- For thermoplastic or lightly crosslinked systems, as here
- Mass loss, leading to film contraction, occurs as far into coating as photodegrading wavelengths can penetrate

“Contraction” model for paint gloss loss and chalking



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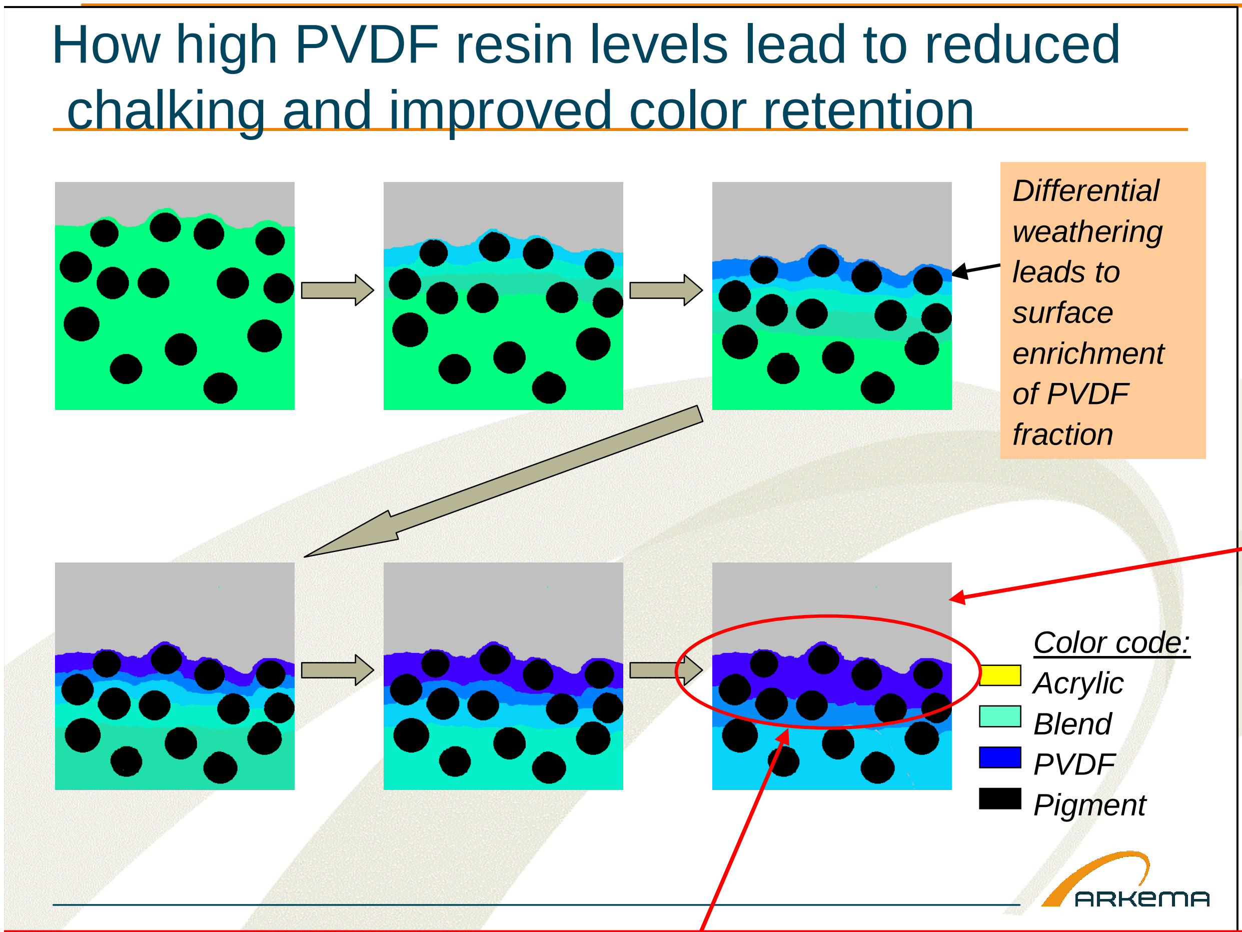
Some predictions of the model:

- **Mass loss usually precedes gloss loss**
- **Gloss loss (surface roughening) precedes chalking**
- **Chalking occurs when surface PVC (pigment volume concentration) = CPVC (critical PVC)- surface pigments are no longer encapsulated**
- **Small color shifts at short time (in neutral direction, usually) result from the higher surface PVC**

Contraction model predictions for blends of a more photoresistant (PVDF) and less photoresistant resin (acrylic)



How high PVDF resin levels lead to reduced chalking and improved color retention

Differential weathering leads to surface enrichment of PVDF fraction

Color code:

- 🟨 *Acrylic*
- 🟩 *Blend*
- 🟦 *PVDF*
- ⬛ *Pigment*

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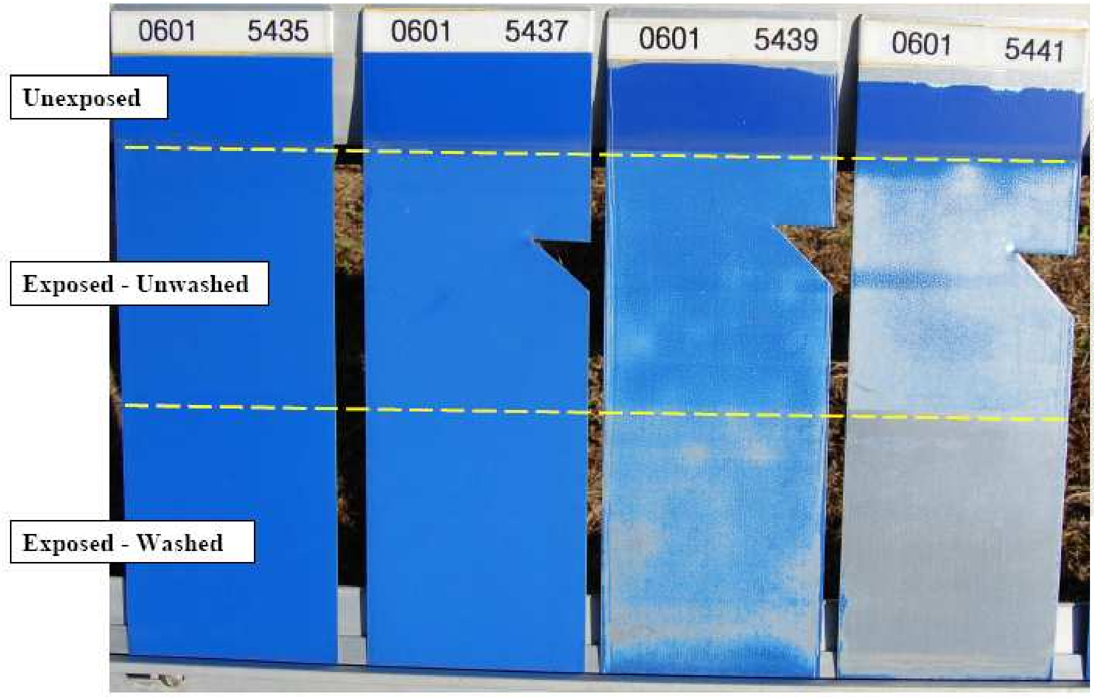
Little further degradation occurs after the near-surface acrylic is depleted

- *If "high enough" PVDF levels are used, the surface PVC stays below the critical PVC even after complete acrylic loss from weathering. Threshold depends on the PVC*
- *If pigments can stay encapsulated by PVDF alone: no chalking and only limited color fade– assuming stable inorganic pigments are used*

PVDF-acrylic ladder, Florida weathering

Waterborne coatings, 12 PVC
Appearance after 7.5 years
South 45º Florida exposure



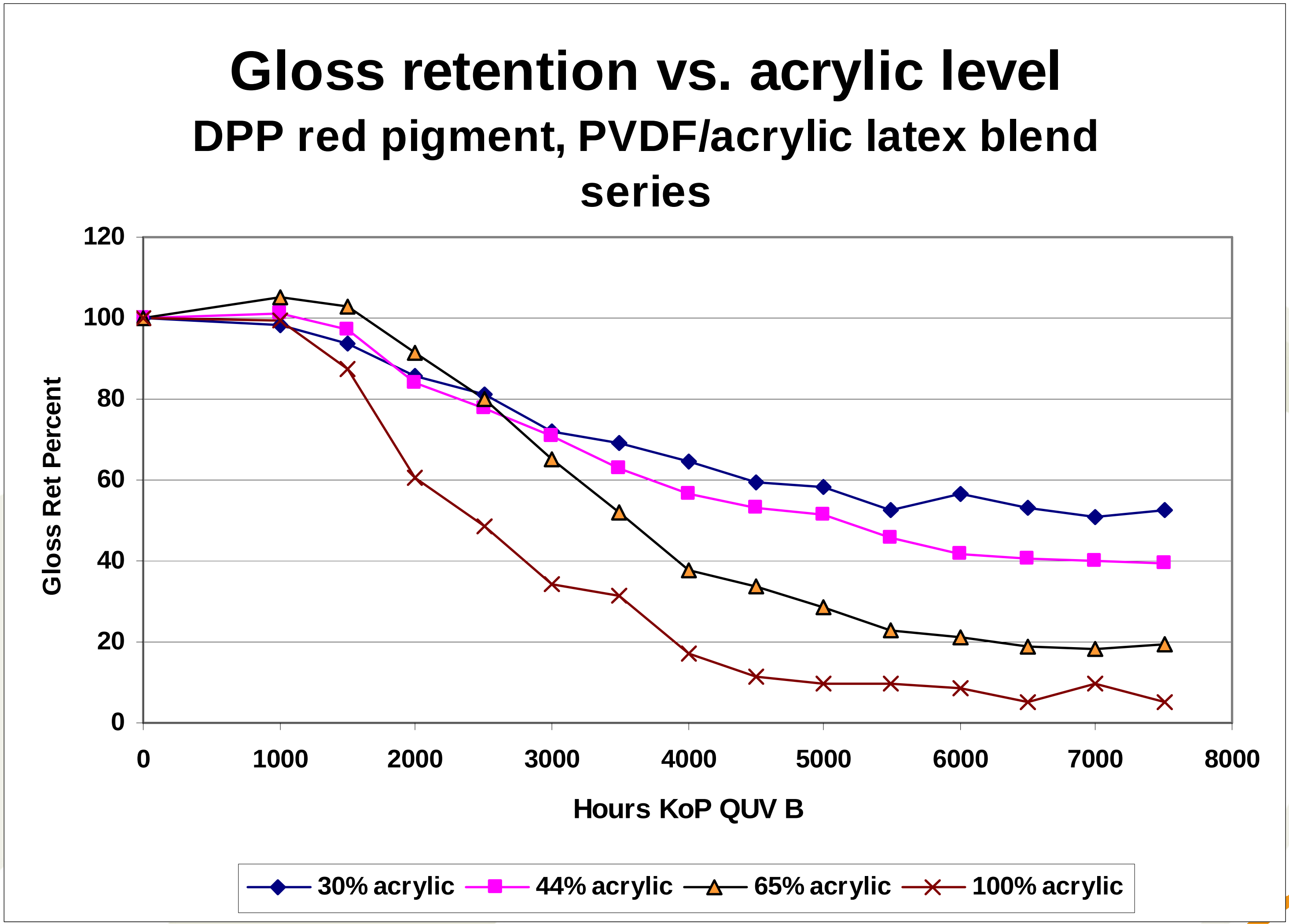
70% PVDF

50% PVDF

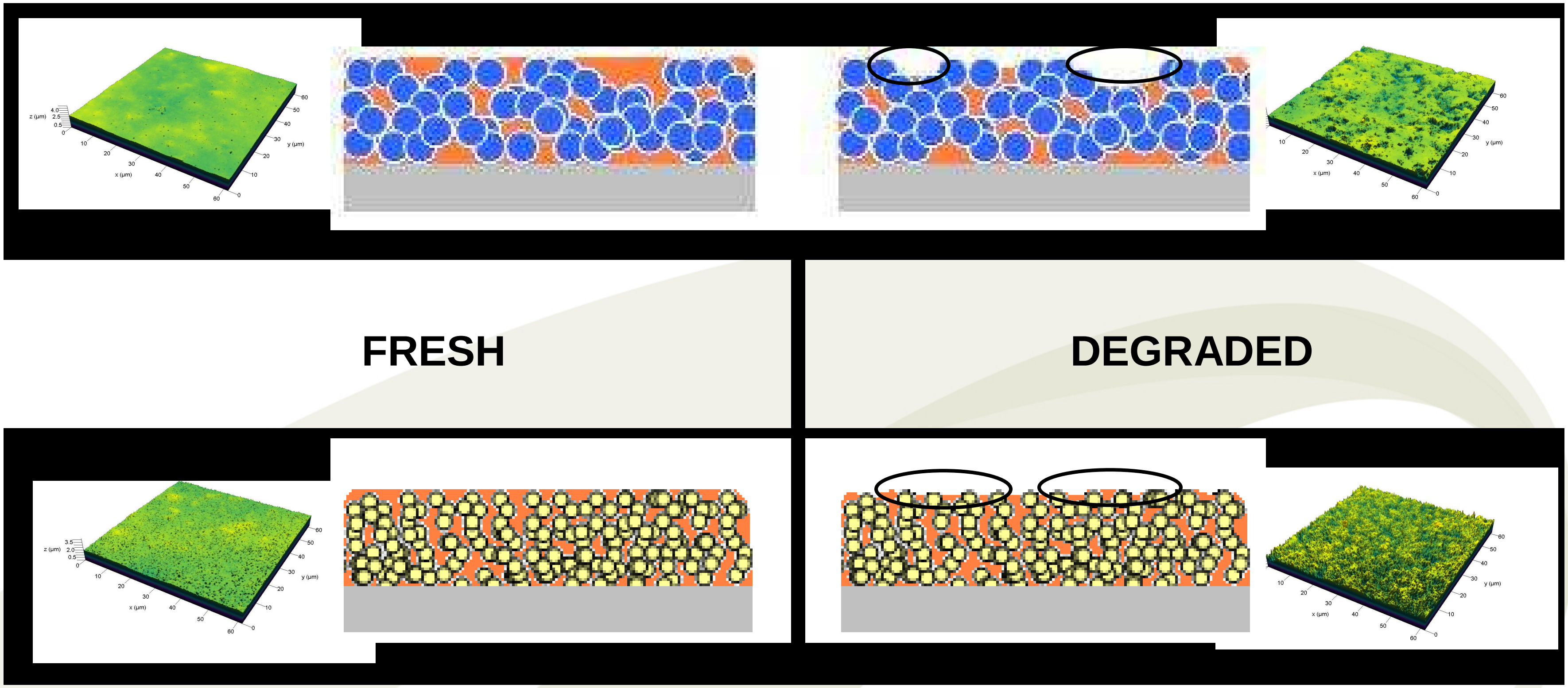
100% acrylics

- *Cobalt blue pigment allows penetration of UV into the binder*
- *Color fade comes only from binder degradation and chalking effects*
- *Color fade rate scales roughly with total acrylic content*
- *No chalking or cracking for systems with 50% or higher PVDF*

Model predicts gloss dropping to a steady state value depending on the PVDF levels



The contraction model is consistent with observed pigment size and pigment dispersion quality effects

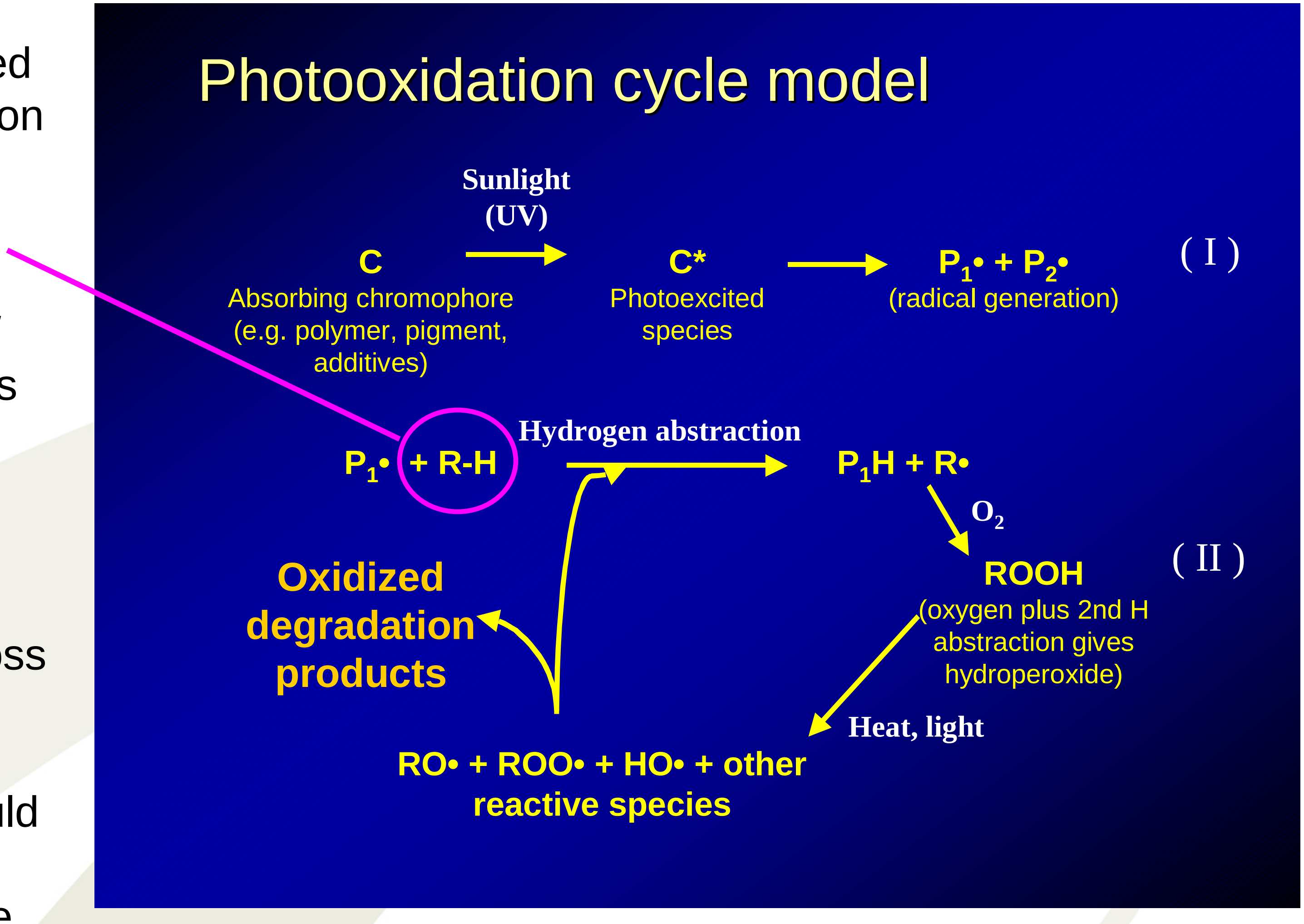


🟧 Binder
⬭ Pit, loss of material
● Pigment Cluster Ø~5µm
○ TiO$_2$

J. Faucheu, K. A. Wood, L.-P. Sung and J.W. Martin, JCT Research Vol. 3, No. 1, 29-39, January 2006

The photooxidation cycle: role of H abstraction

- Rate of –OOH formation is related to the concentration of most abstractable protons–
- For PVDF resin/ acrylic blends, this is proportional to the binder acrylic fraction
- The degradation rate– for binder loss and organic pigment destruction– should therefore be proportional to the *total acrylic level*



Photooxidation cycle model

C
Absorbing chromophore
(e.g. polymer, pigment, additives)

Sunlight (UV)

C*
Photoexcited species

$P_1\bullet + P_2\bullet$
(radical generation)

(I)

$P_1\bullet$ + R-H

Hydrogen abstraction

$P_1H + R\bullet$

O_2

ROOH
(oxygen plus 2nd H abstraction gives hydroperoxide)

(II)

Heat, light

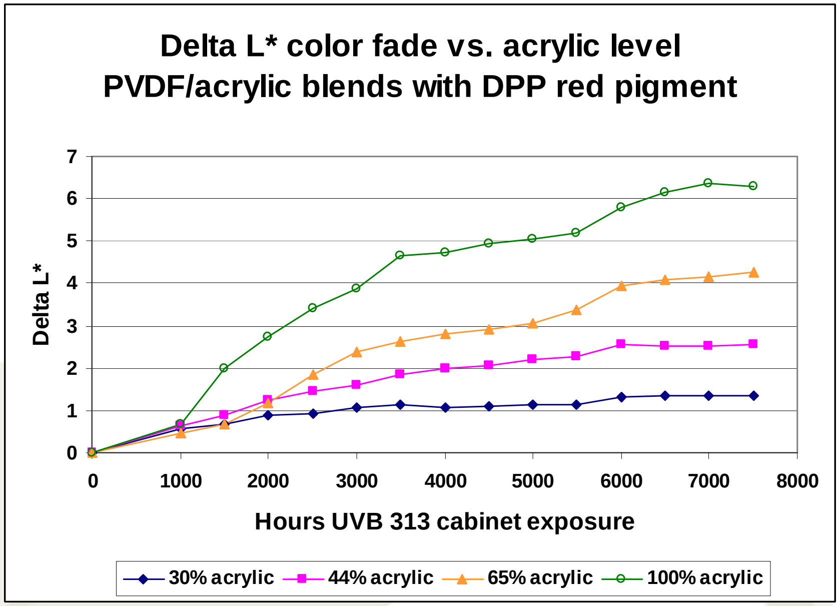
RO• + ROO• + HO• + other reactive species

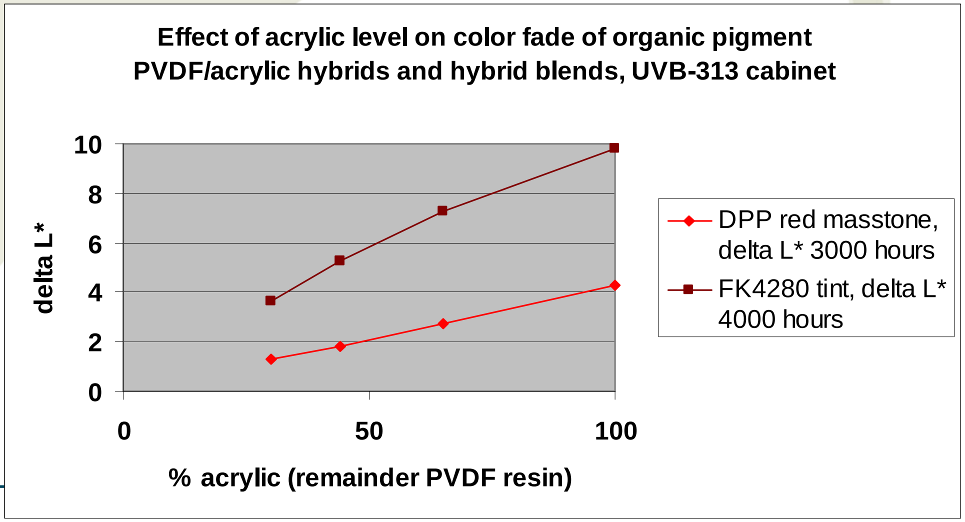
Oxidized degradation products

For organic pigments, color fade rate should be proportional to the binder acrylic content

- *For a specific organic pigment, undergoing color fade from photooxidative attack*
- *Same mechanism would apply to relative gloss loss rate regardless of pigmentation type, if the contraction model is correct*

PVDF: acrylic ratio	Total wt% acrylic resin	Rate of color fade (neat acrylic = 100%)	Color fade lifetime vs. lifetime in neat acrylic
0:100 (baseline)	100%	100%	1.0x
20:80	80%	80%	1.25x
40:60	60%	60%	1.66x
50:50	50%	50%	2.0x
70:30	30%	30%	3.3x





Role of TiO_2 and other photocatalytically active pigments

- TiO_2 particles both protect the binder (polymer continuous phase) by blocking UV, AND initiate binder degradation through photocatalytic sites on the particle surface
- Grades designed for exterior applications have low photocatalytic activity, but residual photoactivity can still be a significant contributor to binder degradation over long periods of time
- For PVDF/acrylic blends, adding TiO_2 therefore tends to accelerate the rate of gloss loss, also organic pigment color fade, compared to the case of masstones (no TiO_2)
- Color fade rates for whites and tint finishes with *inorganic* pigment are low, since colored pigment is not attacked by the photoradicals

Summary of quantitative model:

- The relative rate of degradation for PVDF/ acrylic blends, compared to acrylics, can be quantitatively estimated using the contraction model plus a simple kinetic model based on the photo-oxidative cycle
- For paints using color-fast inorganic pigments, chalking and dramatic color fade can be prevented by using a high enough PVDF level (such that PVC < CPVC even if all acrylic is removed)
- Gloss loss rate, plus color fade rate for organic pigments, is roughly proportional to the total fraction of acrylic in the binder
- TiO_2 net impact is complex: a tradeoff between protective effects (UV blocking) and photocatalytic contribution

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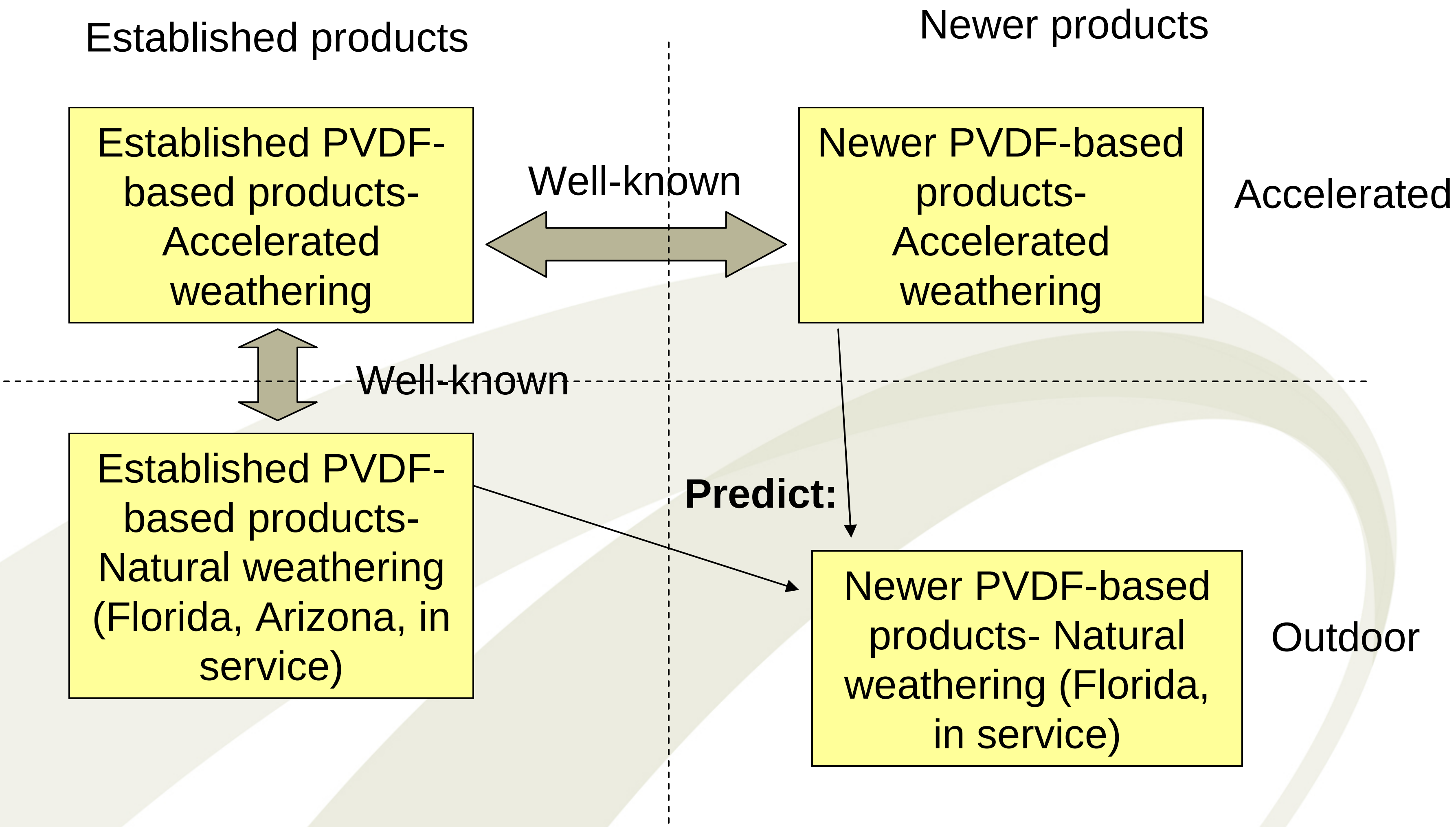
Our general practical approach



Established products

Newer products

Established PVDF-based products- Accelerated weathering

Well-known

Newer PVDF-based products- Accelerated weathering

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Predict:

Established PVDF-based products- Natural weathering (Florida, Arizona, in service)

Newer PVDF-based products- Natural weathering (Florida, in service)

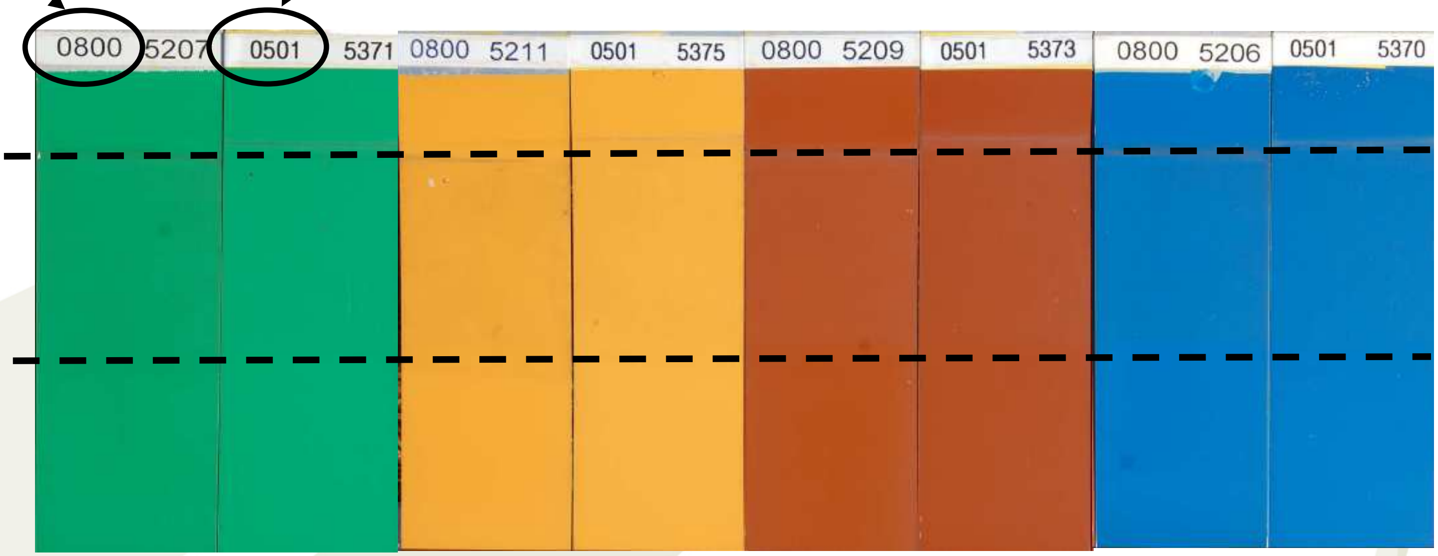
Outdoor

A specific strategy for our new products- guided by our weathering model

- Verify that resin blend morphology is similar to the morphology of established products with a long outdoor exposure track record
- Formulate with proven raw materials which are also used with the established products
- Screen formulations mainly using UVB exposure since surface attack of acrylic component will mimic what happens outdoors at long times
- Monitor parallel outdoor exposures to look primarily for unanticipated new failure modes
  - Outdoor exposure should also verify that expectations of similar weathering for similar formulations are correct

Comparison of new and old PVDF platforms

9 Years South Florida Exposure



New waterborne

Traditional high temp. bake

Unexposed

Exposed Unwashed

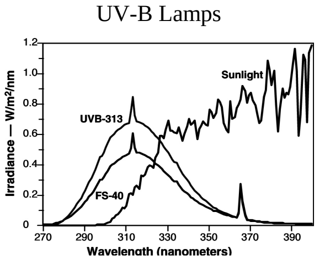
Exposed Washed

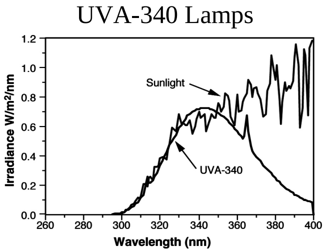
Panel photos taken December 17, 2009

Meet AAMA 2605 10-Year Florida Color, Gloss, and Chalking

Main accelerated weathering options

- Solar Concentrator
  - ASTM-G90
  - Doesn't "get water right"- plus some heat problems
  - Some value for qualification (AAMA 625 for composite window profiles)
- Xenon arc
  - ASTM G155
  - Closest spectral match to sunlight across UV + visible
  - Traditional cycles don't "get water right"
- Fluorescent cabinet
  - ASTM G154
  - Spectral output may differ considerably from solar
  - Option of longer condensation cycles





Relative costs of common accelerated techniques

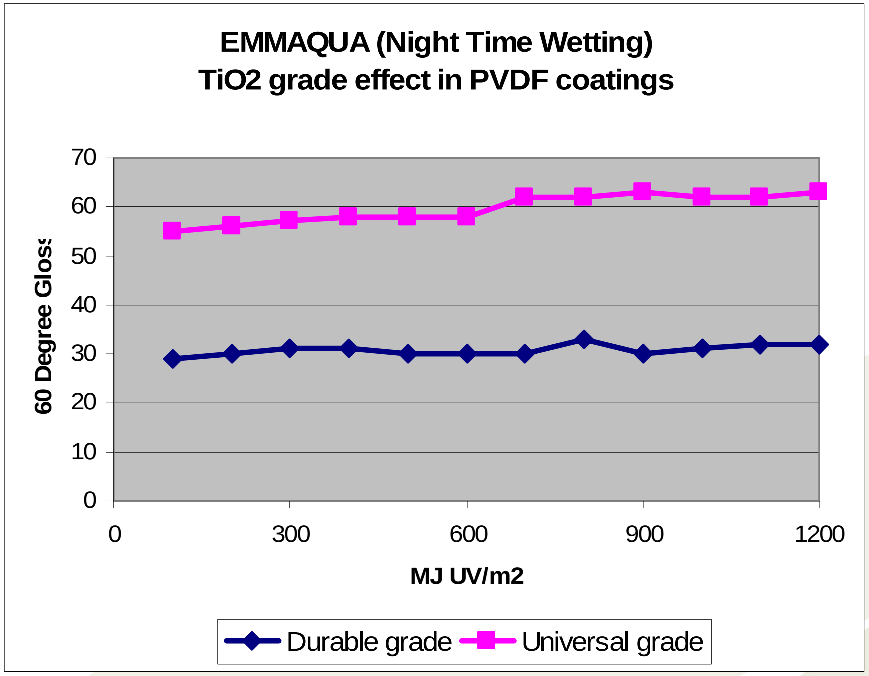
	Xenon Arc ASTM G155	UV Fluorescent ASTM G154	Solar Concentrator ASTM G90
Approximate cost/ standard size sample/year (Outdoor: $5-15/sample/year)	**$145**	**$38**	**$180**
Can use half samples to lower cost?	Yes	Yes	No
Approximate acceleration factor vs. Florida	??? Depends	??? Depends	4x (realistically, for AAMA 625 qualification)

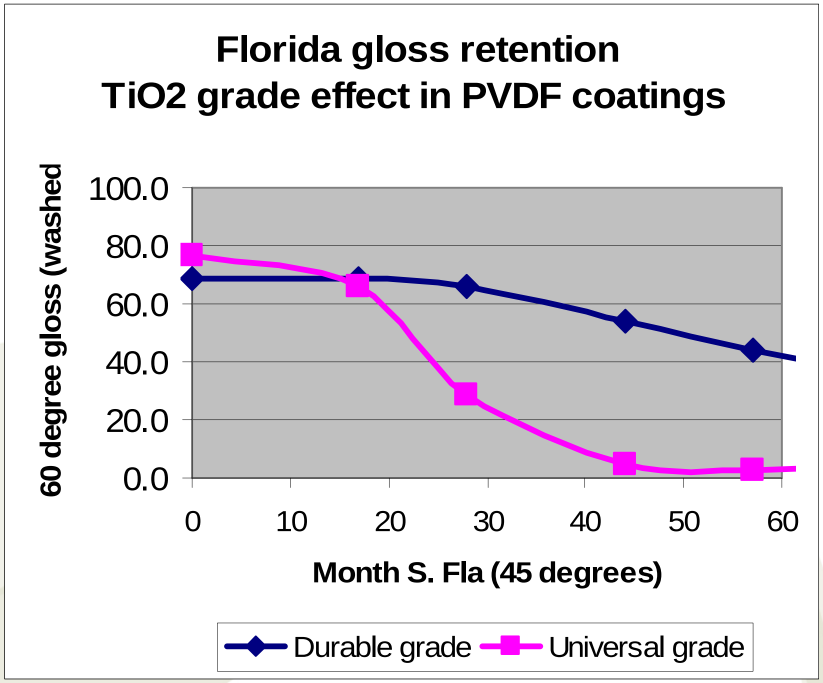
When can we get away with using UVB fluorescent testing?

Our group's historical experience:

- For similar formulations (same % PVDF in binder, same pigment at same loading level), long term color shifts are comparable across product platforms– but accelerated color shifts are often smaller than Florida color shifts, for comparable gloss retention (inorganic pigments)
- Minimal film erosion and chalking in nearly all cases, similar to Florida, as long as film formation is adequate (generation of PVDF continuous phase);
- Rates of gloss loss correlate less well across product platforms (heat, humidity effects?)
- UVB testing does NOT work well to rank TiO_2 grades for weatherability

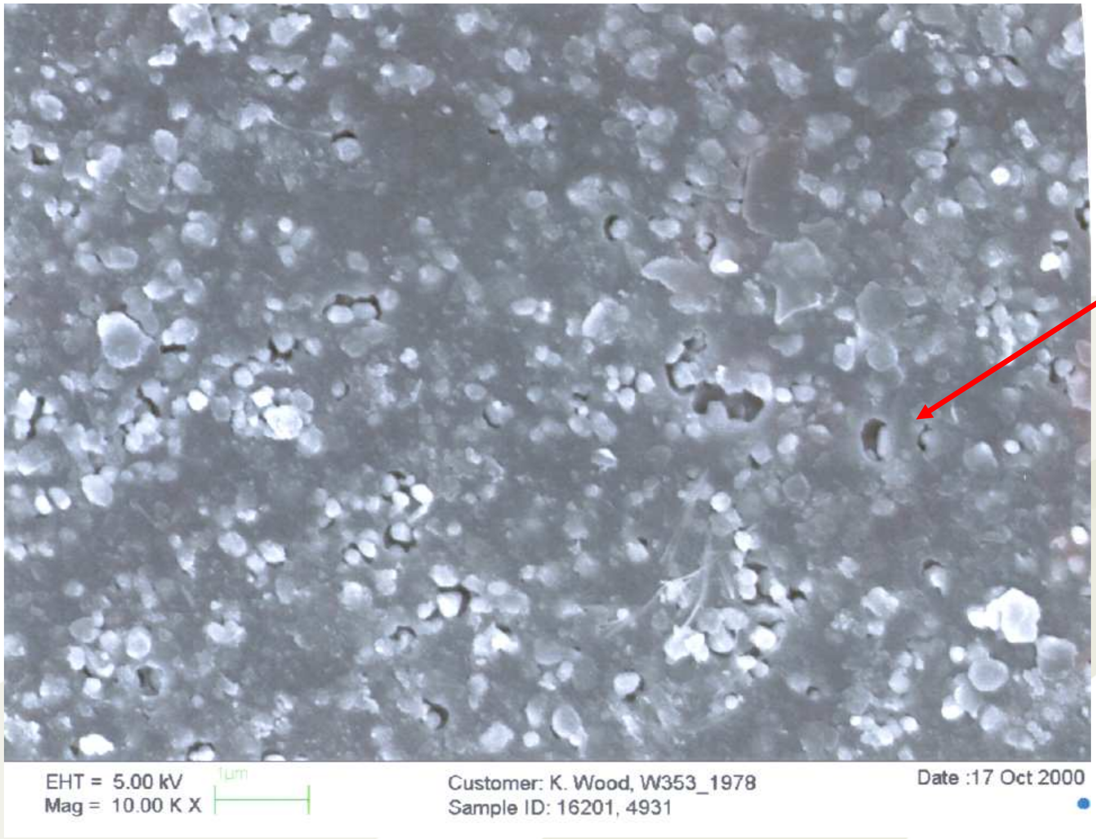
TiO_2 grades- a particular challenge





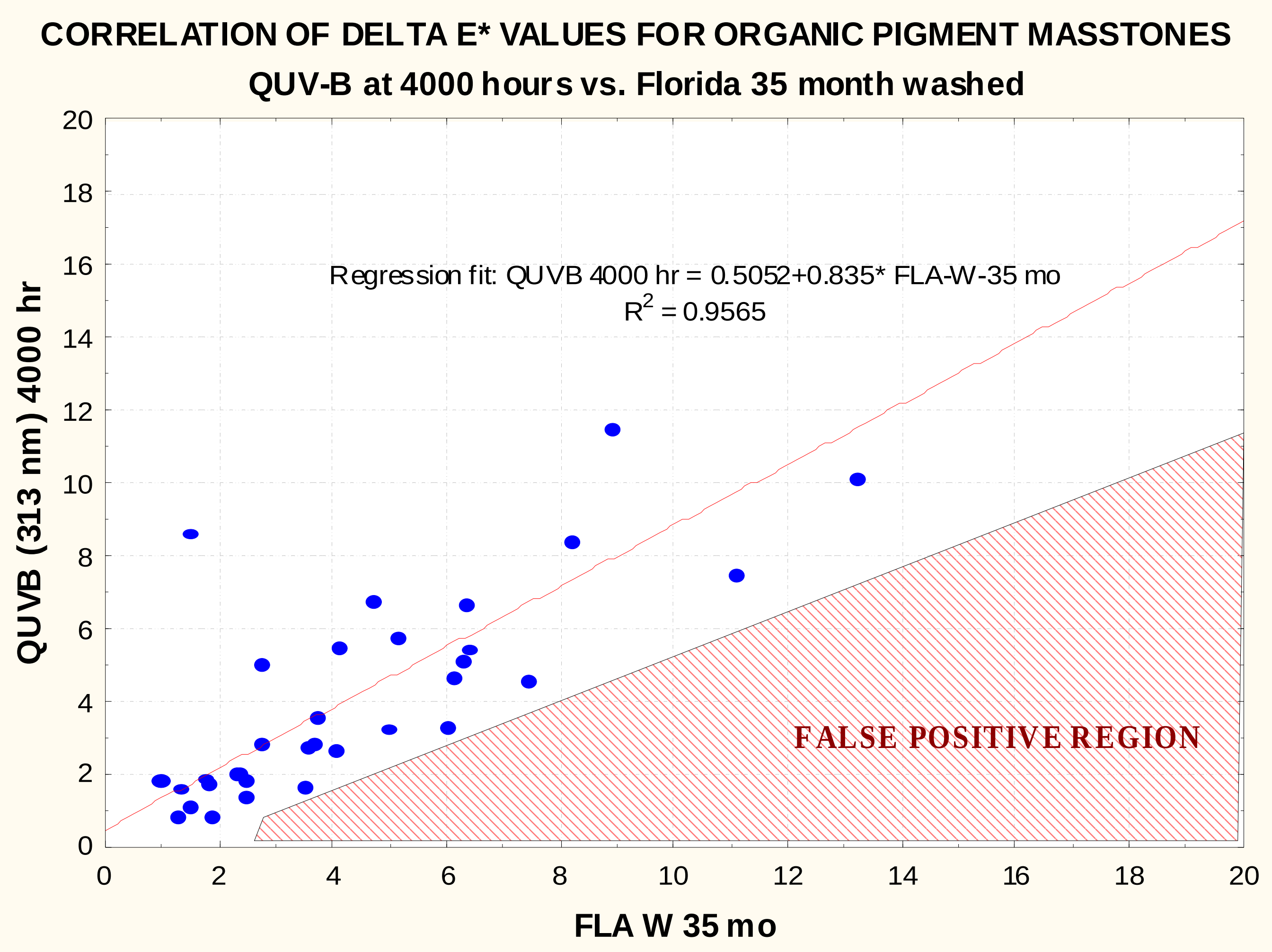
- Neither UVB fluorescent testing, nor Solar concentrator testing, accurately ranks TiO_2 grades for weatherability in 70% PVDF systems (false positive for universal grade, for AAMA 624 qualification!)

TiO_2 grades and photocatalytic activity



- The more durable the binder, the less important is the TiO_2 protective effect, but the more one needs to worry about residual photocatalytic activity from the pigment
- Water plays an important role in photoradical generation
- Photoradical generation rate likely scales not linearly with light intensity but rather like $I^{0.5}$
- Degradation does not have x-y homogeneity

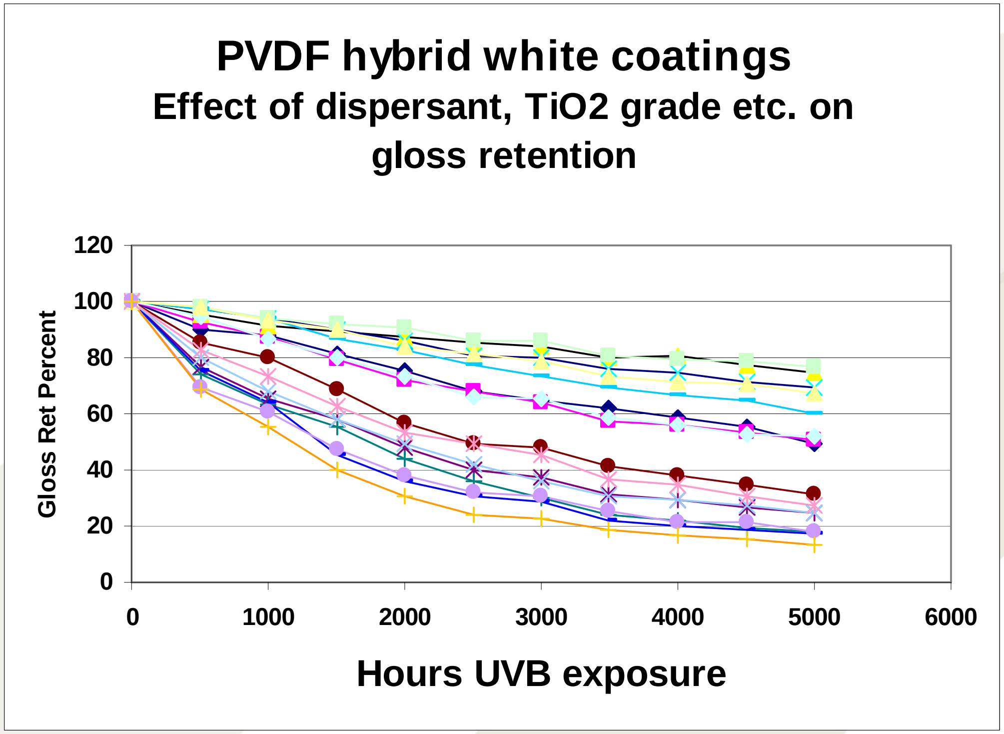
Organic pigment color fade- UVB exposure <u>does</u> accurately predict Florida for PVDF systems, surprisingly!

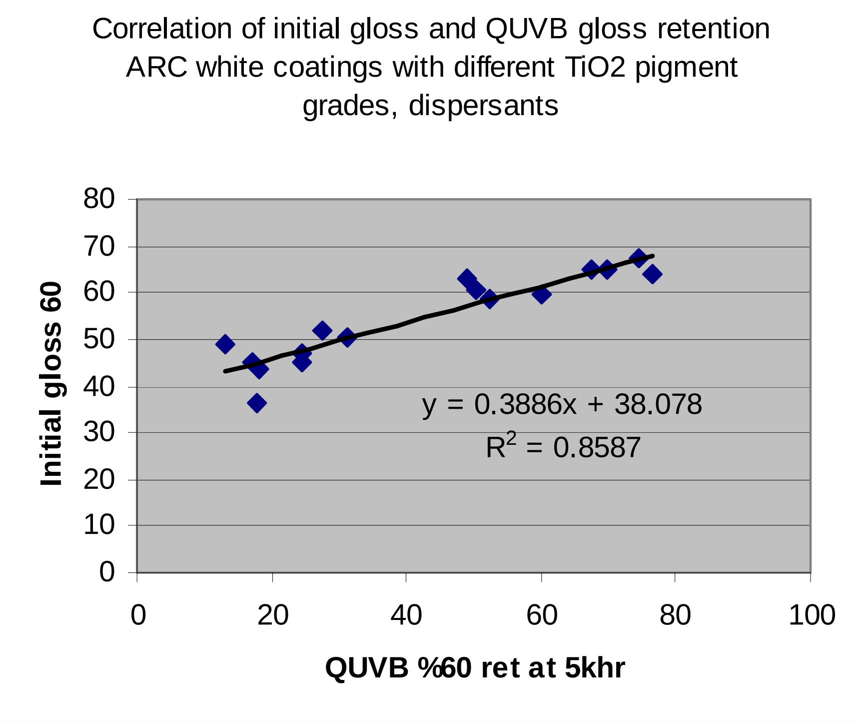


- Florida vs. UVB: Spearman R = 0.90
- No “false positives”
- Acceleration factors range from 3-20, but are greater for more durable organic pigments

UVB exposure reproduces the sensitivity of gloss retention to the uniformity of the pigment dispersion

- A 2^4 DOE study looking at TiO_2 grade, dispersant, and bake temperature/annealing effects
- Initial gloss levels were between 36 and 68, reflecting different degrees of quality of the dispersion





When can we get away with using UVB fluorescent testing?

Most important info needed for warranty considerations

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When can we get away with using UVB fluorescent testing?

Room for improvement!

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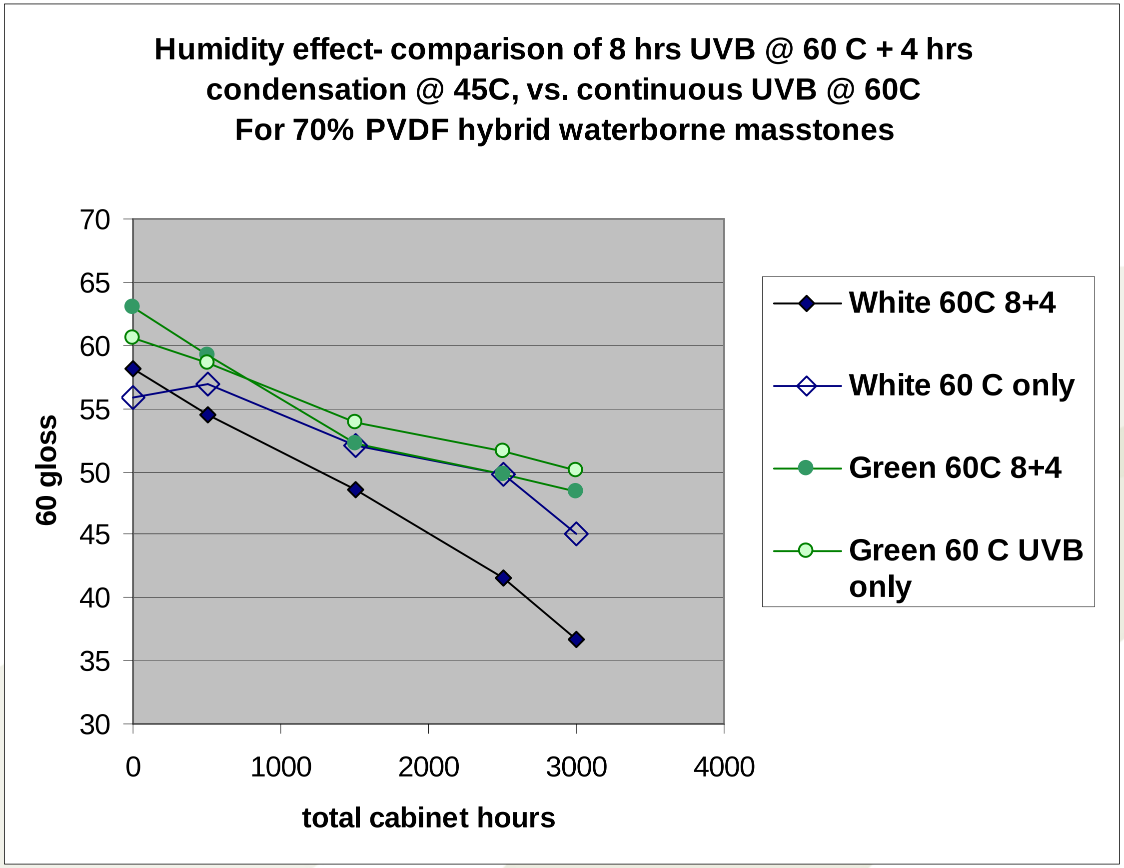
A fluorescent cabinet “high throughput” experiment

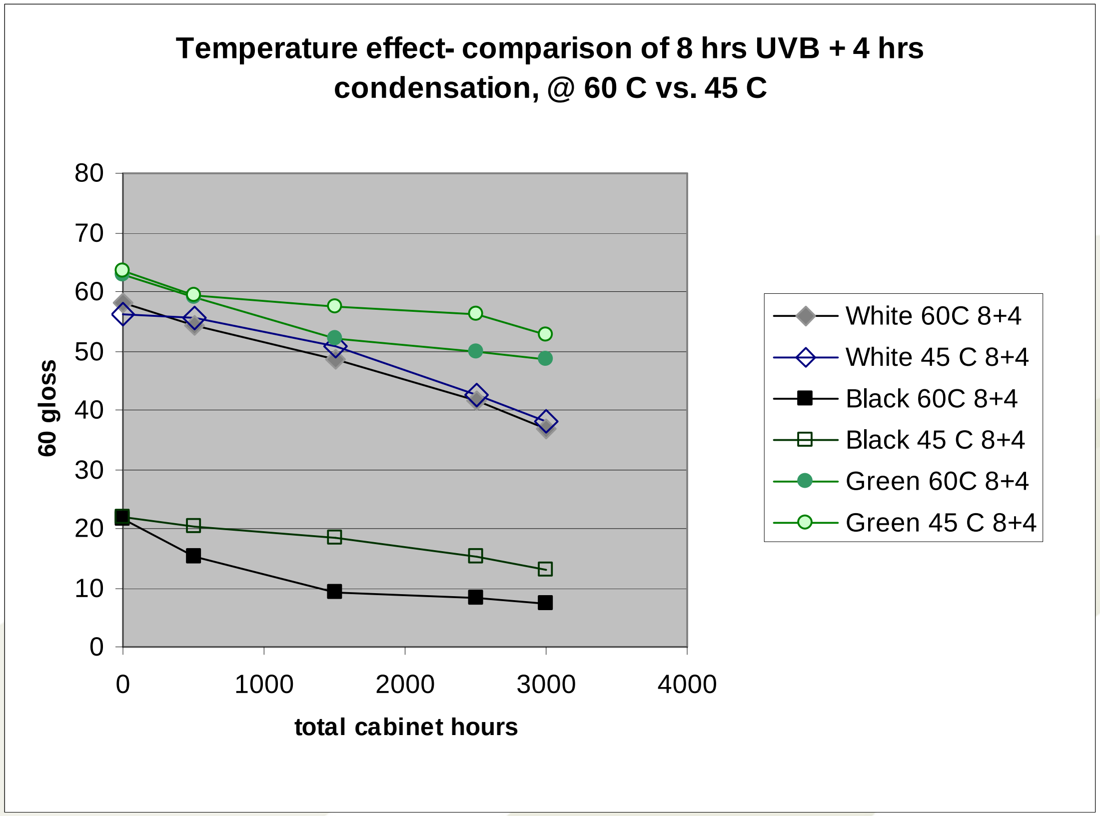
- Run UV fluorescent cabinets in parallel under different conditions of temperature and humidity
- Our particular experiment used UVB bulbs and compared:
  - Normal cycle: 8 hours light @ 60 C, 4 hours condensation @ 45 C
  - Cycle without humidity: continuous @ 60 C
  - Lower temperature cycle: 8 hours light@ 45 C, 4 hours condensation @ 45 C

Humidity effect, 70% PVDF waterborne systems



- For green mass-tone (inorganic green pigment), 4 hours light ≈ 4 hours condensation (no light!)
- For white, cycling 4 hours condensation is more aggressive than 4 hours light (dry)

Temperature effect,
70% PVDF waterborne systems



- Little effect of temperature for white coatings
- A larger effect for darker colors: degradation is faster at higher temperature
- Range of conditions tested was not enough to distinguish photocatalytic and thermal effects

Next steps

- Investigate new humidity cycle for xenon arc unit, with PVDF-based coatings (does it more accurately rank TiO_2 grades; does it predict the magnitude of color fade for PVDF masstones?)
- Can we invent an alternate fluorescent cabinet cycle, which more accurately reproduces the magnitude (and direction) of color fade for PVDF masstones?

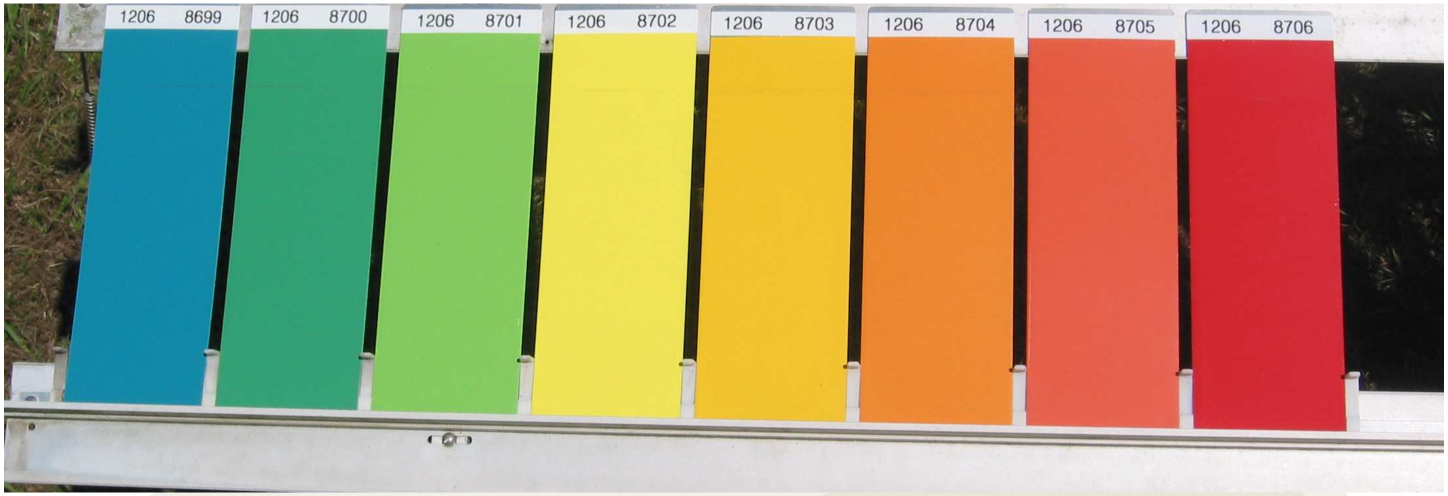
Concluding remarks

- UVB testing (coupled with Florida data for older PVDF products) allows a reliable estimate of color fade, chalking and erosion for new PVDF products, formulated with weatherable inorganic pigments
- Using fluorescent cabinets running multiple cycles is a cost-effective way to gain mechanistic insights about weathering kinetics, and understand (and mitigate?) limitations of accelerated cycles

KYNAR® PVDF technology- traditional and new

New KYNAR Aquatec® emulsion technology for low VOC coatings

Kynar Aquatec®



Proven performance: KYNAR 500® PVDF

COAT WITH CONFIDENCE
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