Solasorb
Plastic UV Protection

High performance UV barrier additives based on highly dispersed metal oxides

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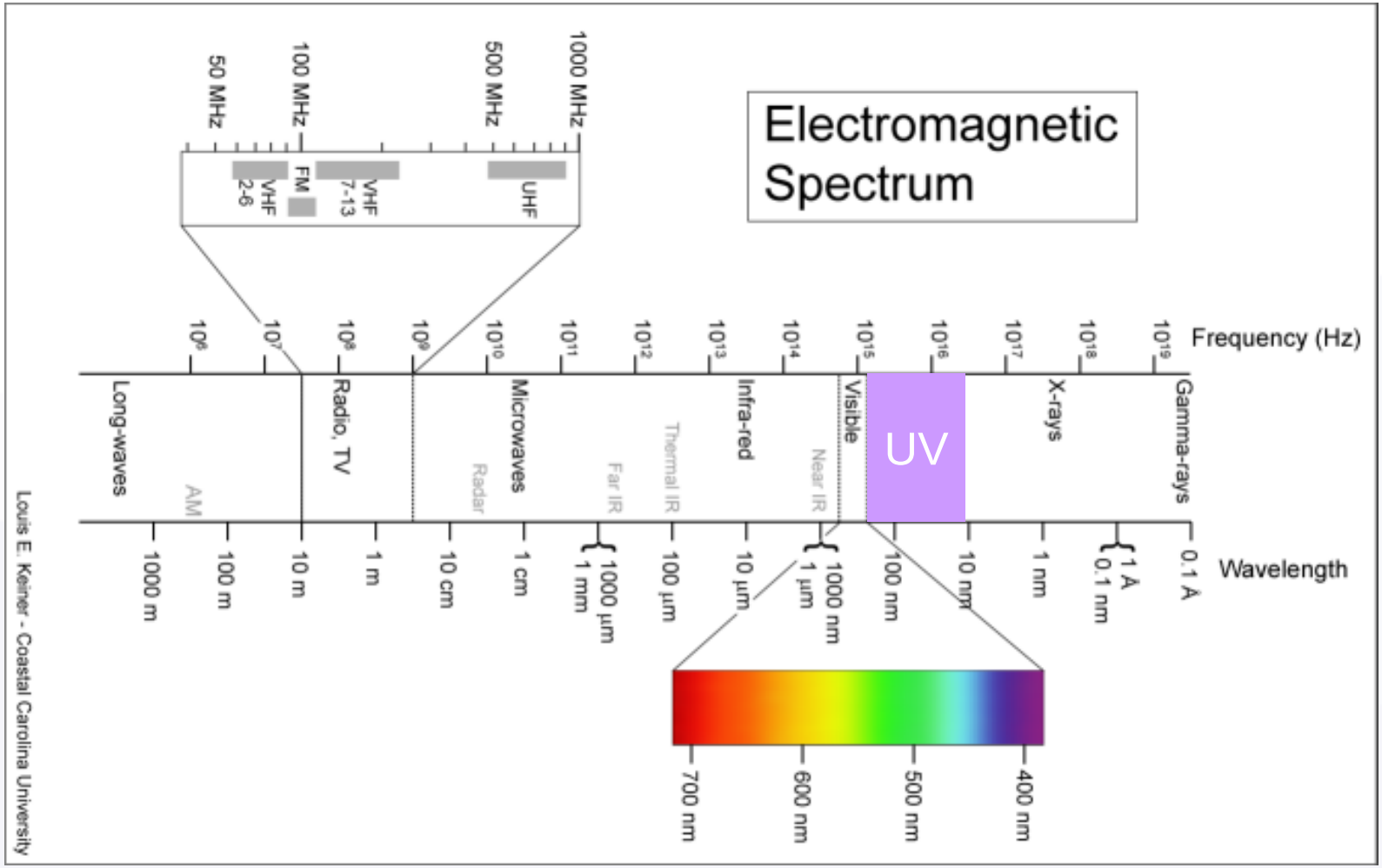
Introduction

- Ultra-Violet can cause damage to polymers & in the case of packaging, to the contents
- UV absorbers are valuable part of the formulator's toolkit to alleviate some of the problems caused by UV
- Metal oxide UV absorbers have been used for many years but have been limited by their effect on optical properties
- **This work intends to demonstrate that well dispersed metal oxide systems offer benefits over existing metal oxides and organic UV absorbers**

What’s UV electro magnetic radiation ?



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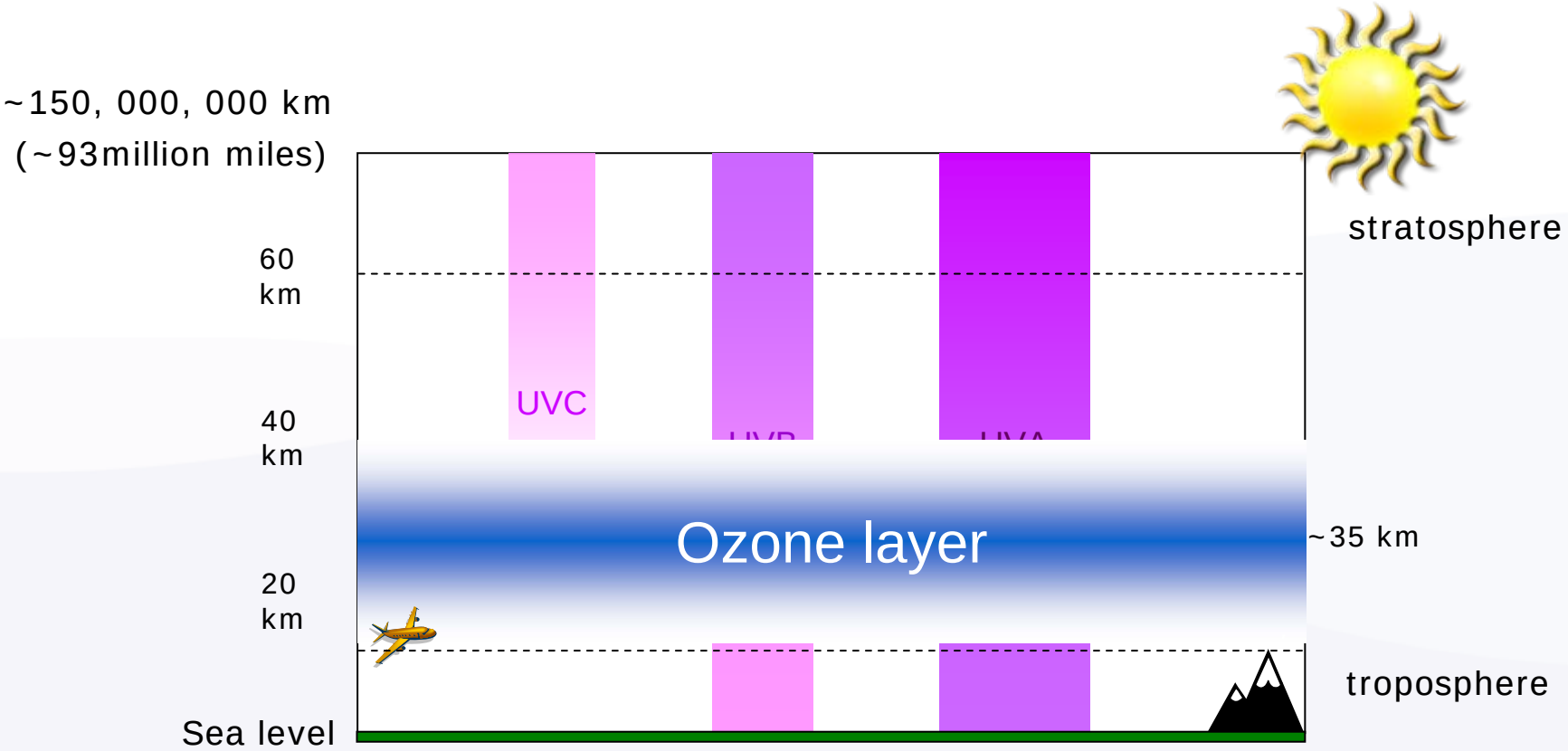
Ultra-Violet radiation

Name	Abbreviation	Wavelength (nm)
Ultraviolet A long wave or black light	UVA	400 – 315
Ultraviolet B or medium wave	UVB	315 – 280
Ultraviolet C short wave or germicidal	UVC	280 – 100
Vacuum Ultraviolet	VUV	200 – 10

- As the wavelength decreases the energy imparted by the radiation increases. More energy = more chemical reactions – Photo-oxidation, photo-degradation
- Each photon of UV light at 250 nm has 4x more energy than Infrared at 1000 nm
- Vacuum UV is stopped by air and UVC is blocked by the ozone layer, but UVA and some UVB from the sun reach the earths surface
- UVB is more damaging but there is much less than UVA

UV exposure at earth's surface



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Why is UV critical to Plastics ?

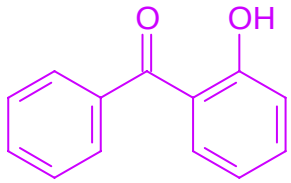
- Damage to the packaging
  - Degradation (chain scission, cross-linking & oxidation)
    - *loss of mechanical properties leading to failure of package integrity*
    - *Change in colour : yellowing or fading*
    - *Generation of "off taste and odour"*
    - *Print fading*
- Damage to the contents of the package
  - Loss of Vitamin content in fruit juice & milk
  - Accelerated oxidation of fats – *rancidity*
  - Colour fading in food, personal care & home products

Strategies to reduce the effects of UV

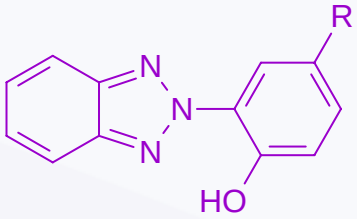
- **UV stabilisers**
  - Work in a similar manner to anti-oxidants by interrupting the breakdown pathway of the substrate material
  - Most commonly used are Hindered Amine Light Stabilisers (HALS)
  - Will only protect the packaging material to which they are added
- **UV absorbers**
  - Absorb or scatter the UV radiation reducing its penetration into the material
  - Two main types
    - Organic usually aryl compounds
    - Ultra-fine particle size metal oxides
  - Ideally will give even absorption over the UV region & no visible absorption or scattering
  - Protect contents of packaging
- **Totally opaque packaging**
  - Metal foil layers, high pigment loadings, metal cans etc

Organic UV absorbers

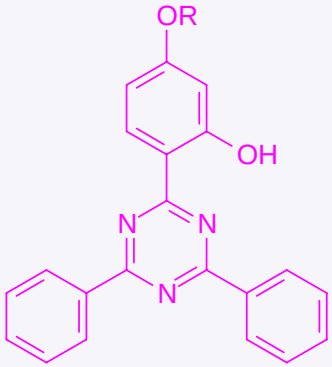
- Benzophenones
- Benzotriazoles
- Triazines



2-hydroxy**benzophenone**



2-hydroxyphenyl**benzotriazole**



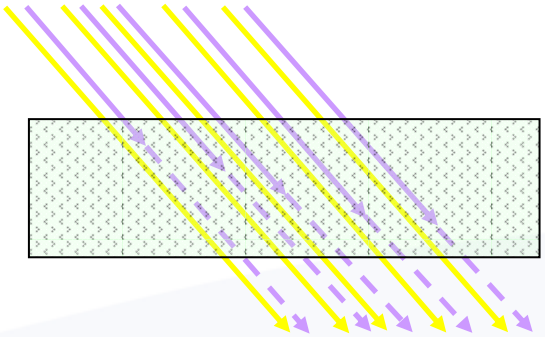
2-hydroxyphenyl**triazine**

Inorganic or metal oxide UV absorbers

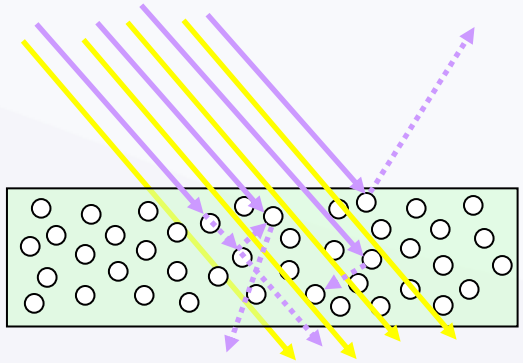
- Titanium dioxide (Titania, TiO_2)
  - Titanium dioxide has some catalytic properties so a coating is normally applied to provide a inactivated surface
  - Has been used in combination with other transition metals to eliminate catalytic activity but this tends to impart an orange-brown colouration (‘doping’)
- Zinc oxide (ZnO)
  - No coating is required, material is also basic in character so can act as an acid scavenger
- Cerium oxides and iron oxides
  - Have been used but impart colour to the polymer

Mode of action of UV absorbers

- **Organics**
  - UV energy is absorbed creating an excited state species
  - Energy is released through proton transfers & rearrangements of tautomeric or mesomeric forms



- **Inorganics**
  - Electrons promoted to an excited state
  - Energy released thermally through a series of relaxations
  - UV light is also scattered

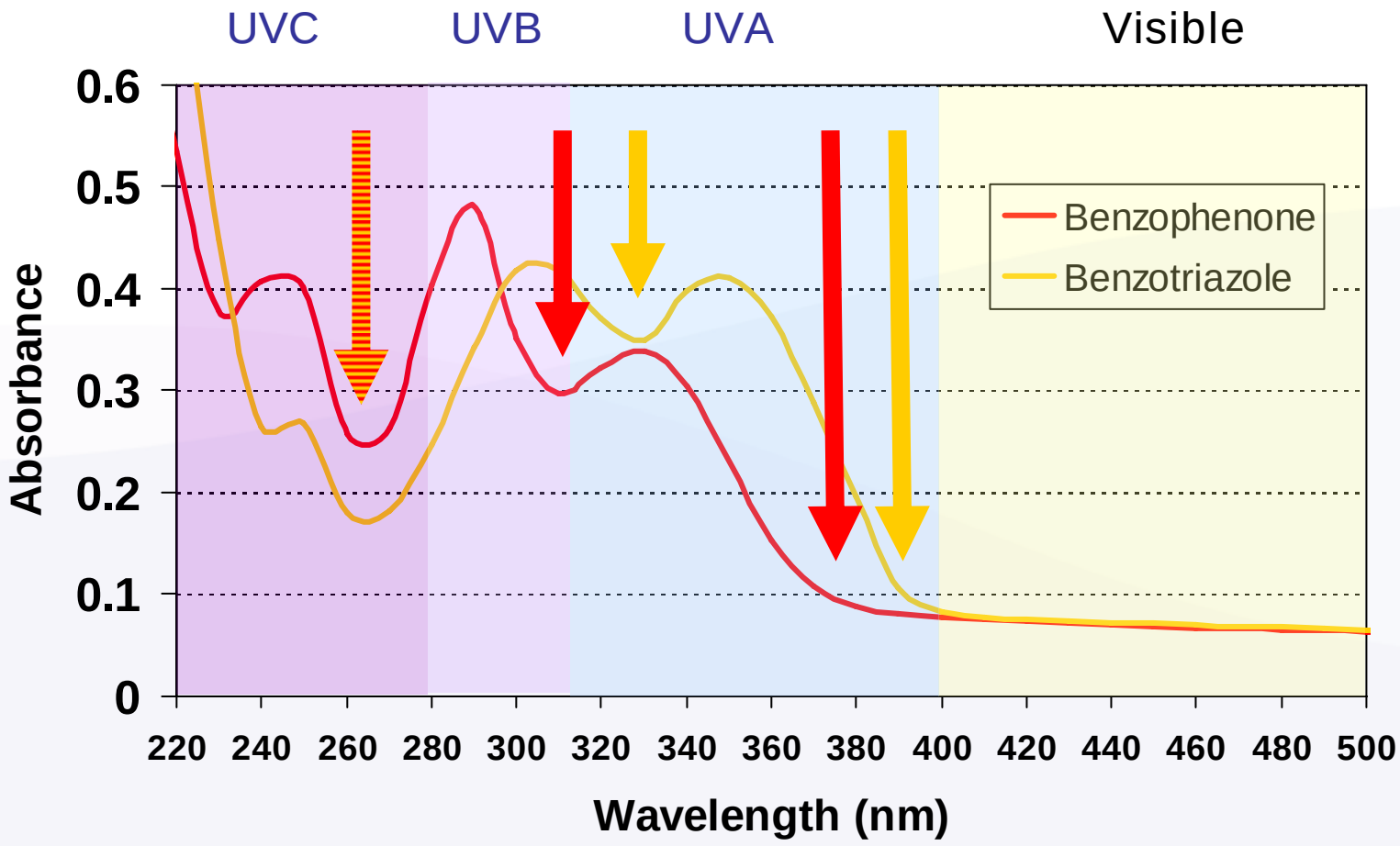


Organic UV absorber properties

- Allow production of high clarity articles
- Can bloom to surface resulting in visible haze
- Can migrate into package contents
- Some impart a yellow colour
- Not all have food approval or have limitations on use
- Cannot achieve full spectrum UV protection with one additive type
- Performance deteriorates with time

Organic UV absorbers

Absorbance varies with wavelength within the UV region



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Inorganic UV absorber properties

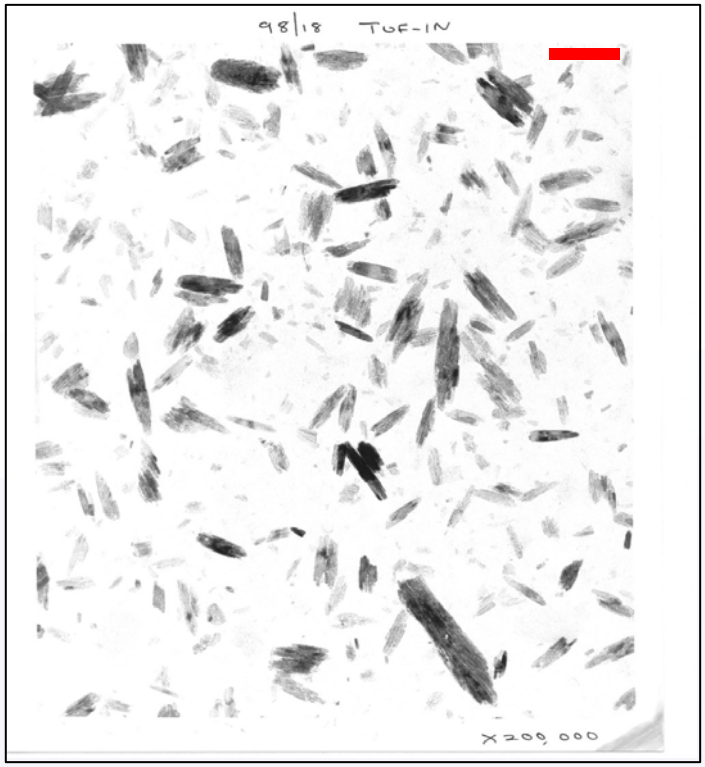
- Some affect on clarity
- Non migratory
- Long lasting properties
- Neutral colour
- Titanium Dioxide & Zinc Oxide have wide ranging food approvals
- Wide UV spectrum protection

Making Inorganic absorbers work better

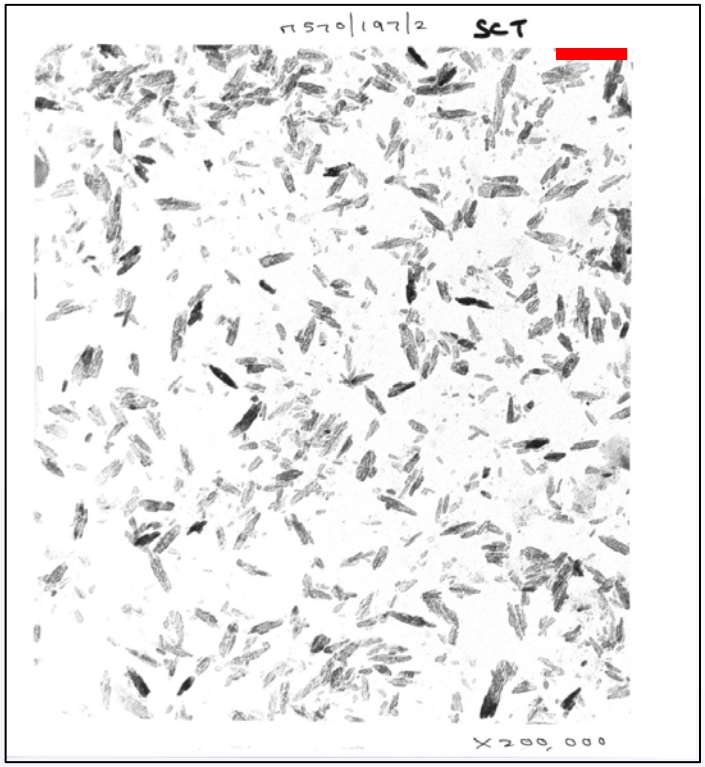
- The concept of Ultra-fine metal oxide UV absorber has been around for sometime, but the additives have not “taken off” in a big way.
  - *Clarity issues*
  - *Low UV absorbance*
- The key to clarity and high UV absorbance is particle size and the key to particle size is dispersion

TEM of TiO_2 particles

Red bar = 100 nm



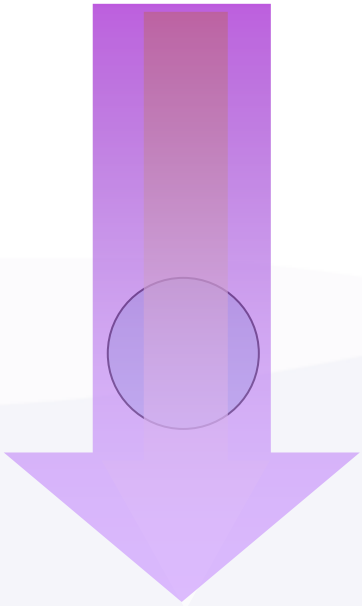
Conventional ultra-fine TiO_2



Solasorb UV 100 TiO_2

Particle size

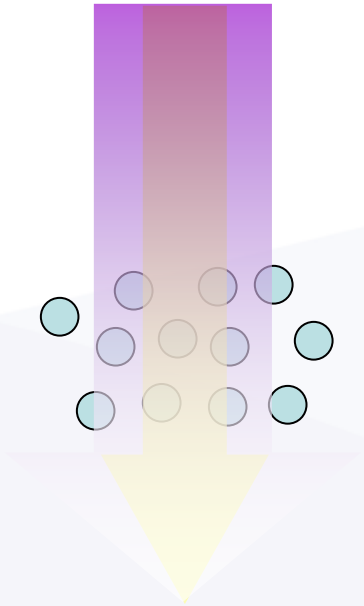
Pigment MO
(~200 nm)



Poor transmission of Visible

Poor barrier to UV

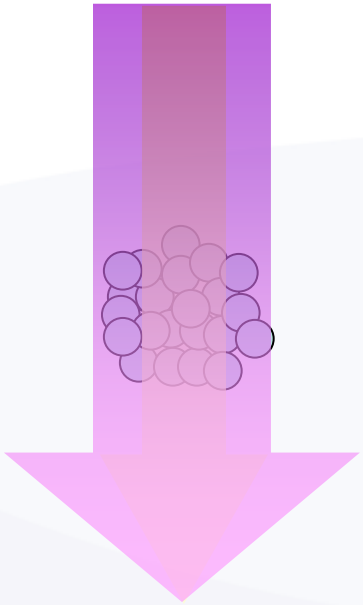
Dispersed MO
(~30 – 60 nm)



Good transmission of Visible`

Excellent barrier to UV

Agglomerated MO
(~200 nm)



Poor transmission of Visible

Poor barrier to UV

Materials tested

- Polymer
  - High pressure LDPE, 0.923 g/cm^3 density, 2 MFI
- Organic UV absorbers
  - Benzophenone type
  - Benzotriazole type
- Metal oxide UV absorbers
  - 4 titanium dioxide powder grades
  - 3 Zinc oxide powder grades
- Croda Solasorb grades
  - Solasorb UV100 (Titanium dioxide dispersion)
  - Solasorb UV200 (Zinc oxide dispersion)

Dispersions

- Solasorb dispersions were prepared by passing the metal oxide through a bead mill with a carrier oil and a polymeric dispersing agent.
  - UV100 contains 45% of an inorganic and organic coated Titanium dioxide particle size average 40 nm
  - UV200 contains 60% Zinc oxide 60nm average

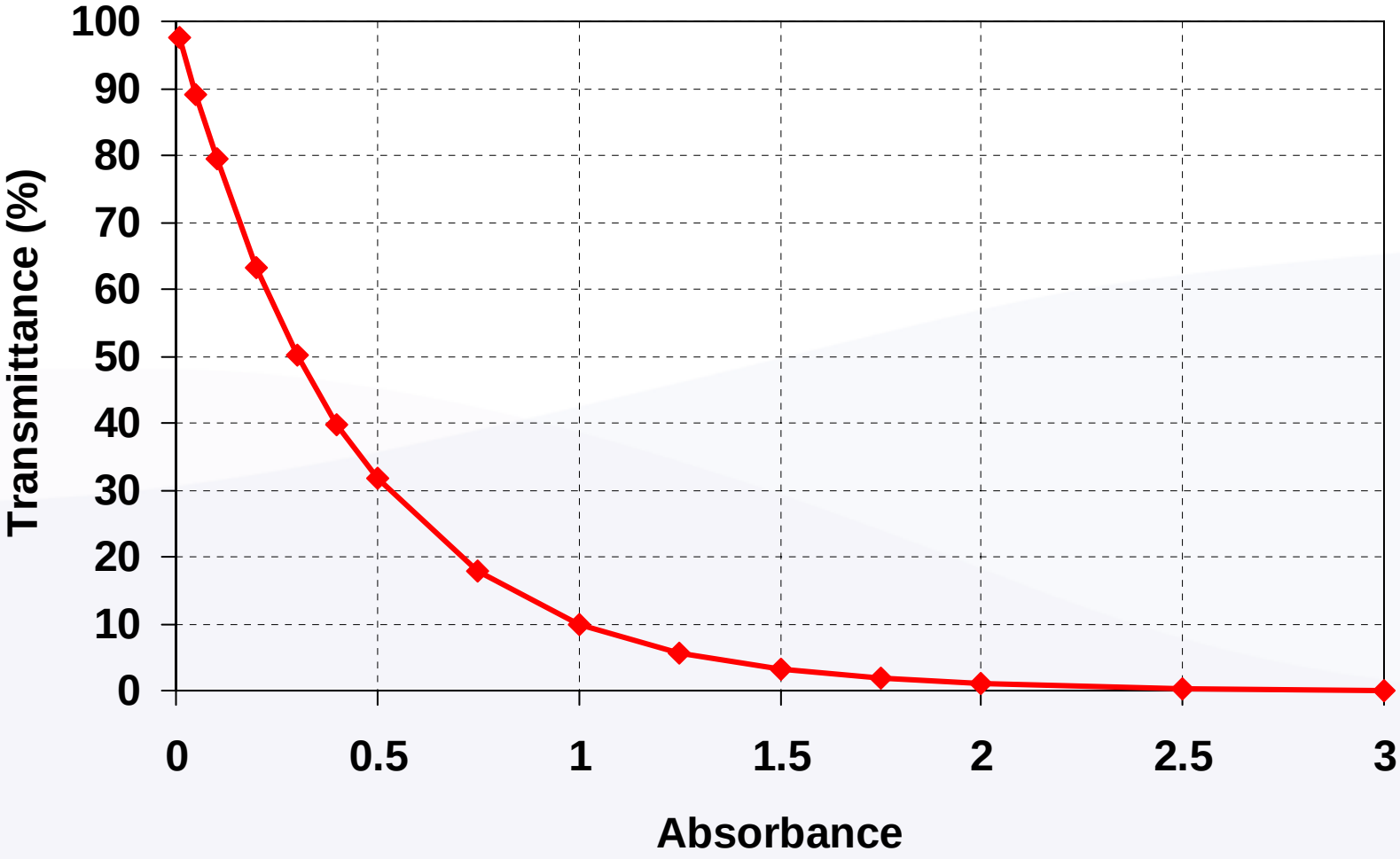
Procedure

- Masterbatches containing 5% w/w solids were prepared of each UV absorber type
- Powdered metal oxides and organic UV absorbers were preblended with powdered LDPE and extruded through a twin screw extruder and the resulting strand cooled in a water bath and pelletized.
- Metal oxide dispersions were mixed with polymer pellets and tumble blended before extrusion in to masterbatch pellets
- The masterbatches were let down to the appropriate concentrations for film production by batch blending with LDPE.
- Films up to 65µm were produced by blown film extrusion (35 mm single screw, 24 l/d, 50 mm die, 3:1 blow ratio). 100 µm film was produced by cast film extrusion through a 150 mm “coat-hanger” die.
- The typical extrusion temperature for all processes was 200° C

Testing

- Absorbance between 200 and 800 nm using a UV / visible spectrophotometer
- Haze measurements were taken on the 35 µm film samples.
- UV resistance of films was assessed using a UV weatherometer QUV type cabinet, UV absorbance was measured at various times of exposure

Conversion of Absorbance to % transmittance



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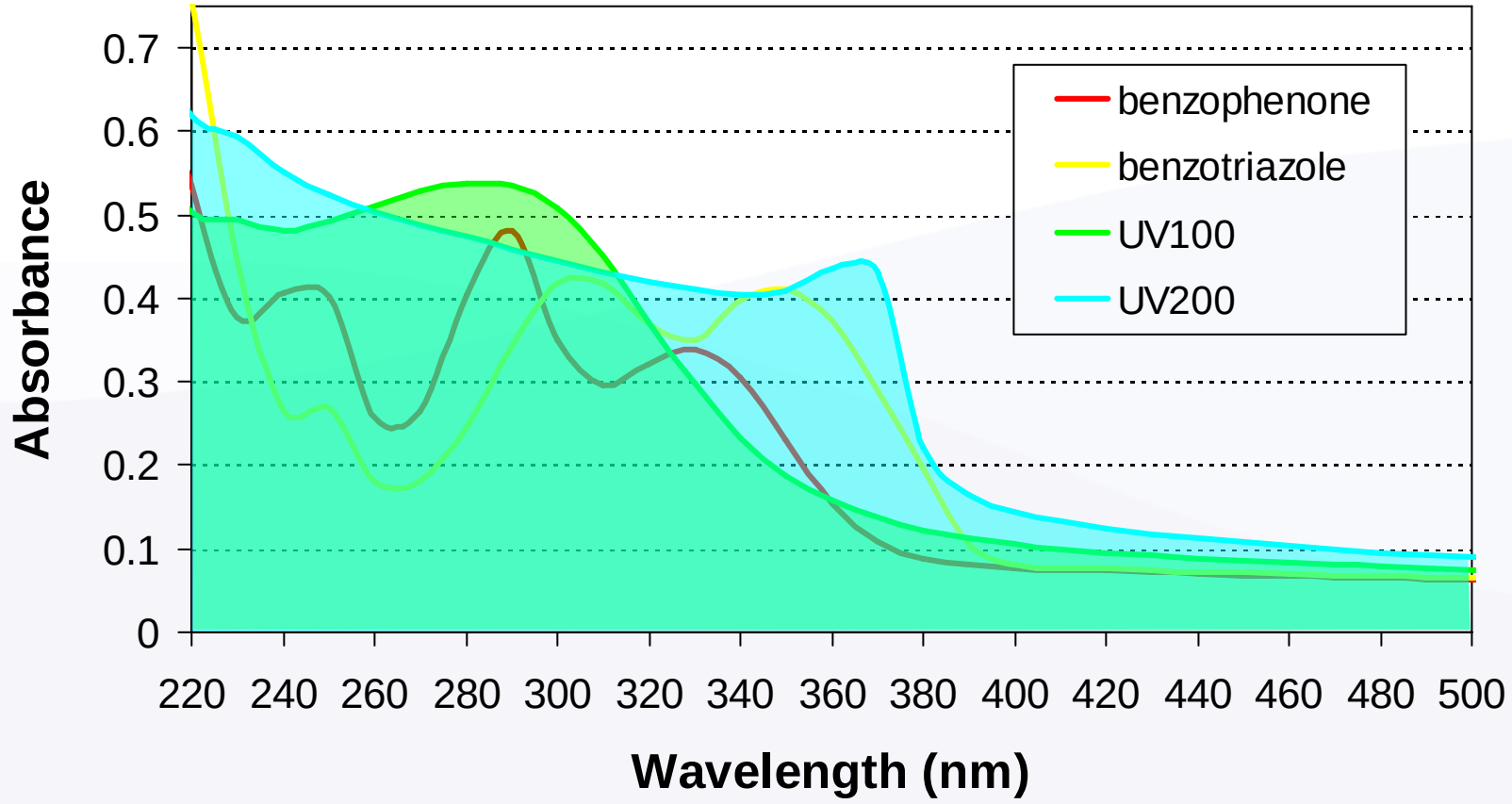
Comparison of UV absorbance profile of organic and inorganic absorbers

Metal oxides give broad spectrum absorbance



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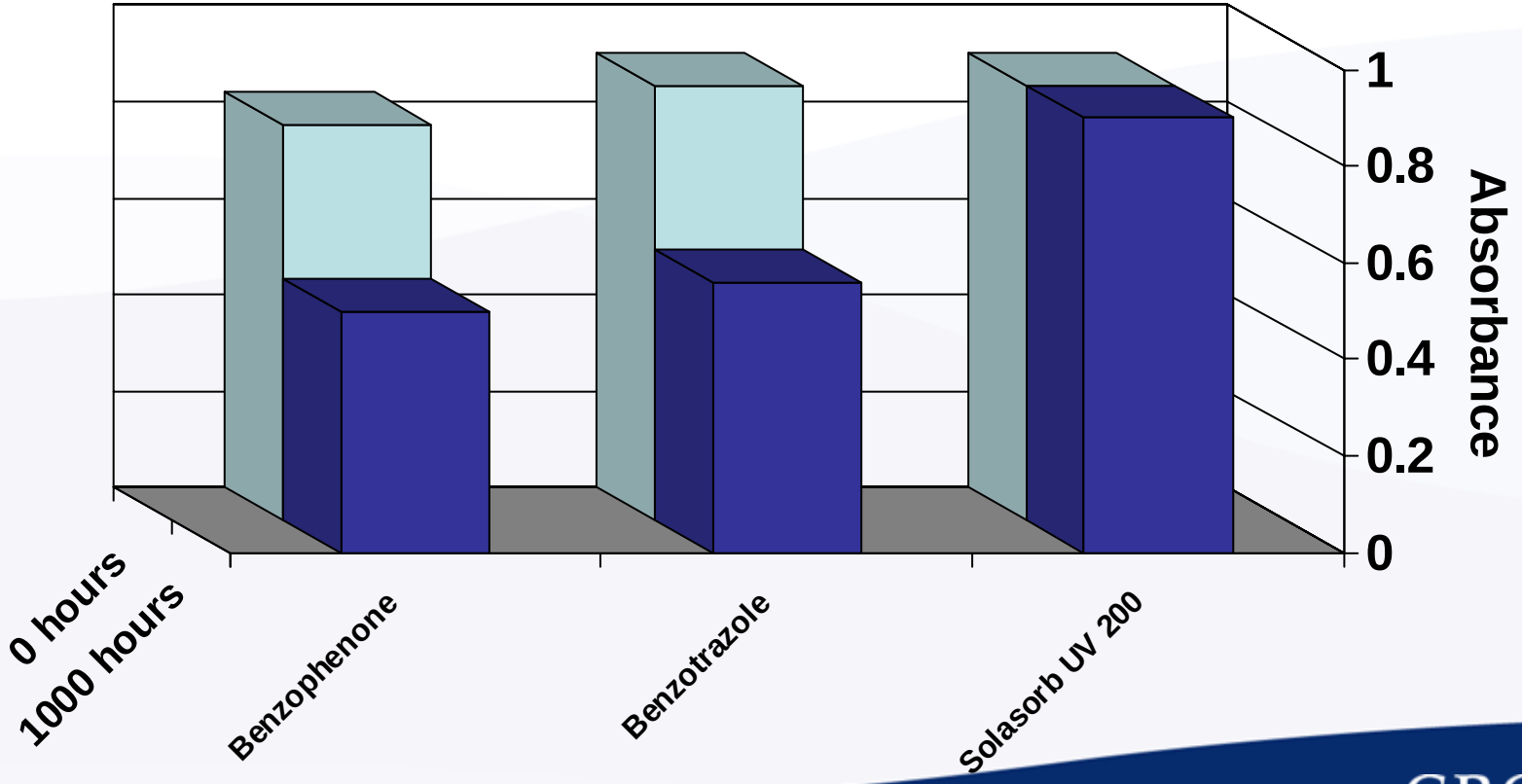
Effect of UV exposure on absorbers

UV absorbance at 320 nm, 65µm LDPE film, UV weatherometer

No reduction in UV absorbance with exposure with metal oxide



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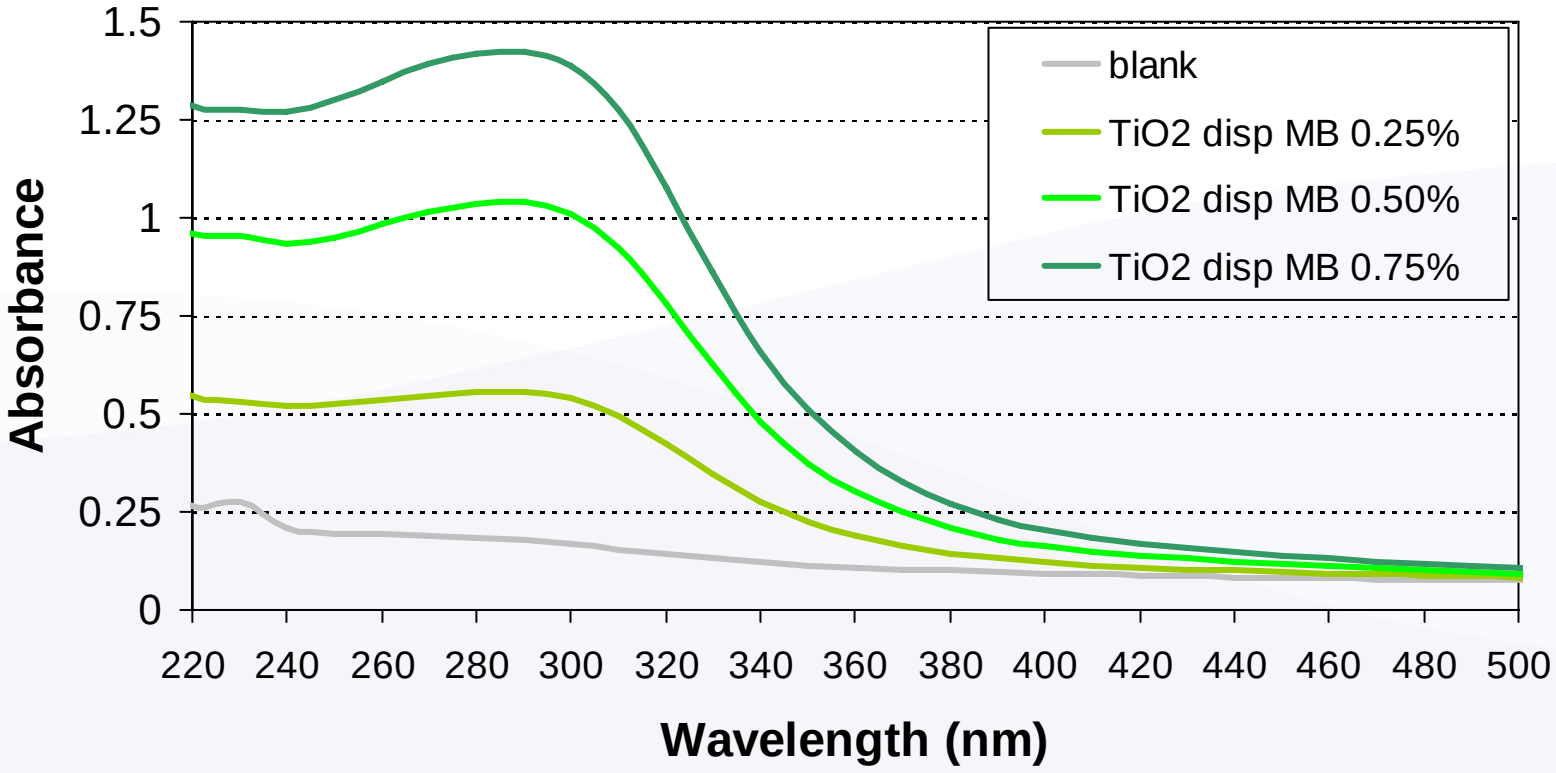
Solasorb UV 100

Effect of concentration on absorbance (% active, 35 µm LDPE film)



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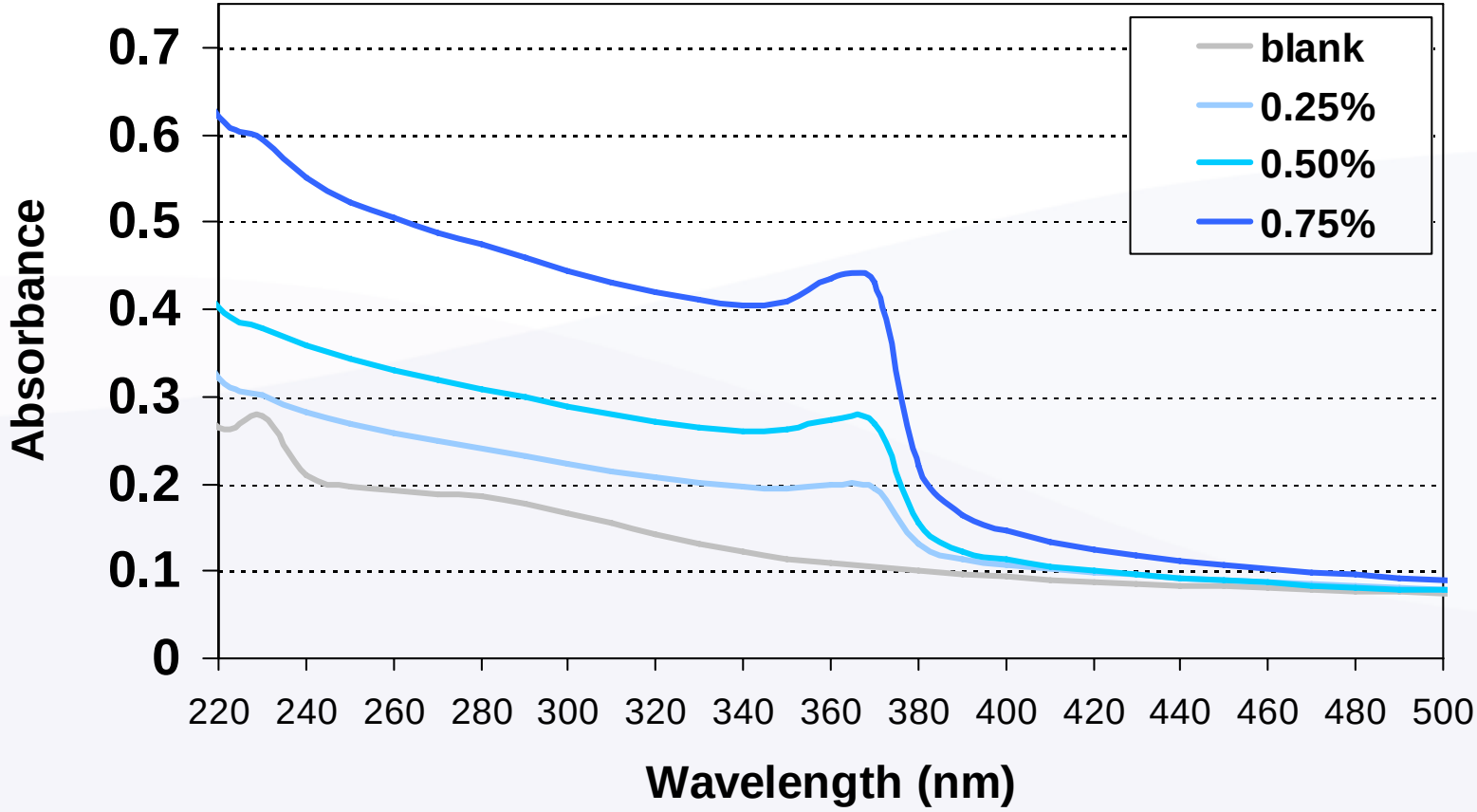
Solasorb UV 200

Effect of concentration on absorbance (% active, 35 µm LDPE film)



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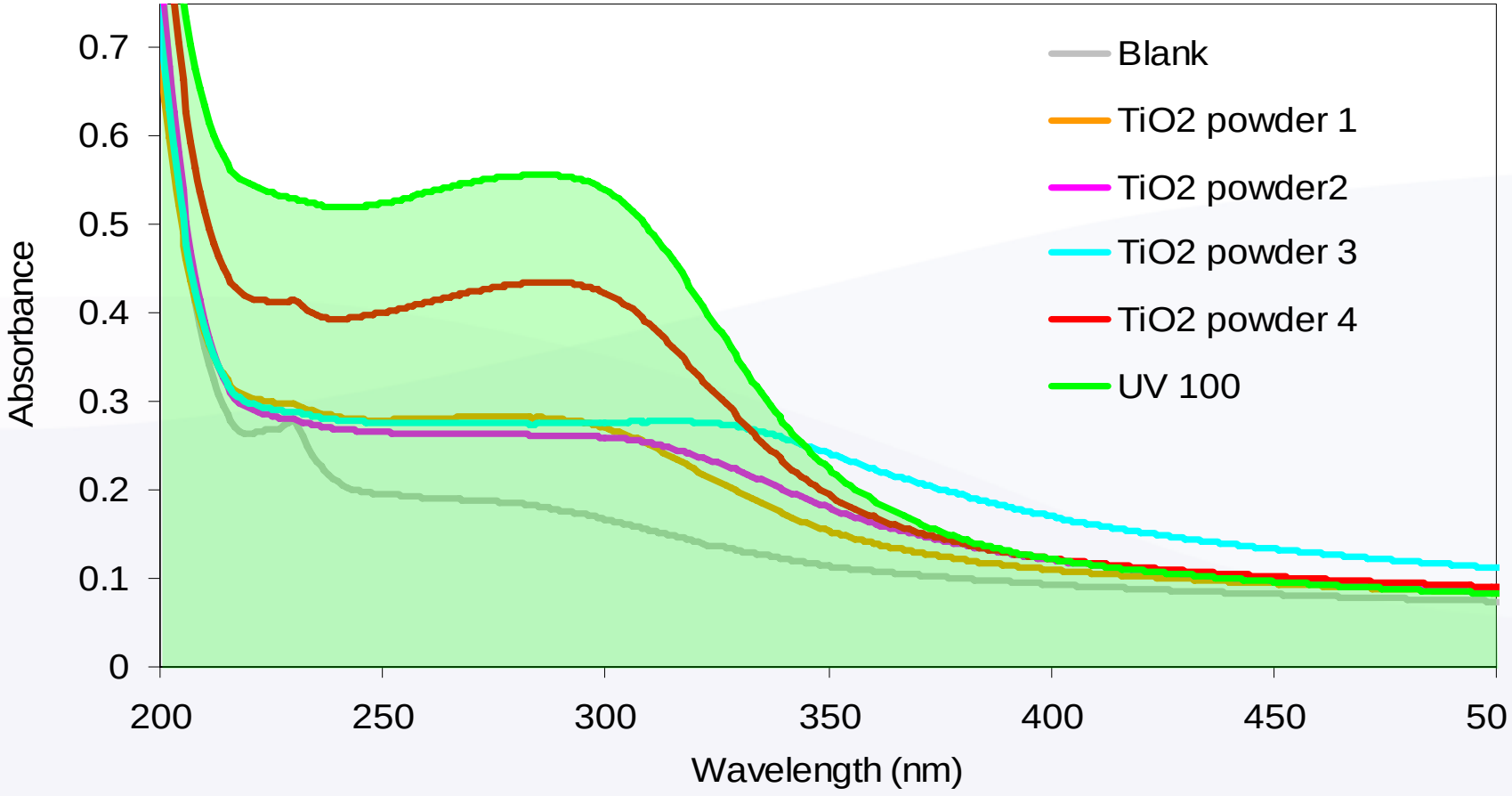
Effect of dispersion : TiO_2

0.25% active loading in polyethylene film (35 μm film thickness)



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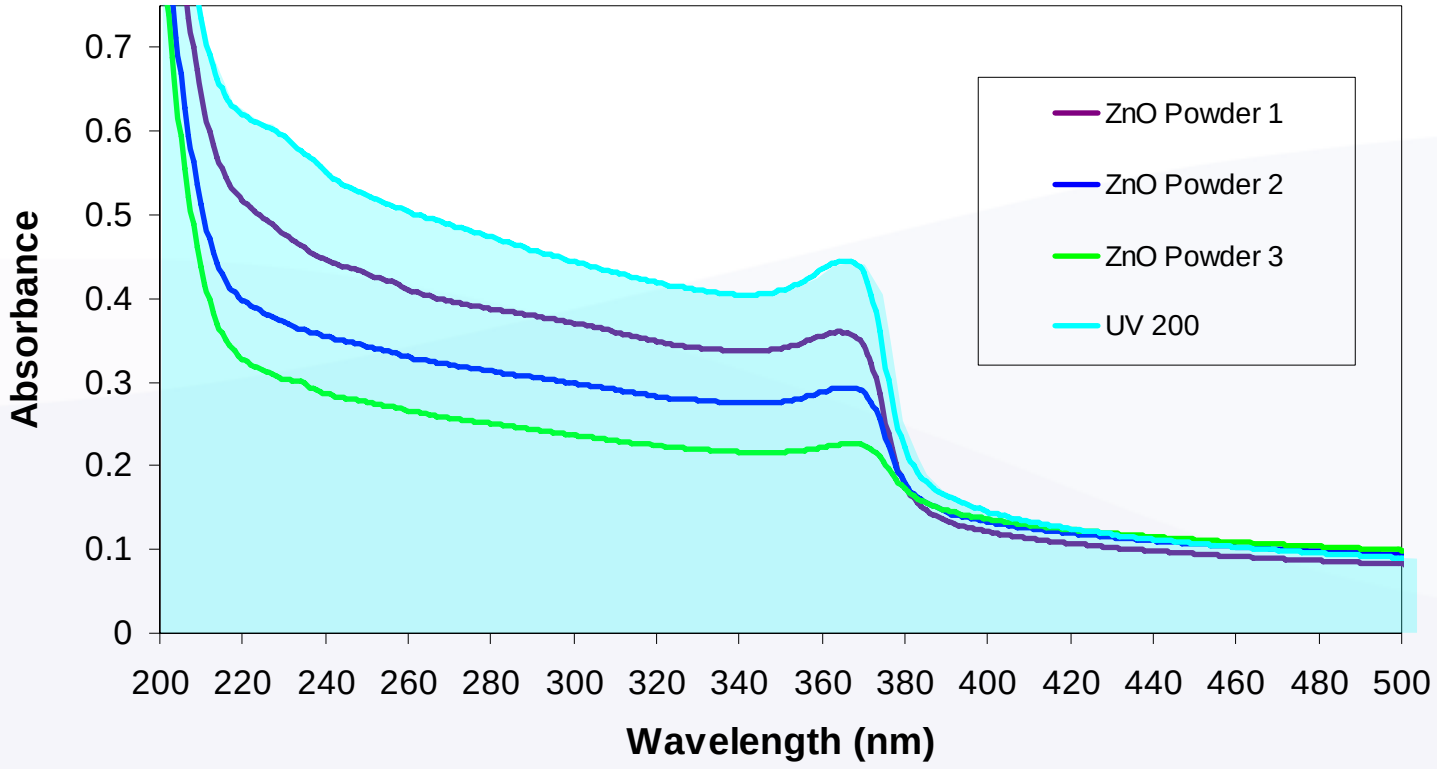
Effect of dispersion : ZnO

0.75% active loading in polyethylene film (35 μ m film thickness)



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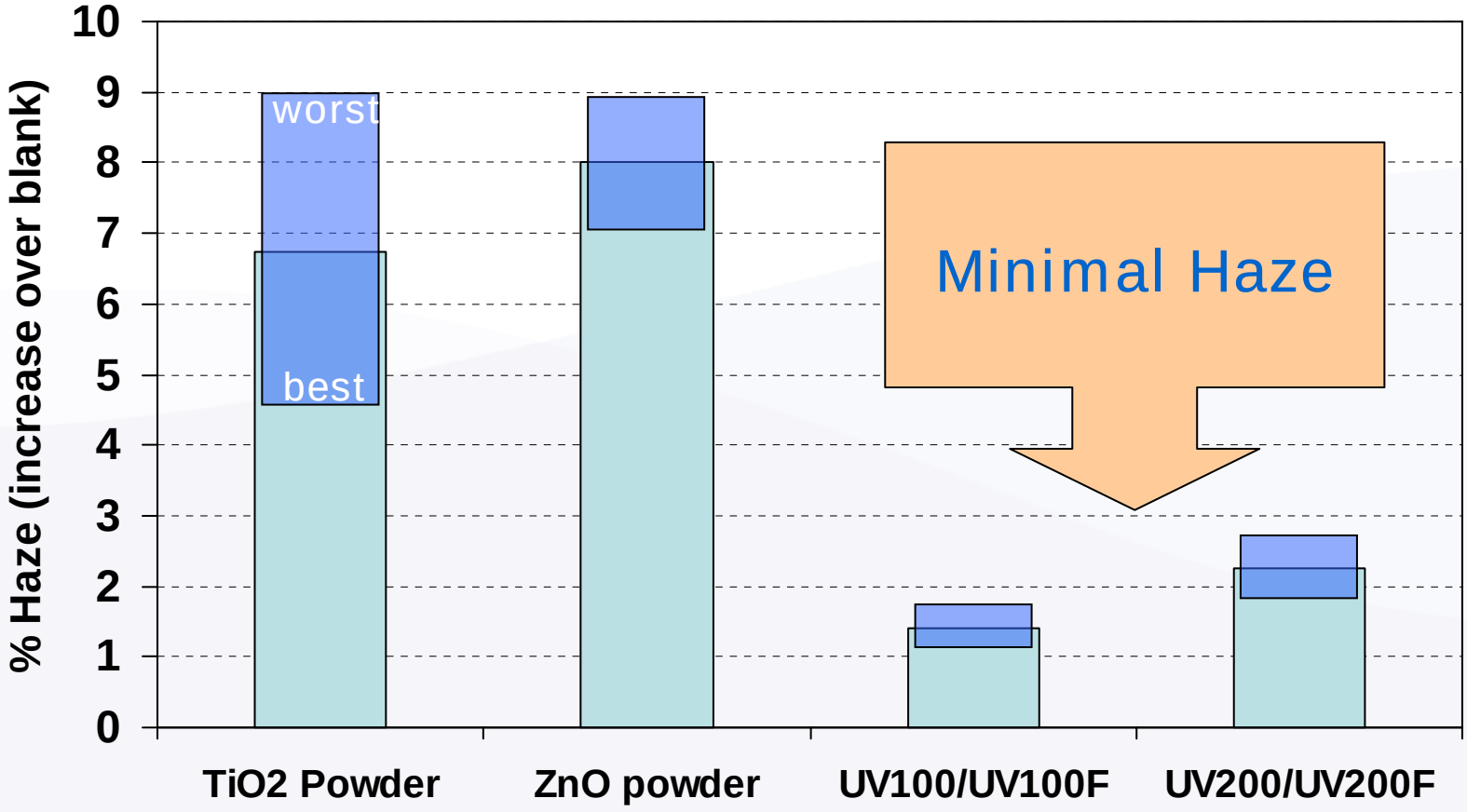
Effect of inorganic UV absorbers on haze

TiO_2 : UV100/100F - 0.25% active, ZnO : UV200/200F 0.75% active (w/w)

35 µm LDPE blown film



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Effect of Inorganic UV absorbers on film clarity

Solasorb 100F TiO_2 powder

It was also noted that film made with TiO2 powder does not lie as flat as that made with Solasorb, this is indicative of a dispersion effect

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Recommendations for use

- **Polymers**
  - Principally aimed at polyolefins and co-polymers: LDPE, LLDPE, HDPE, PP, EVA
  - Not tested yet in PS, PC, PET etc, may need some reformulation but worth a try
- **Durable applications**
  - Solasorb UV200
- **Non-food applications**
  - Solasorb UV100/200 or combinations
  - For improved clarity Solasorb UV100 + organic UV absorber may be a useful option
- **Food Contact applications**
  - Solasorb UV100F / UV200F combinations
  - For longer term full spectrum coverage Solasorb UV200F is preferred
  - Solasorb UV100F may give better clarity but an organic UV absorber may be used in combination to give full spectrum coverage
- **Not designed for HALS replacement**
- **Solid concentrates in a polymer carrier also available**

Addition Levels

- It is difficult to give an *absolute* addition level as the thickness of the article is a key factor, but in 75µm film to achieve <10% transmittance (Absorbance > 1) at 300 nm add:
  - Solasorb UV100 0.50 – 0.60 % *(or Atmer 7352 1.0 – 1.2%)*
  - Solasorb UV100F 0.55 – 0.65 % *(or Atmer 7354 1.1 – 1.3%)*
  - Solasorb UV200 1.20 – 1.30 % *(or Atmer 7353 2.4 – 2.6%)*
  - Solasorb UV200F 1.20 – 1.30 % *(or Atmer 7355 2.4 – 2.6%)*
- These figures are an just an approximate guide

Summary

- Dispersed metal oxides provide an effective UV absorber system
  - Long lasting performance
  - Wide spectral absorbance range
  - Good optical performance
- Advantages over other metal oxide powders
  - Lower haze
  - Better UV absorbance per unit of active added
  - Neutral colour when compared to some metal oxides
- Advantages over organic UV absorbers
  - The active in Solasorb does not migrate out of the polymer
  - No loss of activity with time
  - Neutral colour when compared with some organics
  - Wide spectral absorbance range (especially UV200 & UV200F)