High performance UV barrier additives based on highly dispersed metal oxides
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 electromagnetic radiation?
Ultra-Violet radiation

- 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 earth's surface
- UVB is more damaging but there is much less than UVA

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultraviolet A long wave or black light</td>
<td>UVA</td>
<td>400 – 315</td>
</tr>
<tr>
<td>Ultraviolet B or medium wave</td>
<td>UVB</td>
<td>315 – 280</td>
</tr>
<tr>
<td>Ultraviolet C short wave or germicidal</td>
<td>UVC</td>
<td>280 – 100</td>
</tr>
<tr>
<td>Vacuum Ultraviolet</td>
<td>VUV</td>
<td>200 – 10</td>
</tr>
</tbody>
</table>
UV exposure at earth’s surface

Ozone layer

~150, 000, 000 km
(~93 million miles)

60 km

40 km

20 km

Sea level

stratosphere

troposphere

UV exposure at earth’s surface

UVC

UVB

UVA

~35 km
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
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

- **UVC**
- **UVB**
- **UVA**
- **Visible**

**Absorbance** varies with wavelength within the UV region. The graph illustrates the absorbance of organic UV absorbers, such as benzophenone and benzotriazole, across different wavelengths (nm) in the UV and visible spectrum. The red line represents benzophenone, while the yellow line represents benzotriazole.
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/cm³ 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 into 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

Absorbance

Transmittance (%)
Comparison of UV absorbance profile of organic and inorganic absorbers

Metal oxides give broad spectrum absorbance
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
Solasorb UV 100
Effect of concentration on absorbance (% active, 35 µm LDPE film)
Solasorb UV 200
Effect of concentration on absorbance (% active, 35 µm LDPE film)
Effect of dispersion : TiO$_2$

0.25% active loading in polyethylene film (35 $\mu$m film thickness)
Effect of dispersion: ZnO

0.75% active loading in polyethylene film (35 μm film thickness)
Effect of inorganic UV absorbers on haze

TiO₂ : UV100/100F - 0.25% active, ZnO : UV200/200F 0.75% active (w/w)
35 µm LDPE blown film
Effect of Inorganic UV absorbers on film clarity

It was also noted that film made with TiO$_2$ powder does not lie as flat as that made with Solasorb, this is indicative of a dispersion effect.

Solasorb 100F     TiO$_2$ powder
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)