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# A New Benchmark in Minimizing $\text{TiO}_2$ Photocatalysis

Huntsman Pigments

25<sup>th</sup> June 2015



- ▶ Introduction
- ▶ Photochemical degradation
- ▶ Photocatalytic degradation
- ▶ Weathering studies
- ▶ Accelerated weathering
- ▶ ALTIRIS<sup>®</sup> infrared reflective pigments

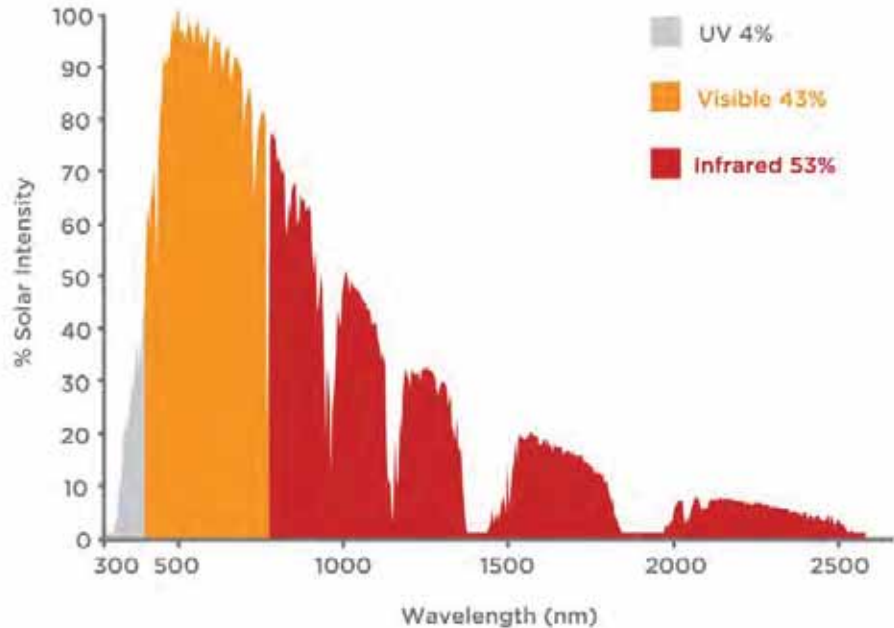
# Introduction

## UV radiation, TiO<sub>2</sub> & Durability

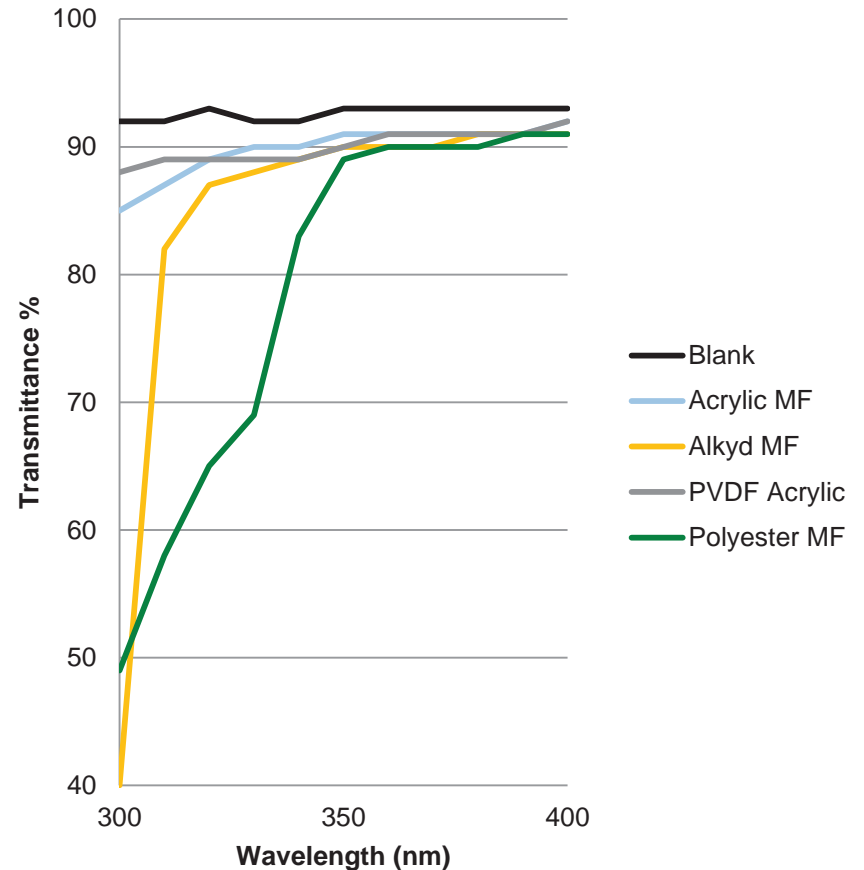
1. Focus here on aspects of durability related to the impact of UV radiation on surface coatings
2. The UV component only accounts for about 4% of solar energy reaching the Earth's surface
3. But each quantum of UV radiation has enough energy to break a chemical bond
4. All solar wavelengths cause heating which can have separate durability consequences



# Solar Spectrum and Resin Absorption



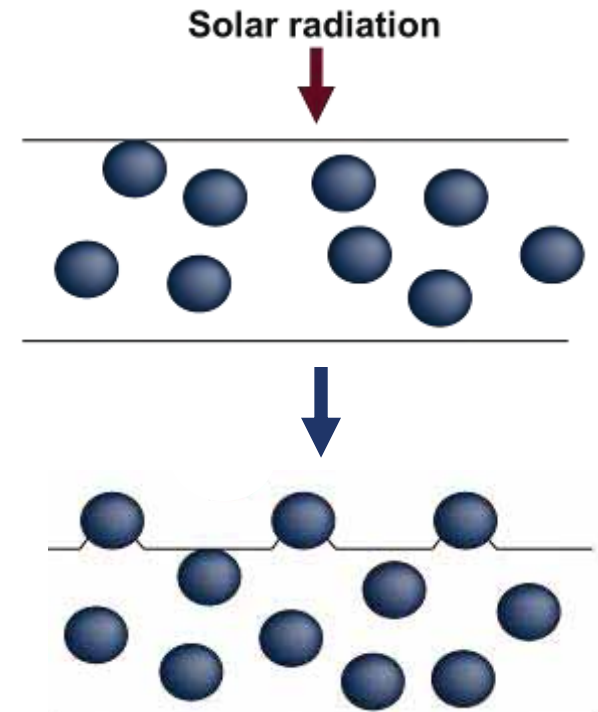
## Solar UV transmittance Spectra of various resins



Binder absorption between 300nm and 400nm represents particular susceptibility to photochemical degradation

# Protecting Resins

- ▶ Resin can be protected by materials which block UV radiation (either by scattering or absorption)
- ▶ Organic UV absorbers provide protection within specific wavelength bands and can be matched to resin types.
  - ▶ However, these are sacrificial limiting the lifetime of the protection
- ▶ Rutile  $\text{TiO}_2$  products provide broad spectrum attenuation, deploying both scattering and absorption to protect resins
  - ▶ They're non-sacrificial
  - ▶ They're available in opaque (pigmentary) and transparent (ultrafine) forms



# But....TiO<sub>2</sub> is a Photocatalyst

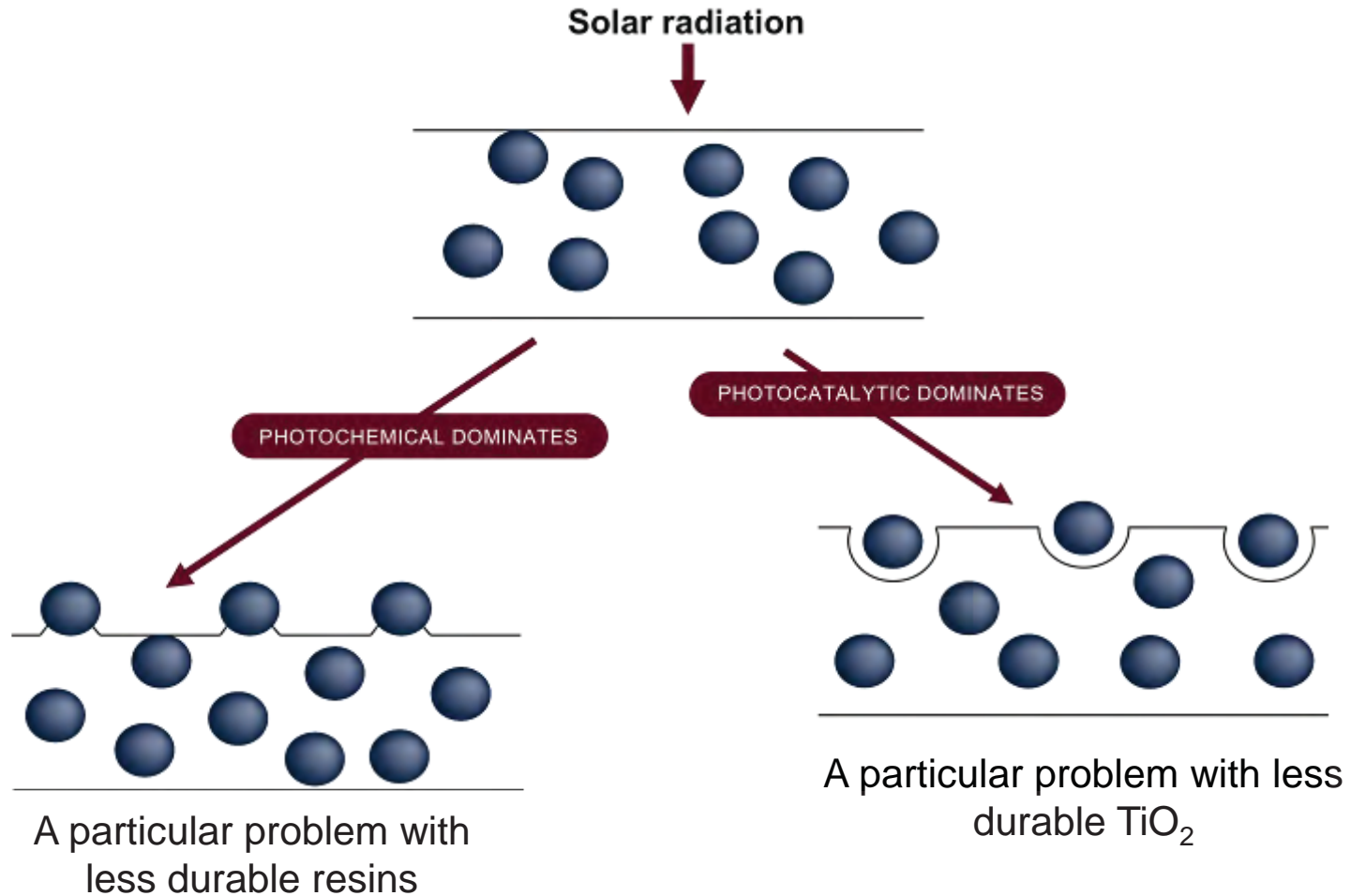
- ▶ When UV radiation is absorbed, electrons and holes are created within the TiO<sub>2</sub> lattice which can, in turn, create radicals at the TiO<sub>2</sub> surface
- ▶ So most TiO<sub>2</sub> is treated to moderate photocatalysis by either doping (which affects whiteness) or by surface treatment

## Radical Mechanisms

- ▶ TiO<sub>2</sub> + UV light  
→ excited electron + positive hole
- ▶ OH<sup>-</sup> + positive hole  
→ OH<sup>·</sup>
- ▶ e<sup>-</sup> + O<sub>2</sub>  
→ O<sub>2</sub><sup>-·</sup>
- ▶ O<sub>2</sub><sup>-·</sup> + H<sub>2</sub>O  
→ OH<sup>-</sup> + HO<sub>2</sub><sup>·</sup>

# Weathering - Role of TiO<sub>2</sub>

- ▶ Both mechanisms result in gloss loss
- ▶ Chalking is promoted by photocatalysis



# Photocatalytic Degradation:

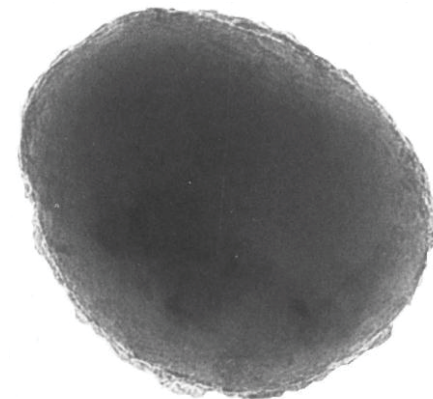
## Limiting $\text{TiO}_2$ Photocatalysis: Coating

- ▶ Charges created within the  $\text{TiO}_2$  lattice must reach the resin to cause problems.
- ▶ One solution is to coat the crystal with an insulating layer
  - ▶ Silica, Zirconia and Aluminium Phosphate provide some protection
  - ▶ Dense silica coatings are particularly effective, providing encapsulation which can be tested by acid solubility
  - ▶ But they are not the perfect answer...

A dense silica coated crystal



A crystal with a non-dense coating





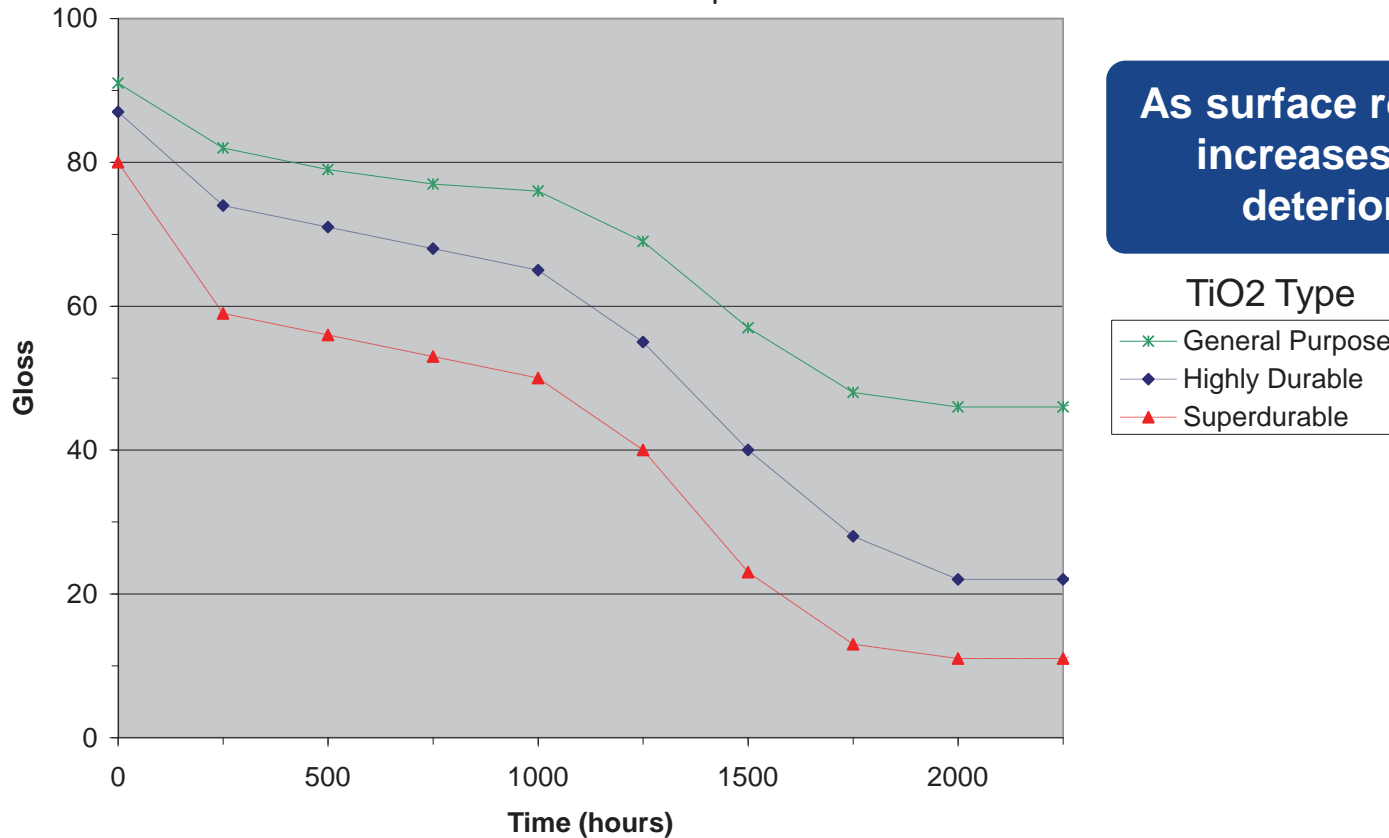
# Weathering Studies



# Weathering

## Role of TiO<sub>2</sub> in a Less Durable Resin System

TiO<sub>2</sub> Grade and Gloss Retention for Alkyd Gloss Paint  
Xenon Exposure



**As surface roughness increases: gloss deteriorates**

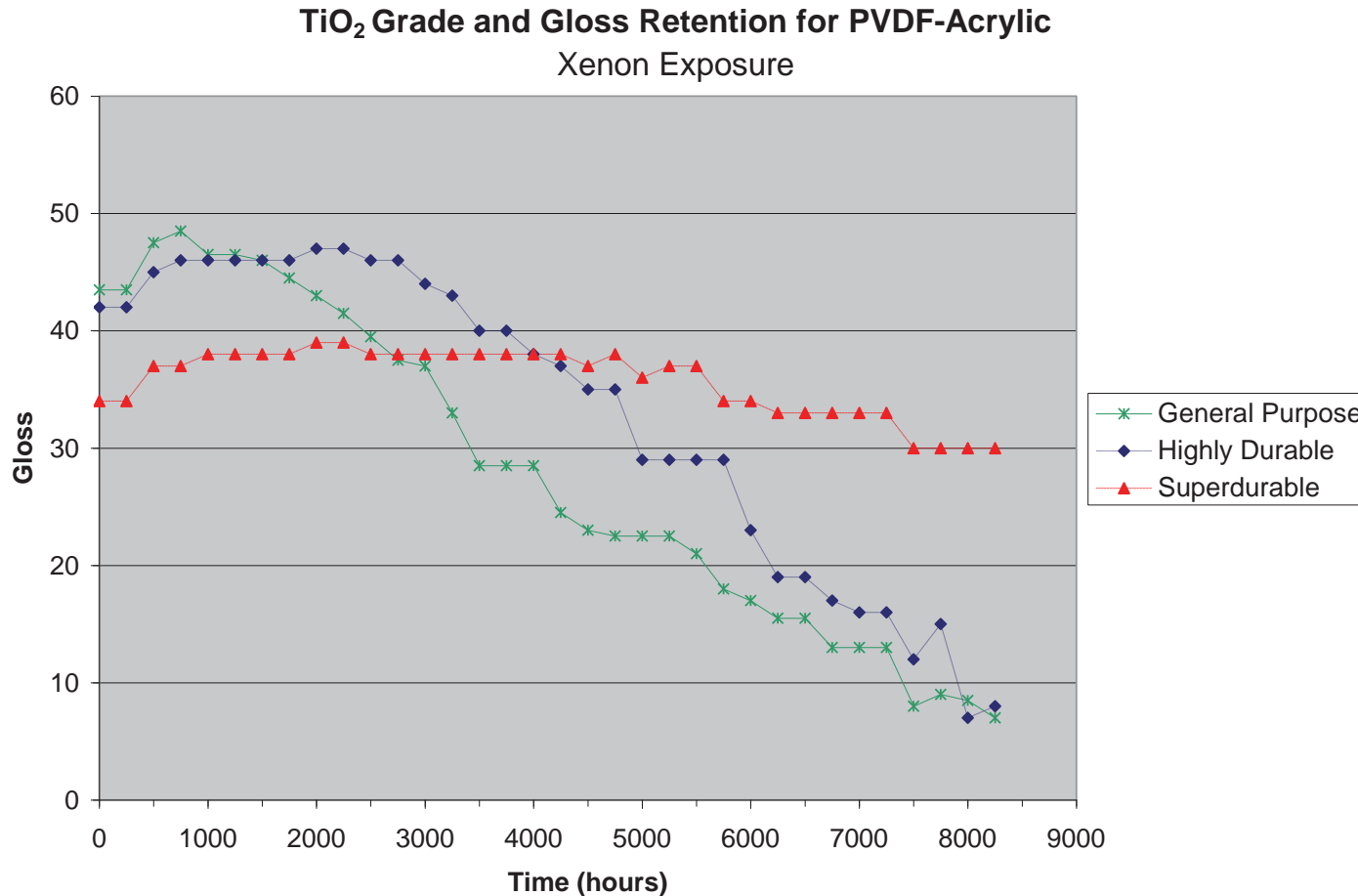
TiO<sub>2</sub> Type

- General Purpose
- Highly Durable
- Superdurable

In less durable systems, heavily coated TiO<sub>2</sub> grades that are more agglomerated provide lower gloss and less protection against photochemical breakdown of resin.

# Weathering

## Role of $\text{TiO}_2$ in a Hyperdurable Resin System

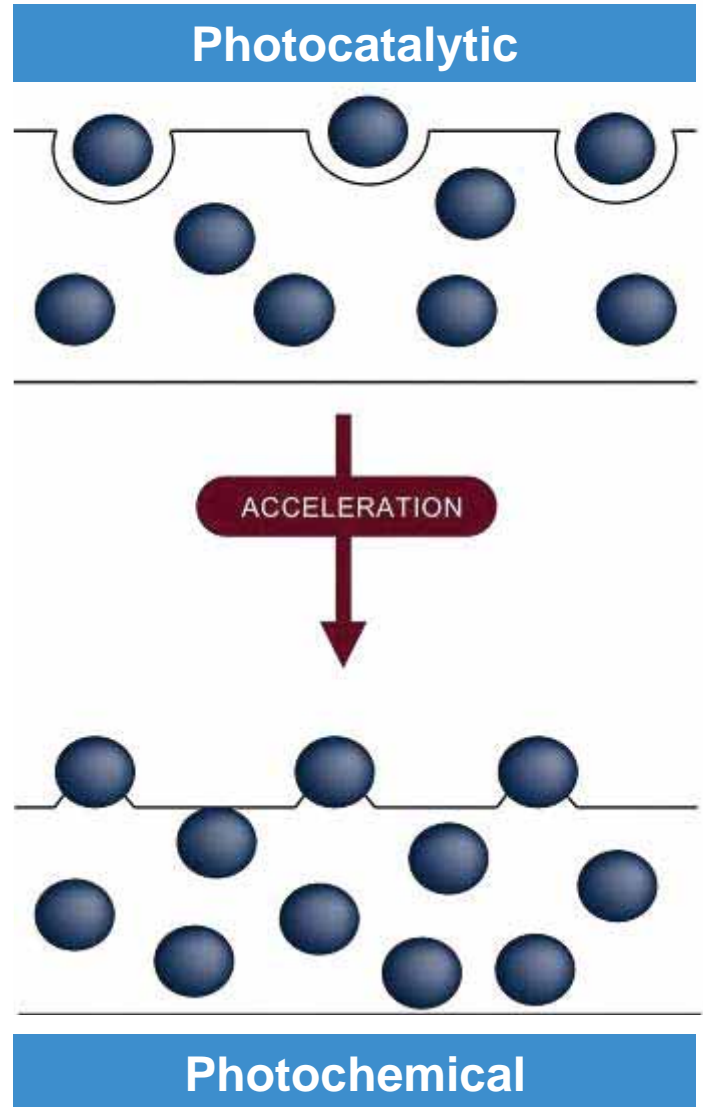
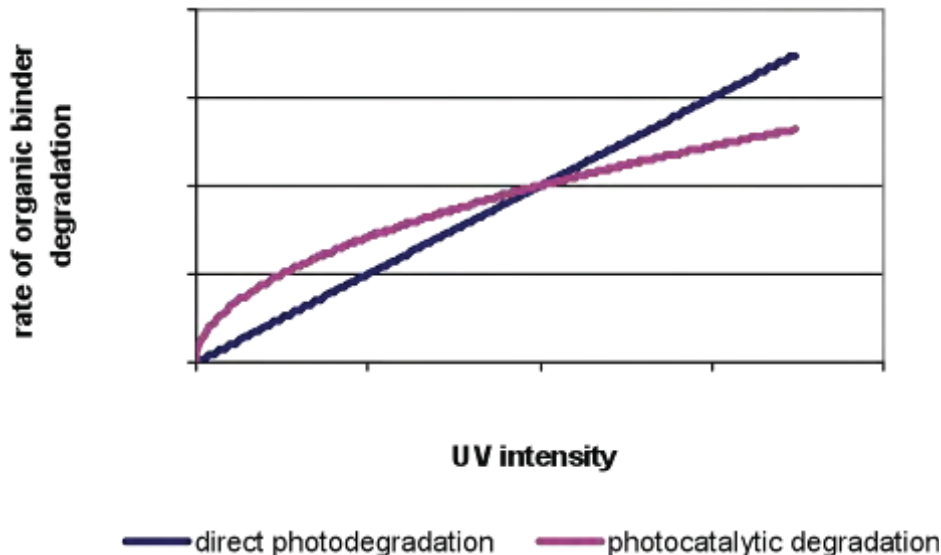


- ▶ In binders of high photostability, where photocatalytic breakdown dominates, surface treatment of  $\text{TiO}_2$  is key
- ▶ Heavily coated/encapsulated  $\text{TiO}_2$  grades are required to maintain durability.

# Weathering

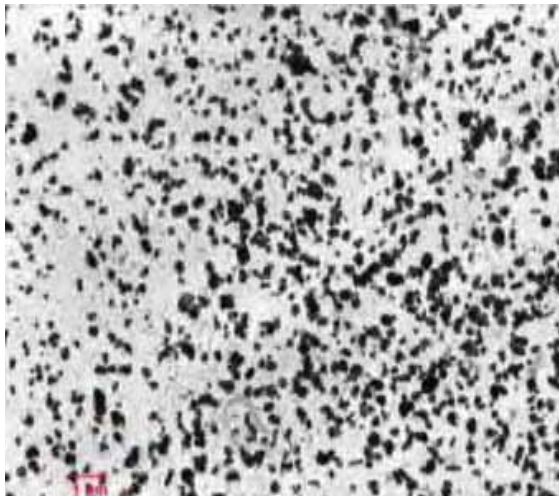
## UV Intensity Considerations

- ▶ Accelerated weathering tests often use high UV light intensities
- ▶ For a given light source
  - Rate of direct UV degradation increases linearly with UV intensity
  - Rate of degradation due to photocatalysis increases with the square root of UV intensity
  - Accelerated weathering can give misleading results

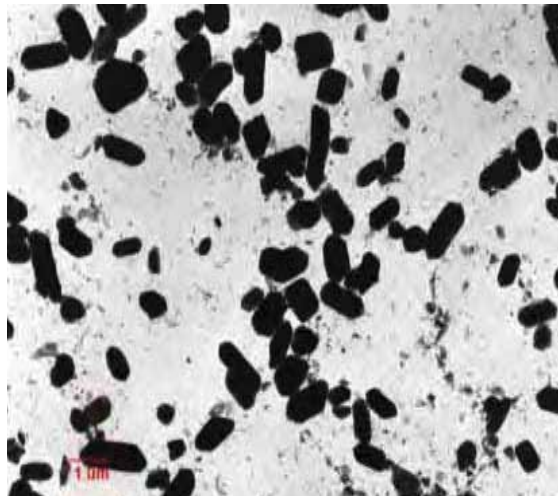


# ALTIRIS<sup>®</sup> Infrared Reflective Pigments

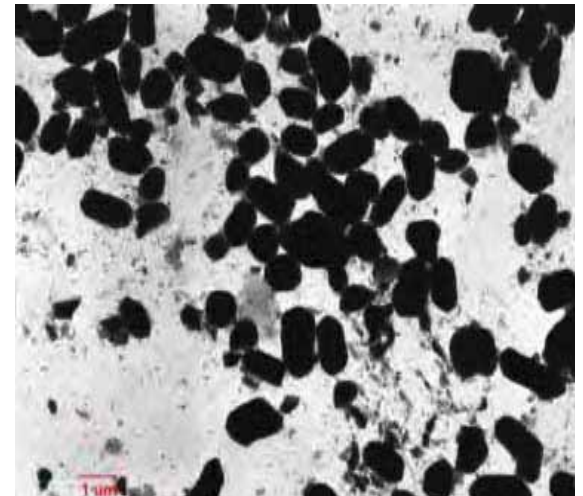
- ▶ Huntsman has introduced ALTIRIS<sup>®</sup> Infrared Reflective Pigments for use in cool coloured coatings and polymers
- ▶ ALTIRIS<sup>®</sup> pigments have larger crystal sizes than conventional TiO<sub>2</sub> to shift the scattering emphasis from visible to NIR wavelengths



Pigmentary rutile titanium dioxide



ALTIRIS<sup>®</sup> 550 pigment



ALTIRIS<sup>®</sup> 800 pigment

# ALTIRIS® Infrared Reflective Pigments

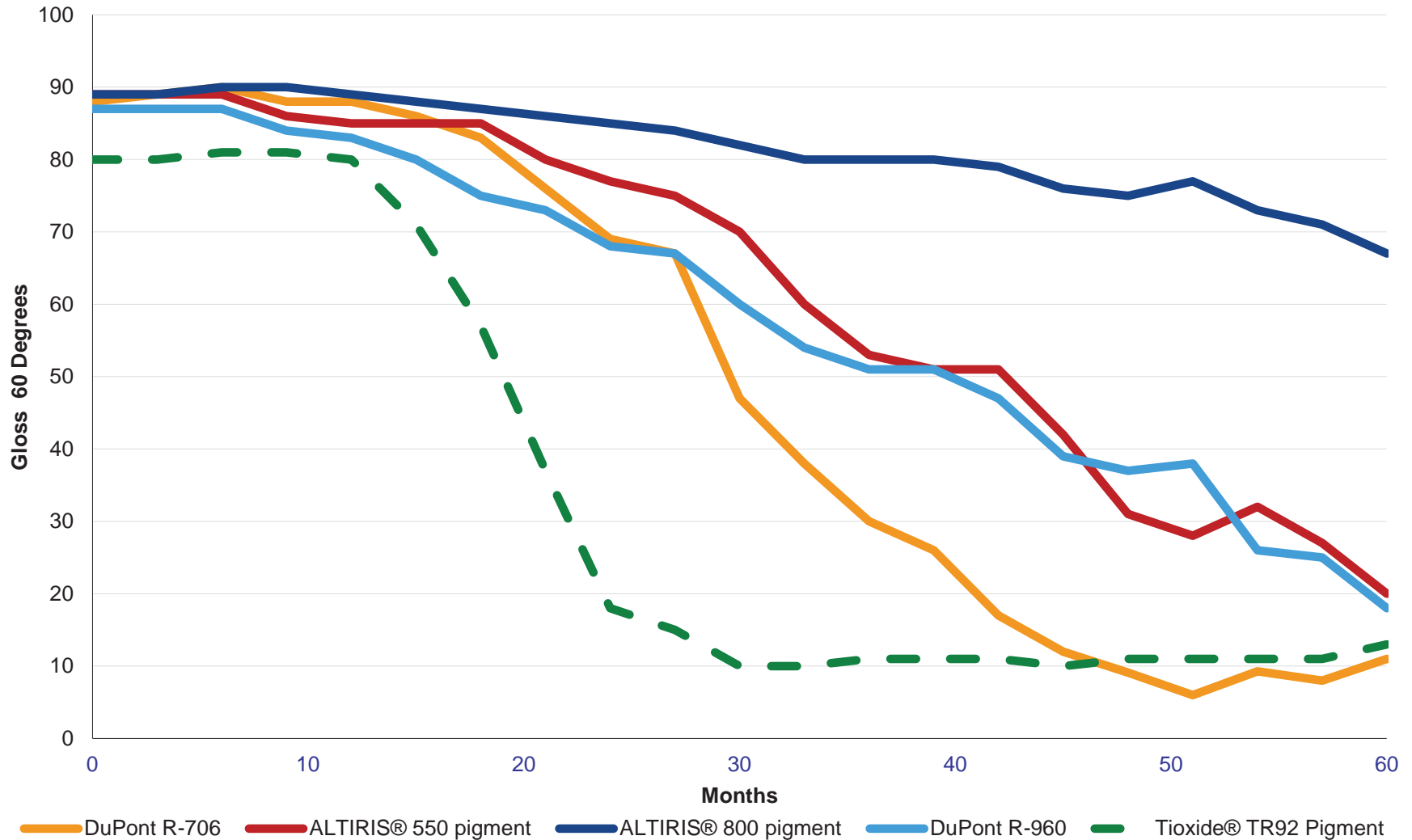
- ▶ ALTIRIS® pigments are designed to be used in surfaces exposed to significant solar radiation
- ▶ Low tint reducing power makes them particularly suitable for use in colored surfaces
- ▶ To provide weather resistance, ALTIRIS® pigments are equipped with an encapsulative dense silica coating
- ▶ Large crystal sizes often promote surface roughness giving poor gloss. Conveniently, the crystal size of ALTIRIS® pigments can help to promote stratification in coatings, opening the possibility to formulate high gloss coatings



# ALTIRIS® Infrared Reflective Pigments

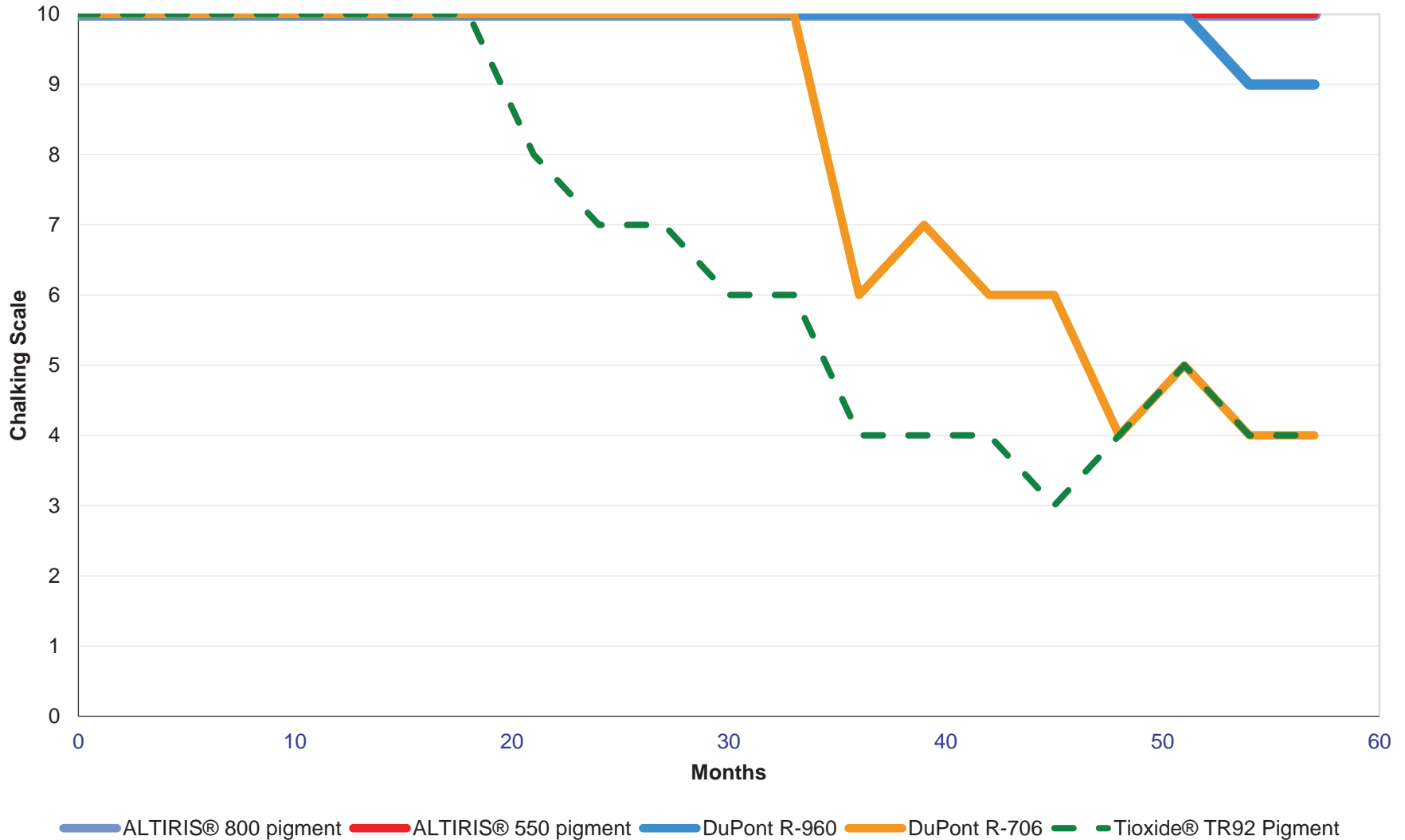
## 5 Years Florida Weathering: Gloss

Polyester-MF (Uralac SN-804, Cymel 303)



# 5 Years Florida Weathering: Chalking

Polyester-MF (Uralac SN-804, Cymel 303)





# New Type of TiO<sub>2</sub>

- ▶ ASTM D476 is produced as an aid to determining fitness for use of TiO<sub>2</sub> pigments for coatings applications
- ▶ From 1<sup>st</sup> Feb there are 8 types of TiO<sub>2</sub> defined in ASTM D476
- ▶ The new Type VIII provides for specification of TiO<sub>2</sub> grades for cool coloured durable coatings
- ▶ We see ALTIRIS<sup>®</sup> Infrared Reflective Pigments fitting comfortably into this new Type



# Summary

- ▶  $\text{TiO}_2$  can help to provide UV protection to resins
- ▶ However, in blocking UV,  $\text{TiO}_2$  can photo-catalyse, producing radical species
- ▶  $\text{TiO}_2$  manufacturers coat  $\text{TiO}_2$  to reduce this tendency
- ▶ The introduction of ALTIRIS<sup>®</sup> pigments has provided a new tool in the ongoing battle against UV degradation
- ▶ ASTM D476 has been modified to allow specification of  $\text{TiO}_2$  suitable for cool colored surfaces



# Thank you!

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