

Weathering of CICPs

Historical PVDF/Acrylic Liquid Coatings
New FEVE Based Powder Coatings

**WE
BRIGHTEN
LIVES**



About Shepherd Color

- Headquartered in Cincinnati, OH
- Active Fourth Generation, Family Owned Business
- World-Class Producer of Complex Inorganic Color Pigments (CICPs)



High Performance Inorganic Pigments

- Complex Inorganic Color Pigments (CICP)
- Not simple oxides
- Calcined at high temperature
- Resistant to
 - Acid/Bases
 - Solvents
 - UV energy
 - High temperatures

Weathering of Colored Inorganic Pigments

- Stable to acids, bases and solvents
- Inert to UV radiation
- Heat-stable to firing temperature

Impervious to Degradation in
Normal Conditions

Thanks for Coming!!!!

Mark Ryan

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LIVES**



The Shepherd Color Company
We Brighten Lives

High Durability Color Pigments in Use

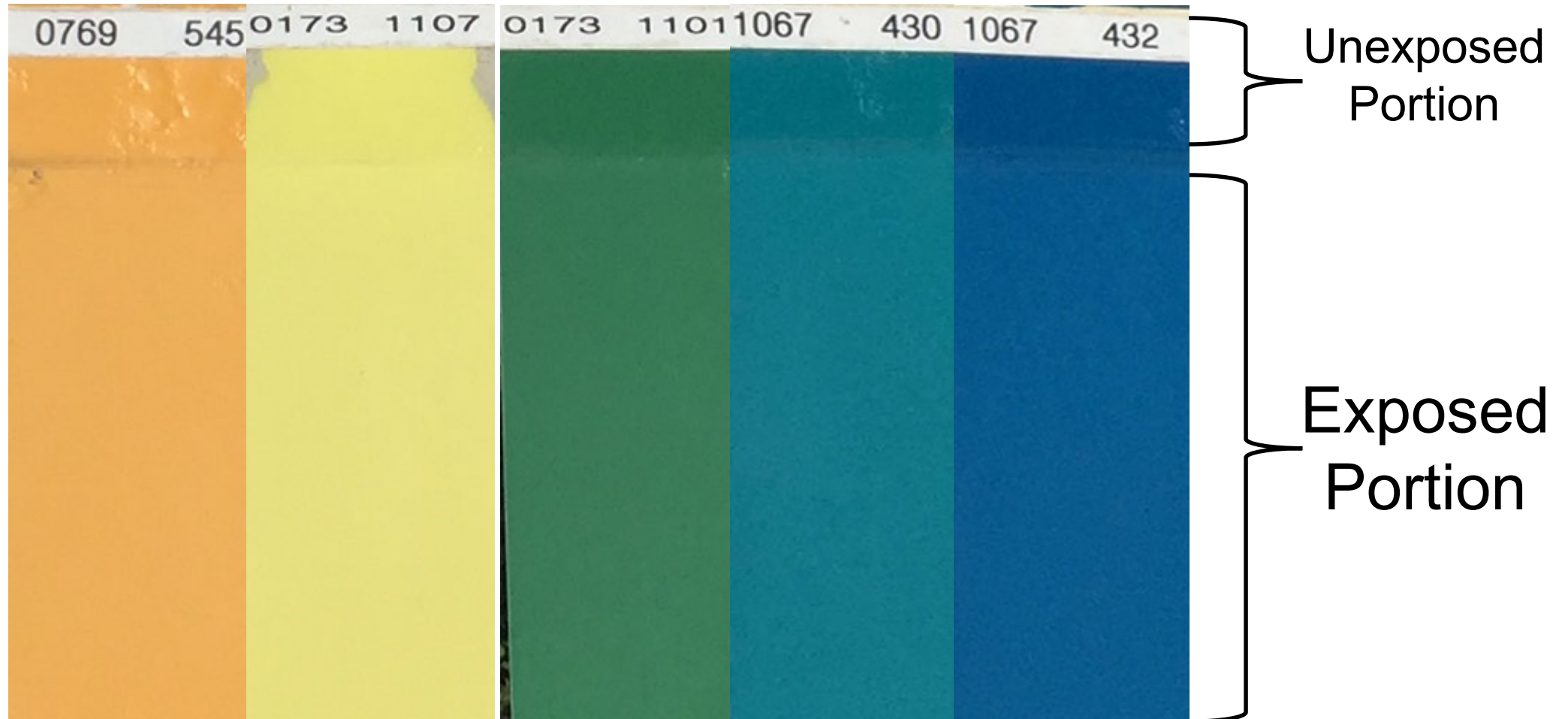
- High heat stable
 - Fully oxidized to firing temperature (standard kiln)
- Resistant to acids & bases
- Insoluble in solvents
- Low surface area
- UV resistant
- Not photoactive like TiO_2 (vibrational mechanism)

- In powder coatings
 - PVDF
 - FEVE
 - Colors

Organic Tints in PVDF/Acrylic



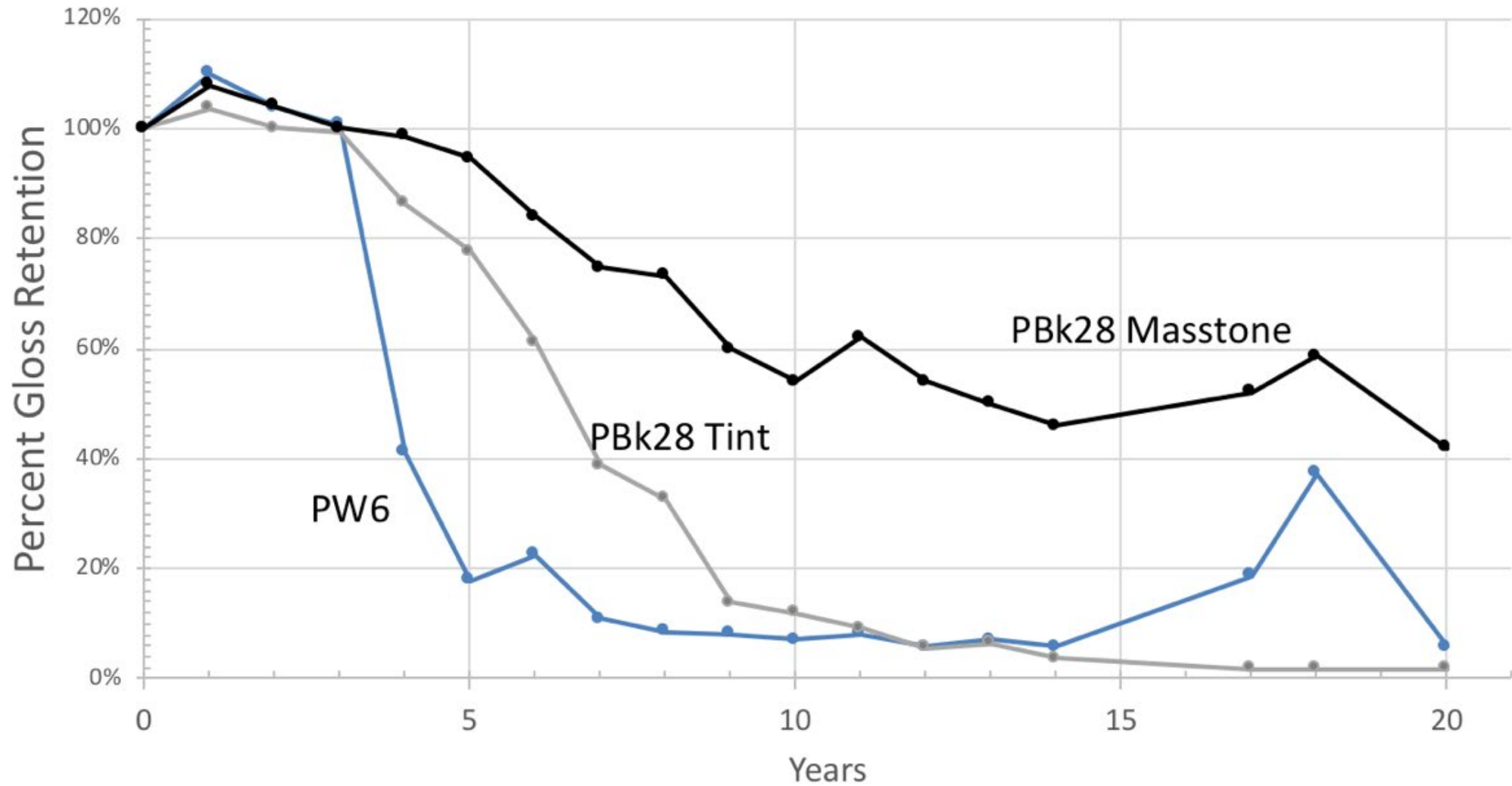
50 year South Florida Exposure PVDF/Acrylic with CICP Pigments



Photos courtesy of Arkema Inc.

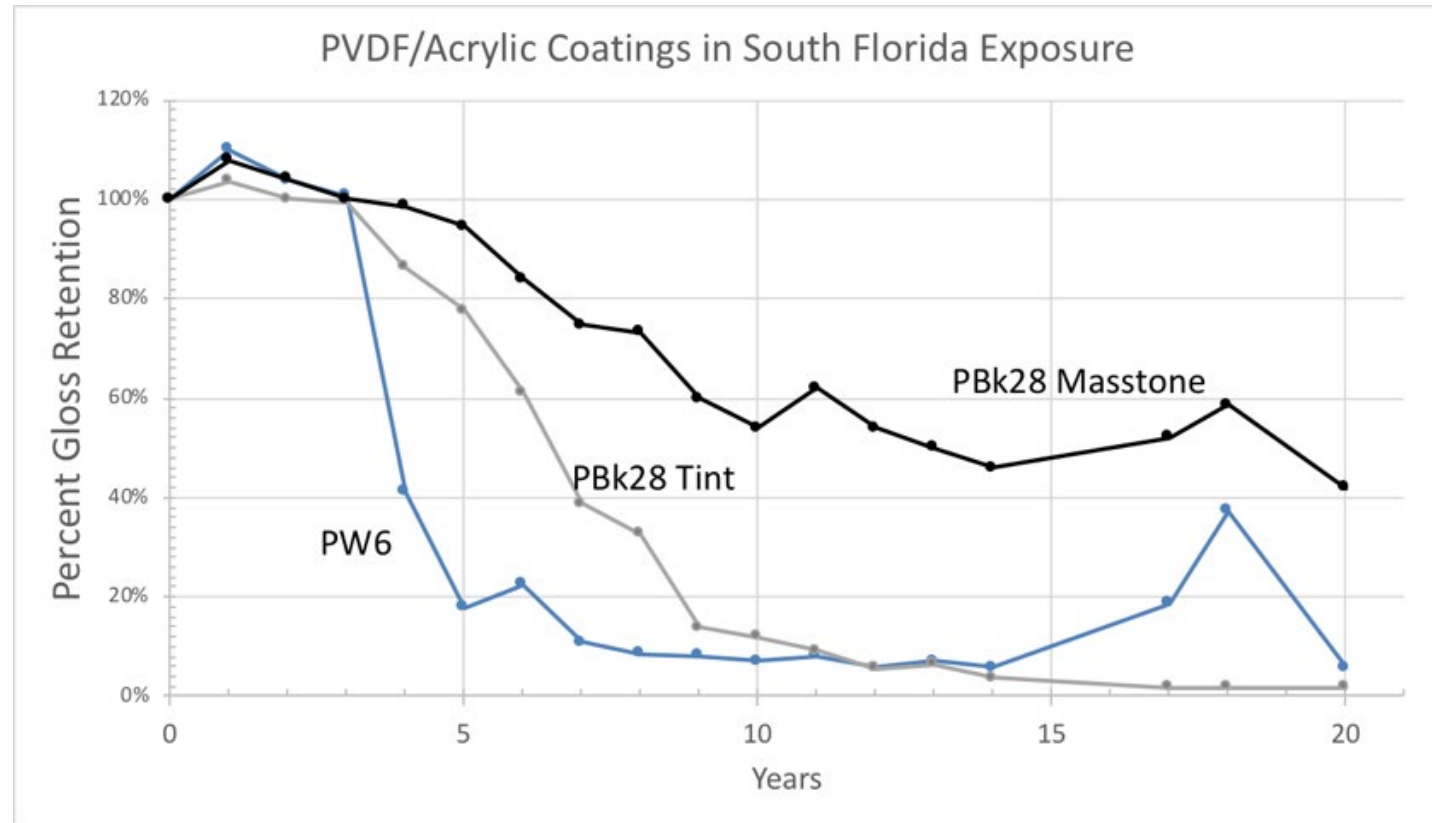
Gloss Change

PVDF/Acrylic Coatings in South Florida Exposure



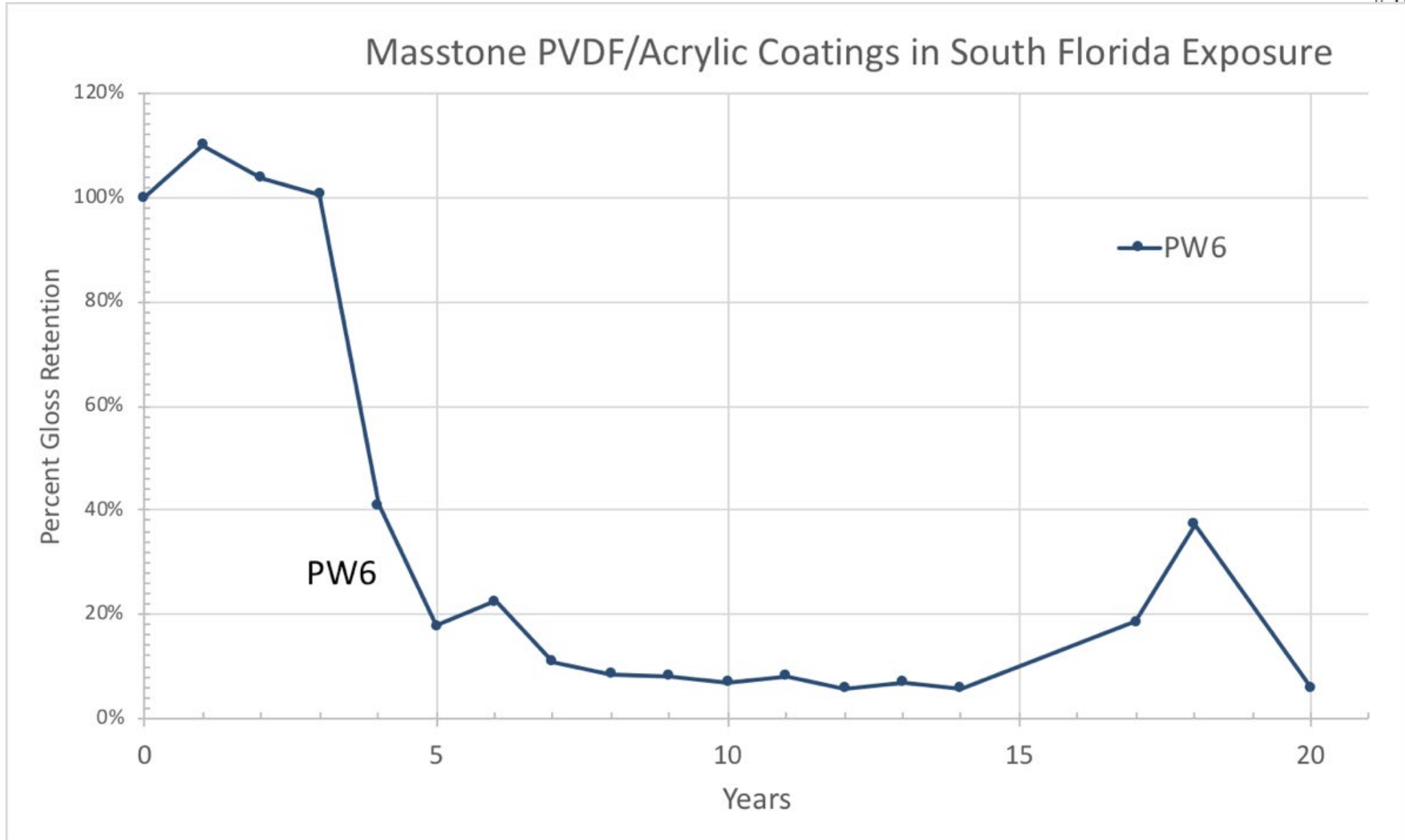
Gloss Change

- TiO₂ lost most gloss
- CACP Black had least
- Black+White middle
- PVDF/Acrylic is highly UV transparent

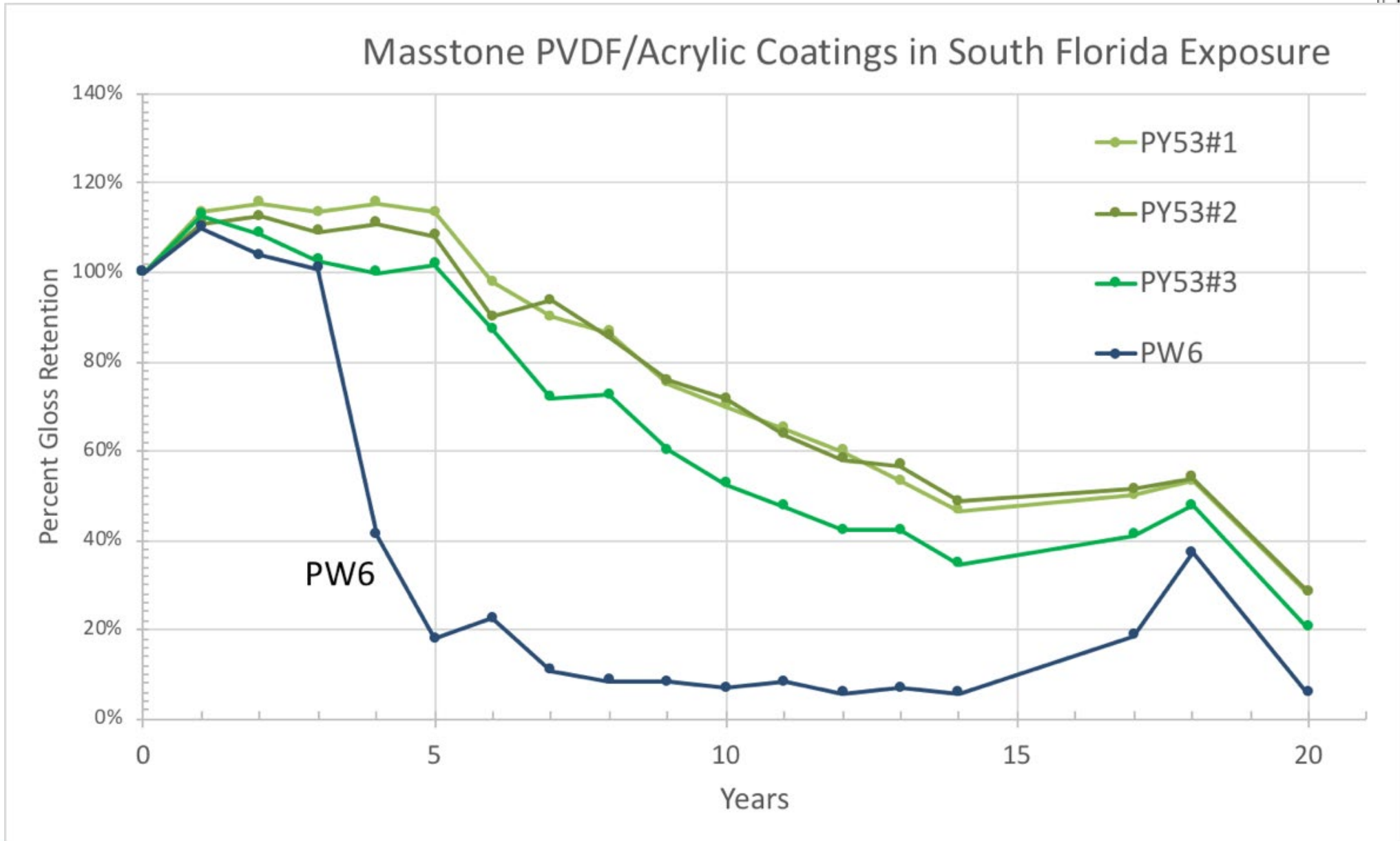


Even though TiO₂ is highly-durable, it has a photocatalytic effect.

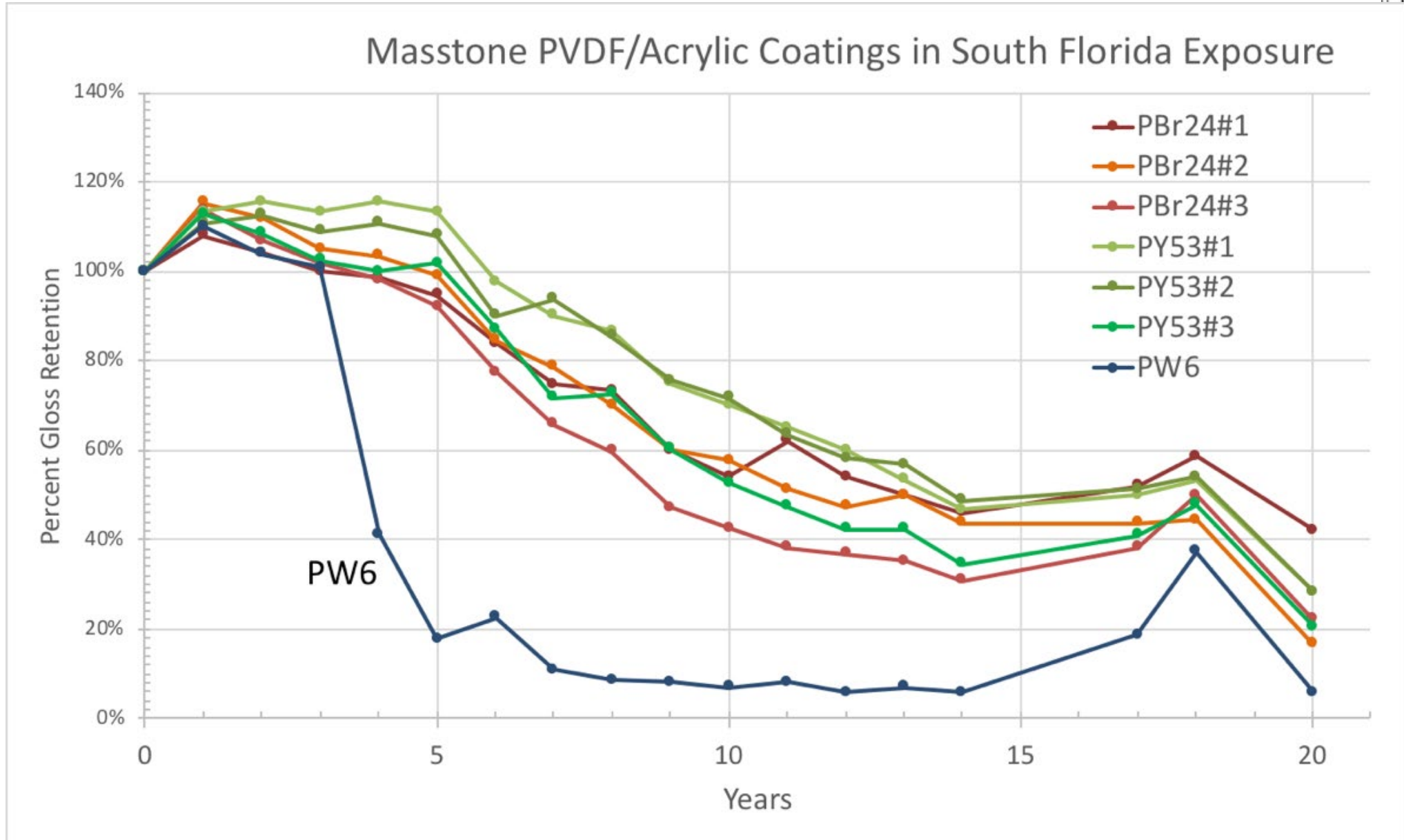
Weathering of Titanate Pigments



Weathering of Titanate Pigments



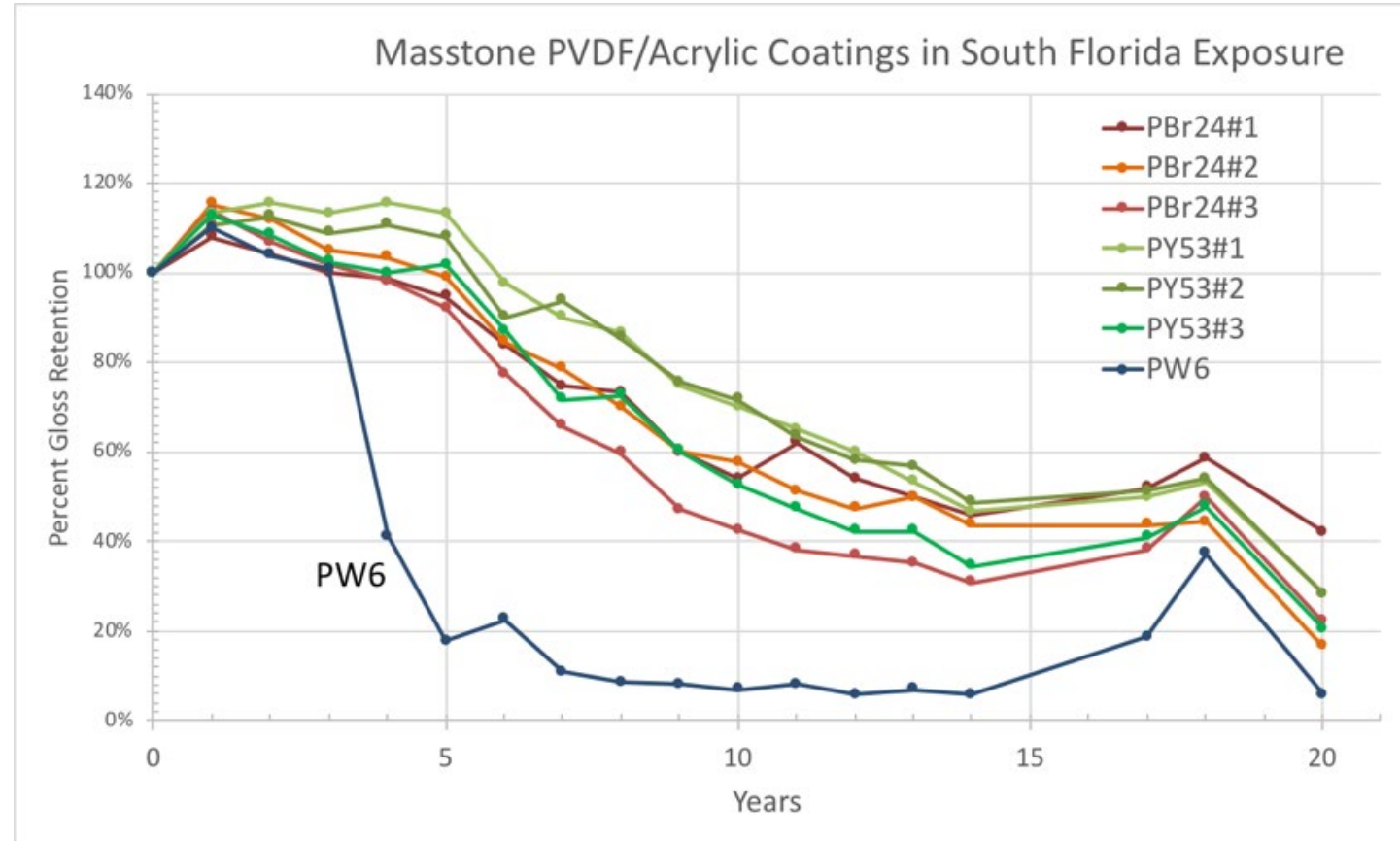
Weathering of Titanate Pigments



Weathering of Titanate Pigments

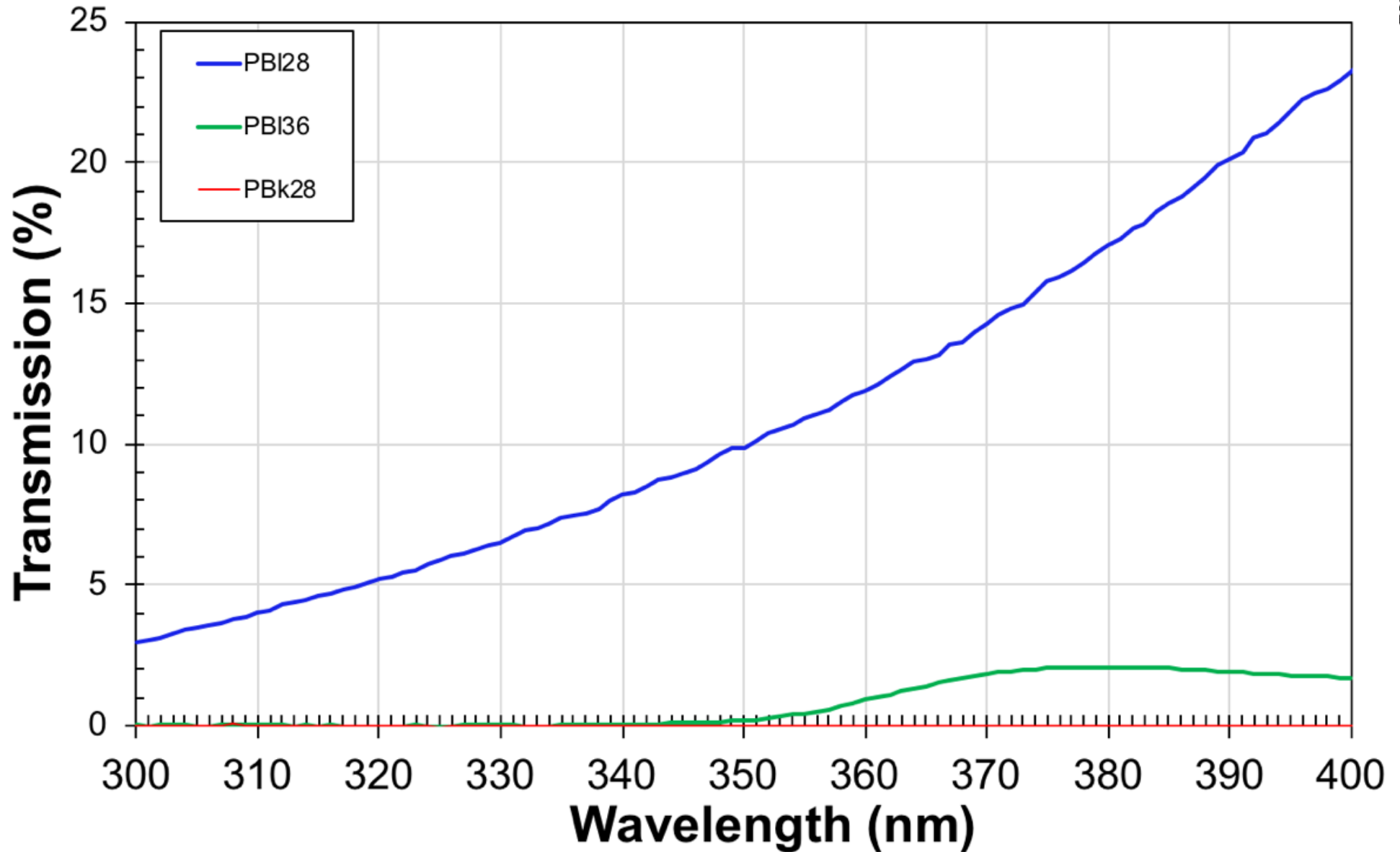


- PW6 Titanium Dioxide
 - TiO_2
 - Rutile
 - Silica coated
- PY53 Nickel Antimony Titanate
 - NiSbTiO_2
 - Rutile
 - Not coated
- PBr24 Chromium Antimony Titanate
 - CrSbTiO_2
 - Rutile
 - Not coated



UV Opacity of Various Pigments

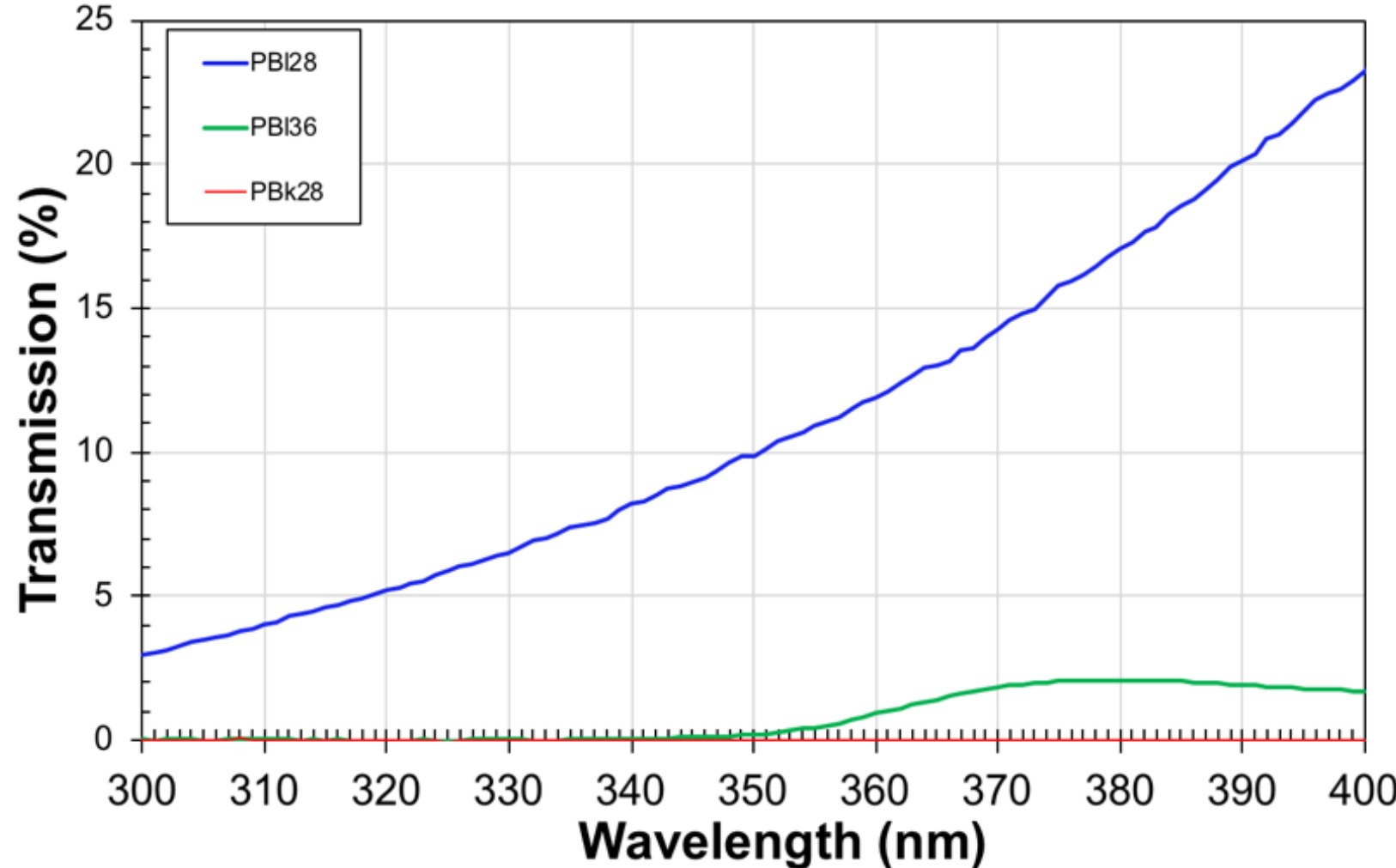
in PVDF/Acrylic $\sim 18\mu\text{m}$ film / $\sim 0.65\text{P/B}$



UV Opacity

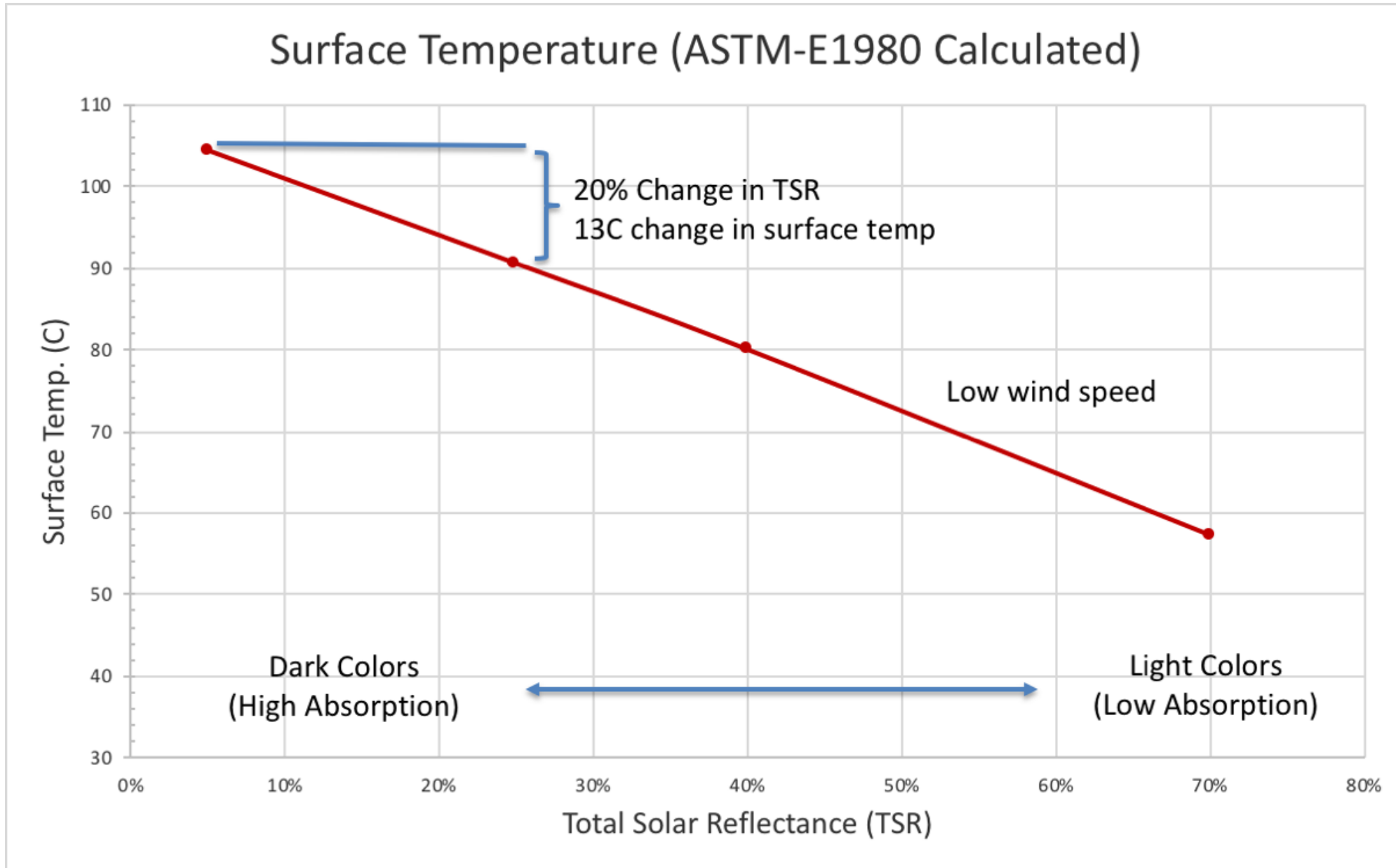


UV Opacity of Various Pigments in PVDF/Acrylic $\sim 18\mu\text{m}$ film / $\sim 0.65\text{P/B}$



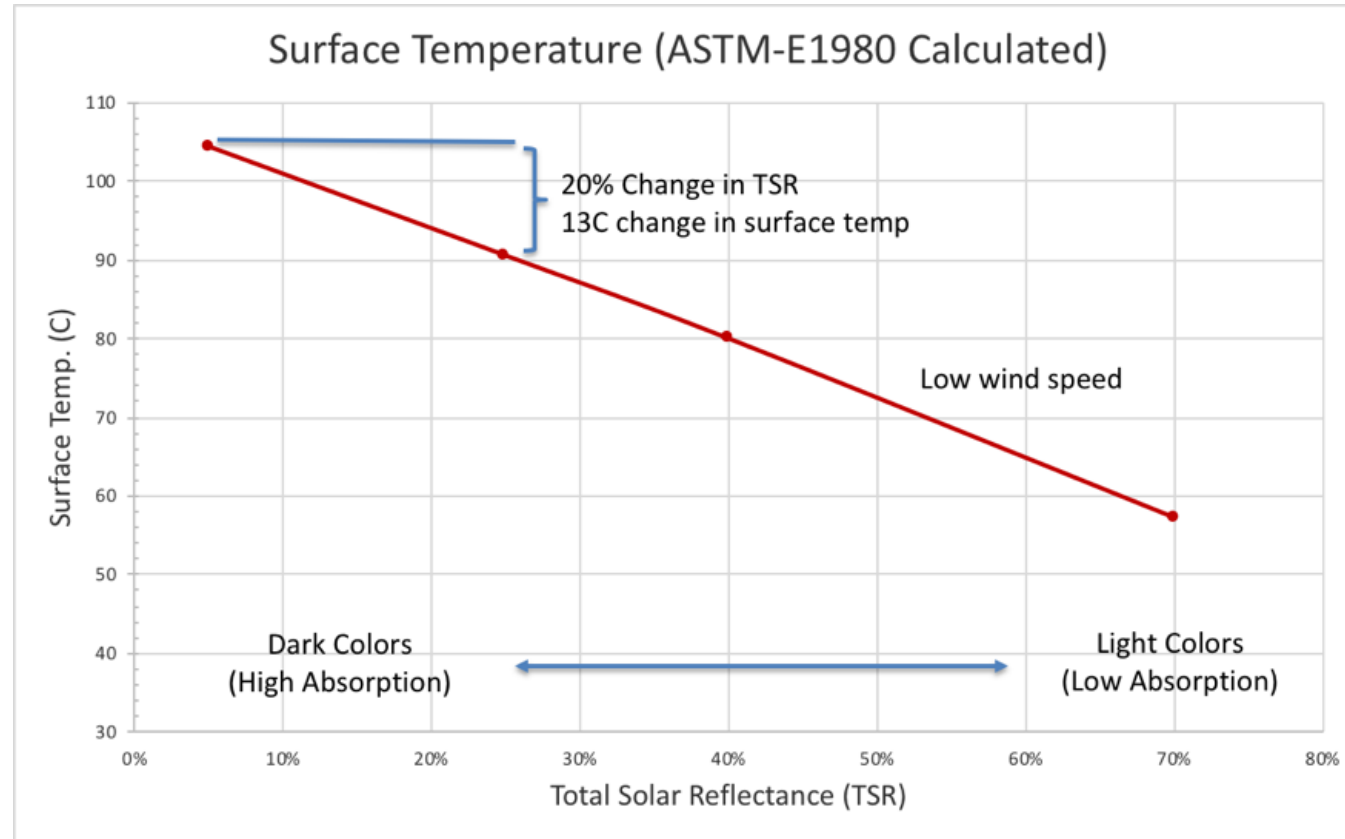
- PBI28
 - Cobalt aluminate
 - High UV transmission
- PBI36
 - Cobalt *chromium*(III) aluminate
 - Much lower UV transmission
- BBk28
 - Copper chromite
 - Relatively no UV transmission

Temperature of Materials in Exposed to Sunlight



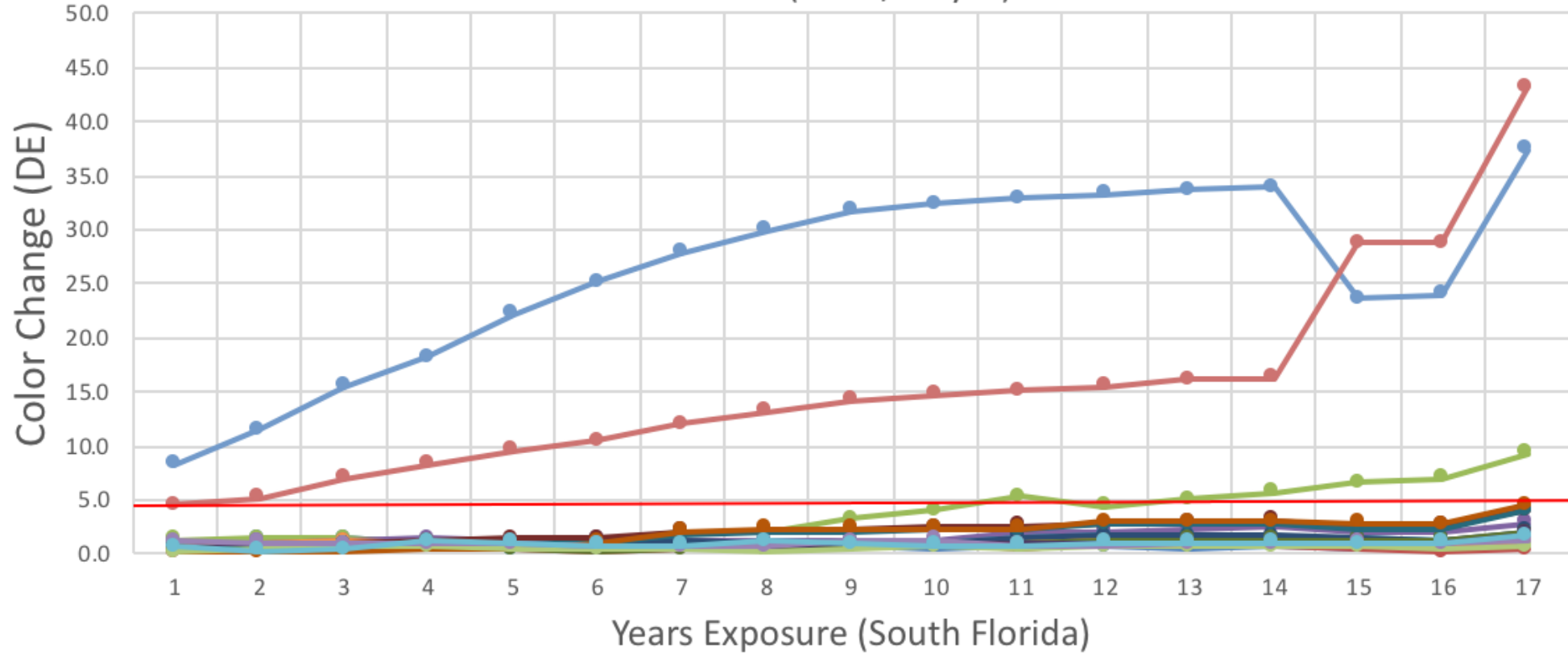
Temperature Influence

- Surface temp depends on
 - Sunlight intensity
 - Reflectivity (TSR)
 - Emissivity
 - Atmospheric conditions
- Sunlight
 - UV and Visible & n-infrared
- Reflect away invisible n-IR
- Critical for heat sensitive r-PVC
- Heat drives other degradation mechanisms



Color Change for Masstone

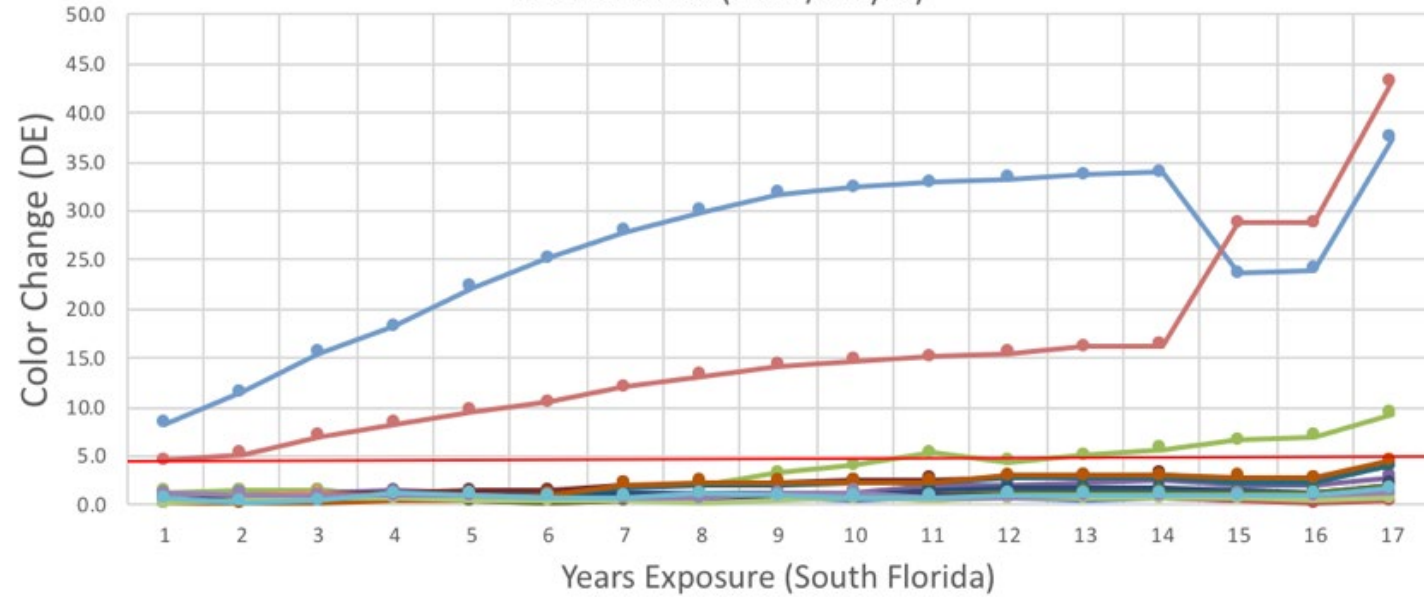
South Florida (PVDF/Acrylic)



- CuCr PBk28
- CoNiZnTi PGr50
- FeCrZnTi PBr33
- MnNH4P2O7 PVi16
- Titanium Dioxide TiO2 PW6
- FeCrNiMn PBk30
- CoCrZnTi PGr26
- MnSbTi PYI164
- Co3(PO4)2 PVi14
- CoAl PBI28
- CoCrAl PBI36
- CrSbTi PBr24
- Chromium Oxide Cr2O3 PGr17
- CoCrAl PBI36
- FeTi PBk12
- NiSbTi PYI53
- Iron Oxide Fe2O3 PR101

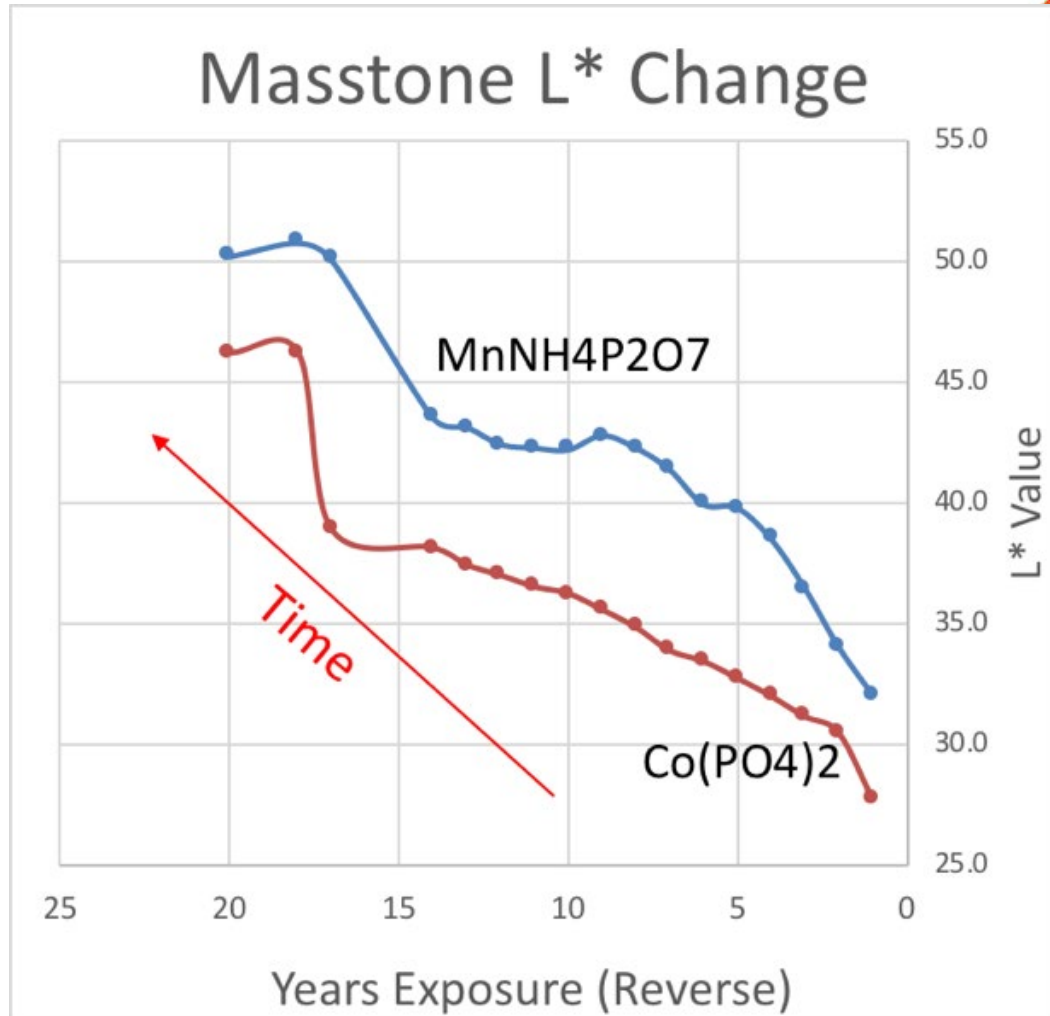
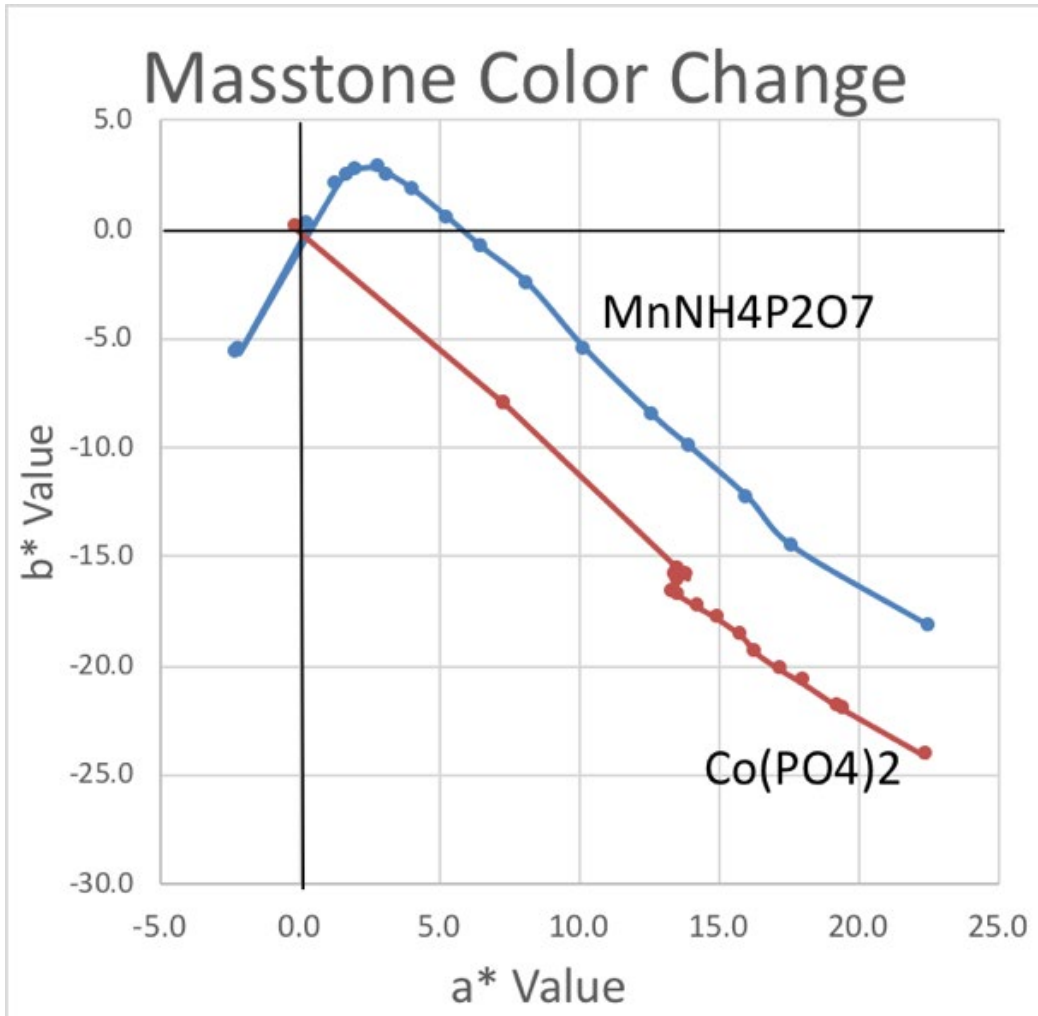
Color Change for Masstone

South Florida (PVDF/Acrylic)



- CuGr PBk28
- FeGr NiMn PBk30
- CoAl PBk28
- CoGrAl PBI36
- CoNiZnTi PGr50
- CoCrZnTi PGr26
- CoGrAl PBI36
- FeTi PBk12
- FeGr ZnTi PBr33
- MnSbTi PYI164
- CrSbTi PBr24
- NiSbTi PYI53
- MnNH4P2O7 PVi16
- Co3(PO4)2 PVi14
- Chromium Oxide Cr2O3 PGr17
- Iron Oxide Fe2O3 PR101
- Titanium Dioxide TiO2 PW6

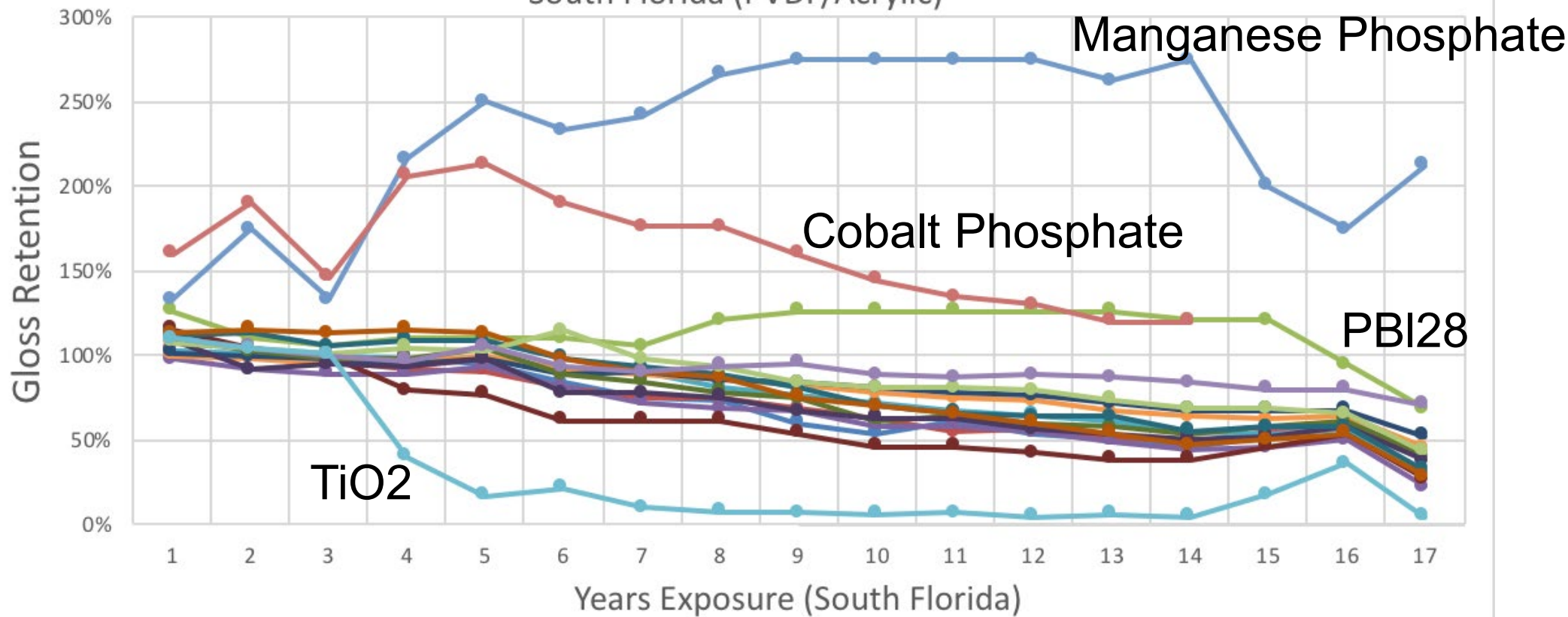
MnNH ₄ P ₂ O ₇ PVi16	26.4	ΔL*	5.6	7.6	10.0	12.0	13.3	13.5	14.9	15.8	16.3	15.7	15.8	16.0	16.7	17.1	13.6	14.3	23.8
	22.6	Δa*	-4.9	-6.5	-8.6	-9.8	-12.3	-14.3	-16.0	-17.2	-18.5	-19.3	-19.7	-20.4	-20.8	-21.2	-14.6	-14.7	-22.2
	-18.2	Δb*	3.6	5.9	8.2	9.6	12.7	15.6	17.3	18.7	20.0	20.7	21.0	20.9	20.7	20.3	12.7	12.5	18.4
		ΔE*	8.2	11.6	15.5	18.3	22.1	25.1	27.9	29.9	31.7	32.4	32.8	33.3	33.7	33.9	23.6	24.0	37.4
	4	ΔG*	1	3	1	5	6	5	6	7	7	7	7	7	7	7	4	3	5
Co ₃ (PO ₄) ₂ PVi14	27.7	ΔL*	2.7	3.4	4.2	5.0	5.7	6.1	7.1	7.8	8.5	8.8	9.2	9.7	10.4	11.1	-18.5	-18.5	-27.7
	22.5	Δa*	-2.9	-3.2	-4.4	-5.2	-6.1	-6.6	-7.4	-8.1	-8.8	-9.1	-8.9	-8.9	-8.9	-8.6	-15.0	-15.0	-22.6
	-24.1	Δb*	2.1	2.3	3.3	4.0	4.7	5.5	6.3	6.8	7.3	7.5	8.0	8.2	8.4	8.2	16.1	16.1	24.2
		ΔE*	4.5	5.2	7.0	8.2	9.6	10.5	12.0	13.2	14.3	14.7	15.1	15.5	16.1	16.3	28.8	28.8	43.1
	10	ΔG*	6	9	5	11	11	9	8	8	6	5	4	3	2	2	N/A	N/A	N/A



MnNH ₄ P ₂ O ₇ PVi16	26.4	ΔL^*	5.6	7.6	10.0	12.0	13.3	13.5	14.9	15.8	16.3	15.7	15.8	16.0	16.7	17.1	13.6	14.3	23.8
	22.6	Δa^*	-4.9	-6.5	-8.6	-9.8	-12.3	-14.3	-16.0	-17.2	-18.5	-19.3	-19.7	-20.4	-20.8	-21.2	-14.6	-14.7	-22.2
	-18.2	Δb^*	3.6	5.9	8.2	9.6	12.7	15.6	17.3	18.7	20.0	20.7	21.0	20.9	20.7	20.3	12.7	12.5	18.4
		ΔE^*	8.2	11.6	15.5	18.3	22.1	25.1	27.9	29.9	31.7	32.4	32.8	33.3	33.7	33.9	23.6	24.0	37.4
	4	ΔG^*	1	3	1	5	6	5	6	7	7	7	7	7	7	7	4	3	5
Co ₃ (PO ₄) ₂ PVi14	27.7	ΔL^*	2.7	3.4	4.2	5.0	5.7	6.1	7.1	7.8	8.5	8.8	9.2	9.7	10.4	11.1	-18.5	-18.5	-27.7
	22.5	Δa^*	-2.9	-3.2	-4.4	-5.2	-6.1	-6.6	-7.4	-8.1	-8.8	-9.1	-8.9	-8.9	-8.9	-8.6	-15.0	-15.0	-22.6
	-24.1	Δb^*	2.1	2.3	3.3	4.0	4.7	5.5	6.3	6.8	7.3	7.5	8.0	8.2	8.4	8.2	16.1	16.1	24.2
		ΔE^*	4.5	5.2	7.0	8.2	9.6	10.5	12.0	13.2	14.3	14.7	15.1	15.5	16.1	16.3	28.8	28.8	43.1
	10	ΔG^*	6	9	5	11	11	9	8	8	6	5	4	3	2	2	N/A	N/A	N/A

Change in Gloss for Masstone

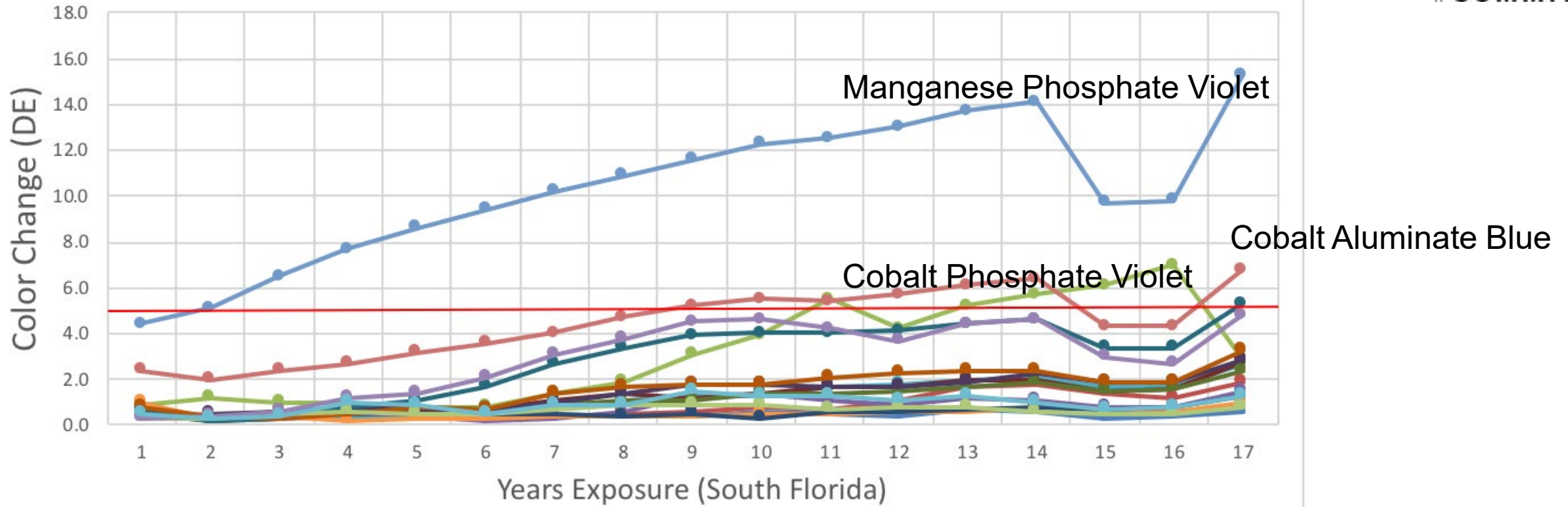
South Florida (PVDF/Acrylic)



- CuCr PBk28
- FeCrNiMn PBk30
- CoAl PBI28
- CoCrAl PBI36
- CoNiZnTi PGr50
- CoCrZnTi PGr26
- CoCrAl PBI36
- FeTi PBk12
- FeCrZnTi PBr33
- MnSbTi PYI164
- CrSbTi PBr24
- NiSbTi PYI53
- MnNH4P2O7 PVi16
- Co₃(PO₄)₂ PVi14
- Chromium Oxide Cr₂O₃ PGr17
- Iron Oxide Fe₂O₃ PR101
- Titanium Dioxide TiO₂ PW6

Color Change for 4:1 Tint

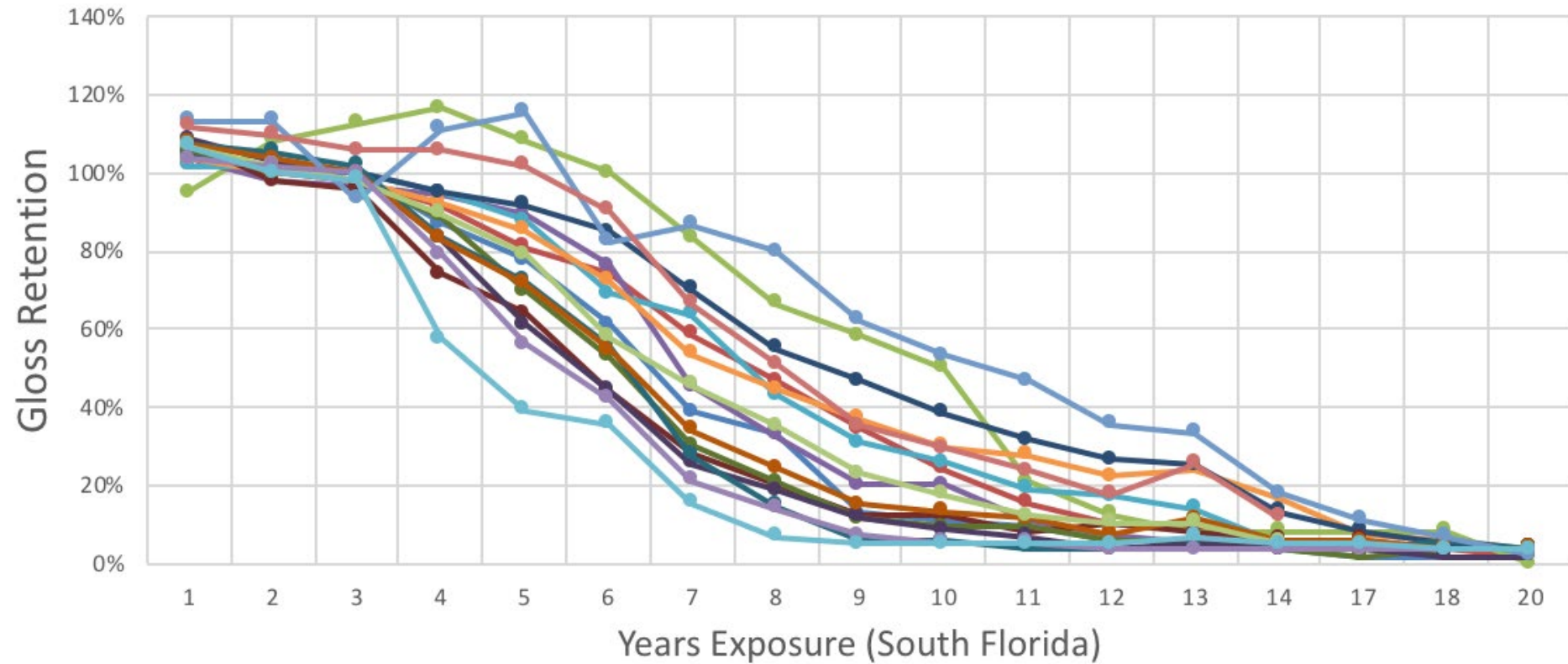
South Florida (PVDF/Acrylic)



- CuCr PBk28
- CoNiZnTi PGr50
- FeCrZnTi PBr33
- MnNH4P2O7 PVi16
- Titanium Dioxide TiO2 PW6
- FeCr NiMn PBk30
- CoCrZnTi PGr26
- MnSbTi PYI164
- Co3(PO4)2 PVi14
- CoAl PBI28
- CoCrAl PBI36
- CoCrAl PBI36
- Chromium Oxide Cr2O3 PGr17
- CoCrAl PBI36
- FeTi PBk12
- NiSbTi PYI53
- Iron Oxide Fe2O3 PR101

Change in Gloss for 4:1 Tint

South Florida (PVDF/Acrylic)



- CuCr PBk28
- CoNiZnTi PGr50
- FeCr ZnTi PBr33
- MnNH4P2O7 PVi16
- Titanium Dioxide TiO2 PW6
- FeCr NiMn PBk30
- CoCrZnTi PGr26
- MnSbTi PYI164
- Co3(PO4)2 PVi14
- CoCrAl PBI28
- CoCrAl PBI36
- CrSbTi PBr24
- Chromium Oxide Cr2O3 PGr17
- FeTi PBk12
- NiSbTi PYI53
- Iron Oxide Fe2O3 PR101

Weathering notes

- Weatherable
 - Except for violets
- In PVDF/Acrylic liquid coatings
 - Most of our weathering studies
 - Masstone and 4:1 tints
 - Findings
 - Masstone keep gloss better than tints (TiO₂ photoactivity?)
 - Cobalt Aluminate (PBI28) have UV transparency issues (primer/substrate attack)

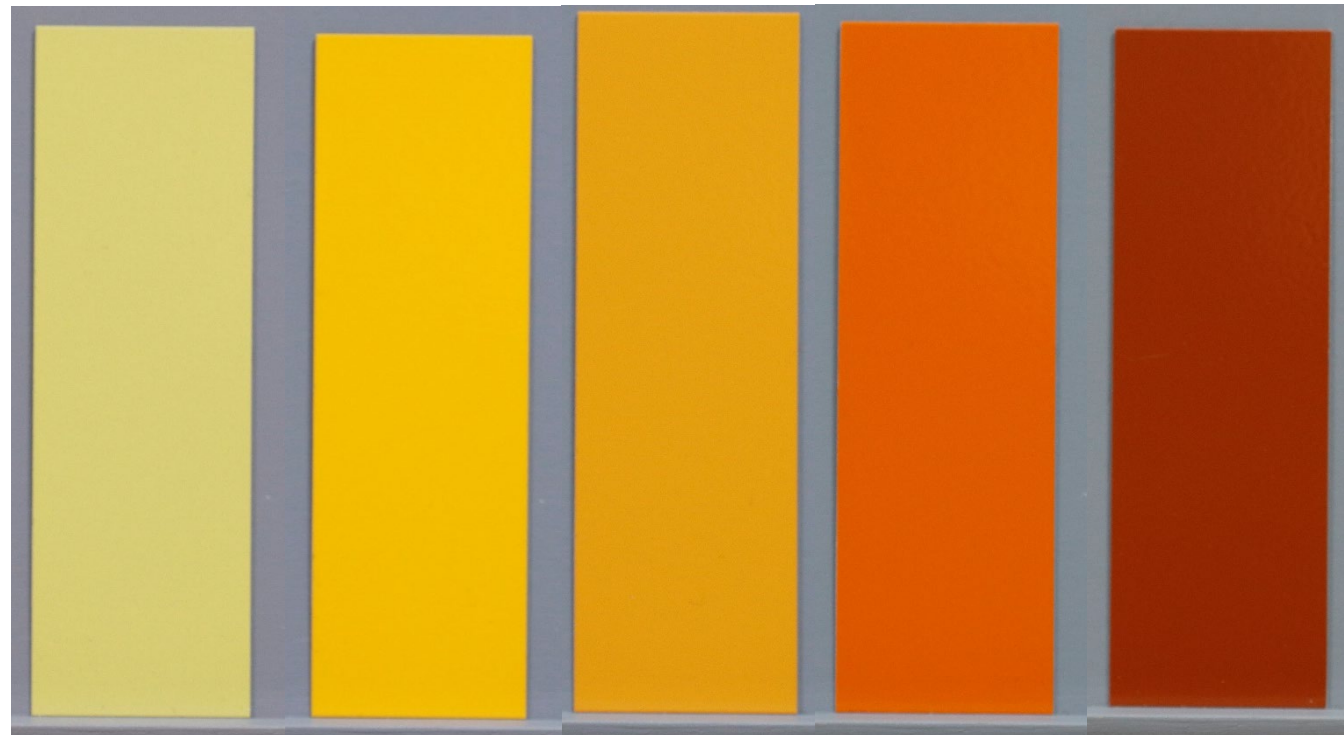
FEVE Testing

- 34 pigments
- 20 different pigment chemistries
- Masstone and 4:1 (white:color)

Testing methods

- QUV-A (ASTM G154-04)
- Emmaqua
- South Florida
- Ohio

Colors



Plus Tints!



QUV-A FEVE Testing



	Masstone Color Change (DE)							
	Hours of Exposure (QUV-A)							
Pigmentation	500	1000	1500	2000	2500	3000	3500	4000
IR Black PBr29	0.3	0.3	0.4	0.4	0.4	0.4	0.6	0.7
Std. Black PBk28	0.2	0.4	0.6	0.7	0.7	0.7	0.8	0.8
Cobalt Blue PBI36	0.9	0.9	1.1	1.0	1.2	1.1	1.4	1.5
Cobalt Green PG50	0.3	0.3	0.5	0.6	0.6	0.6	0.7	0.7
RTZ Orange PY216	0.5	0.9	0.8	0.8	0.8	1.1	1.0	1.2
Chrome Titanate PBr24	0.4	0.8	0.8	0.7	0.7	0.9	0.8	0.9
NTP Yellow PY227	0.6	1.1	1.0	1.0	1.0	1.3	1.3	1.4
	4:1 Tint Color Change (DE)							
	Hours of Exposure (QUV-A)							
Pigmentation	500	1000	1500	2000	2500	3000	3500	4000
IR Black PBr29	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
Std. Black PBk28	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cobalt Blue PBI36	0.3	0.3	0.3	0.3	0.4	0.3	0.3	0.3
Cobalt Green PG50	0.2	0.2	0.3	0.2	0.4	0.3	0.3	0.3
RTZ Orange PY216	0.2	0.4	0.4	0.4	0.4	0.5	0.4	0.5
Chrome Titanate PBr24	0.2	0.3	0.4	0.4	0.4	0.5	0.5	0.5
NTP Yellow PY227	0.3	0.5	0.6	0.6	0.7	0.8	0.8	0.9

Emmaqua FEVE Testing



Emmaqua Weathering			
	Masstone Color Change (DE)		
	Emmaqua (MJ Exposure)		
Pigmentation	290	580	870
IR Black PBr29	0.7	0.6	1.1
Std. Black PBk28	0.3	0.4	0.4
Cobalt Blue PBI36	1.1	1.3	1.8
Cobalt Green PG0	0.4	0.5	0.7
RTZ Orange PY216	0.1	0.1	0.5
Chrome Titanate PBr24	0.4	0.4	0.2
NTP Yellow PY227	0.5	0.6	0.4

	4:1 Tint Color Change (DE)		
	Emmaqua (MJ Exposure)		
Pigmentation	290	580	870
IR Black PBr29	0.3	0.3	0.3
Std. Black PBk28	0.3	0.3	0.3
Cobalt Blue PBI36	0.5	0.5	0.6
Cobalt Green PG0	0.2	0.2	0.2
RTZ Orange PY216	0.2	0.3	0.2
Chrome Titanate PBr24	0.3	0.4	0.4
NTP Yellow PY227	0.6	0.9	0.9

290MJ/m2 roughly equivalent to 1 Year weathering

Ohio Weathering



	Masstone Color Change (DE)		
	Ohio (years)		
	0.5	1	2
Pigmentation			
IR Black PBr29	0.3	0.2	0.5
Std. Black PBk28	0.3	0.3	0.1
Cobalt Blue PBI36	0.9	0.8	0.9
Cobalt Green PG50	0.2	0.2	0.2

	4:1 Tints Color Change (DE)		
	Ohio (years)		
	0.5	1	2
Pigmentation			
IR Black PBr29	0.2	0.2	0.2
Std. Black PBk28	0.2	0.2	0.1
Cobalt Blue PBI36	0.4	0.3	0.3
Cobalt Green PG50	0.2	0.2	0.3

South Florida FEVE Weathering



Masstone Color Change (DE)

Pigmentation	South Florida (Months)	
	6	12
IR Black PBr29	0.4	0.4
Std. Black PBk28	0.1	0.3
Cobalt Blue PBI36	0.8	1.0
Cobalt Green PG50	0.5	0.4
RTZ Orange PY216	0.2	0.2
Chrome Titanate PBr24	0.1	0.4
NTP Yellow PY227	0.3	0.8

4:1 Tints Color Change (DE)

Pigmentation	South Florida (Months)	
	6	12
IR Black PBr29	0.1	0.1
Std. Black PBk28	0.1	0.1
Cobalt Blue PBI36	0.3	0.3
Cobalt Green PG50	0.2	0.3
RTZ Orange PY216	0.1	0.2
Chrome Titanate PBr24	0.1	0.5
NTP Yellow PY227	0.5	1.0

Weathering findings

- PBk26 (CuMnFe) didn't weather as well as PBk28 (expected)
- PG50- Lithium modified versions weathering well (unexpected)
- Standard versus Easily-dispersed grades (hoped for)
 - DE within tenths in QUV-A, Emmaqua
- Looking to do more correlation work with more SF weathering



Thanks!

- Everyone at the Powder Coating Research Group
- AGC Chemicals for FEVE resin
- Brian Schwer and Doug Goetz at Shepherd Color Tech Serv lab

You for attending!



Shepherd

The Shepherd Color Company
We Brighten Lives