New high performance and sustainable UV stabilizer solutions for waterborne coatings

ABRAFATI 2013
SAO PAULO, BRAZIL
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– 3. High performance UV stabilizer dispersions for water-based coatings

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1. Introduction to Clariant BU Additives
A world leader in specialty chemicals

<table>
<thead>
<tr>
<th>KEY FACTS</th>
<th>End 2012</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sales 2012 (CHF m)</td>
<td>21,202</td>
</tr>
<tr>
<td>EBITDA 2012 (CHF m) before exceptionals</td>
<td>802</td>
</tr>
<tr>
<td>Net income 2012 (CHF m)</td>
<td>211</td>
</tr>
<tr>
<td>Dividend 2012 (CHF/share)</td>
<td>0.33</td>
</tr>
<tr>
<td>More than 100 Group companies worldwide</td>
<td></td>
</tr>
<tr>
<td>Represented in 76 countries worldwide</td>
<td></td>
</tr>
<tr>
<td>4 Business Areas</td>
<td></td>
</tr>
<tr>
<td>7 Business Units reported in</td>
<td></td>
</tr>
<tr>
<td>13.3%</td>
<td></td>
</tr>
<tr>
<td>21202 employees (incl. discontinued operations)</td>
<td></td>
</tr>
<tr>
<td>6038</td>
<td></td>
</tr>
</tbody>
</table>
Clariant’s products and services are grouped into four Business Areas

**Care Chemicals**
includes Industrial & Consumer Specialties, food additives & the future Industrial Biotechnology business

**Catalysis & Energy**
includes Catalysts and Energy Storage businesses

**Natural Resources**
includes Oil & Mining Services and Functional Minerals businesses

**Plastics & Coatings**
includes Additives, Pigments and Masterbatches businesses
Clariant focus on value creation with innovative and customized solutions

Clariant provides a desired performance in customer products

With innovative and customized solutions

We create added value by appreciating the needs of our customers – with competitive and innovative solutions.
The Additives Business Unit is an important supplier of products with functional effects for plastics, coatings and printing inks.

The product range includes:

- **Flame retardants**: halogen free products for use in intumescent coatings and engineering thermoplastics for E&E applications.

- **Waxes**: broad product range serving plastics, coatings, inks, adhesives and special applications.

- **Polymer Additives**: light stabilizers, antioxidants and antistatics for effects in plastics, coatings and many other applications.
2. Degradation of coatings & mechanisms of UV stabilization
Degradation of coatings under light / UV exposure

- Simplified scheme of degradation

  gloss reduction
  yellowing of binder
  embrittlement, cracking
  blistering
  sub-chalking delamination
  fading of organic pigments

Air pollutants
- UV-light
- O₂
- Moisture

reduction of film thickness

clearcoat
basecoat
surfacer
Degradation of coatings under light / UV exposure

- Picture of an exposed metallic coating (car hood)
- Picture of an exposed clear coated wood panel

not exposed  exposed
Degradation of coatings under light / UV exposure

- Mechanisms of polymer degradation

  after crosslinking

  after UV-exposure

- UV radiations are damaging light for polymers
- Oxidation is induced by light → photo-oxidation process
Degradation of coatings under light / UV exposure

- Two chemical classes of UV stabilizers are available from Clariant:

1. **UV Absorbers**
   Principle: absorption (filter effect) of damaging UV light and converting its thermal energy into a non-destructive heat before it starts degrading the polymer.

2. **Radical Scavengers (HALS)**
   Principle: trapping of radicals before further reactions leading to degradation of the polymer matrix.
UV Absorbers – Mechanisms of stabilization

- How do UV Absorbers work?
  - They follow a physical principle, commonly described as “Beer-Lambert law”, which translates the fact that light intensity is decreasing in a non-linear way when going through the coating layer.

![Diagram showing light intensity through different film thickness and concentration](image)

- too low film thickness
- optimal film thickness and concentration
- too low concentration
UV Absorbers – Mechanisms of stabilization

– Comparison of different UV Absorbers

<table>
<thead>
<tr>
<th></th>
<th>UV-C</th>
<th>UV-B</th>
<th>UV-A</th>
<th>visible</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td>0,8</td>
<td>0,6</td>
<td>0,4</td>
<td>0,2</td>
</tr>
</tbody>
</table>

Absorption as a function of wavelength (nm):
- Oxalanilide
- Benzophenone
- Triazine
- Benzotriazole
- Halogen. benzotriazole
HALS – Mechanisms of stabilization

- HALS are organic molecules based on the same piperidine structure

![Chemical Structure]

\[ R' \quad R'' \]

\[ \text{tetra-methyl-piperidine} \]

R is the key substituents which determines the speed of activation and the basicity

\[ R = \]

- \(-H\) not substituted
- \(-\text{CH}_3\) methylated
- \(-\text{O} - R'\) etherified
- \(-\text{C} - \text{CH}_3\) acylated

R’ and R” control secondary properties (e.g. compatibility, solubility, volatility etc.)
HALS – Mechanisms of stabilization

- HALS are protecting indirectly the substrate
Mechanisms of UV stabilization – UV Absorbers and HALS contribute to multiple protection

<table>
<thead>
<tr>
<th>Chemical type</th>
<th>UV Absorbers</th>
<th>Radical Scavengers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Benzophenones, Benzotriazoles, Triazines, Oxalanilides</td>
<td>Sterically Hindered Amines (HALS)</td>
</tr>
<tr>
<td>Mechanism of action</td>
<td>Absorbing UV radiations (physical principle)</td>
<td>Trapping free radicals (chemical reaction)</td>
</tr>
<tr>
<td>To protect what?</td>
<td>Interior &amp; exterior coatings</td>
<td>Exterior coatings</td>
</tr>
<tr>
<td>To protect where?</td>
<td>Entire coating layer, basecoat</td>
<td>Mainly at surface of coatings</td>
</tr>
</tbody>
</table>
| To protect against what? | • Colour change  
• Blistering  
• Loss of adhesion | • Gloss reduction  
• Cracking  
• Chalking |
3. High performance light stabilizer dispersions for water-based coatings
Regulation compliance is driving the coatings industry towards waterbornes

- In Europe and USA mainly, paints and coatings producers have been asked to switch to alternative technologies to reduce VOC emissions.

- Increasingly more stringent maximum VOC content limit values for paints and coatings are and will be required.

- Today, solutions exist to make production processes compliant to the directives:
  - Retaining solventborne technology → high solids coatings
  - UV-curing technology → 100% UV or waterborne UV
  - Powder coatings
  - Waterborne coatings
Application of waterborne coatings

- Most commonly used binders

<table>
<thead>
<tr>
<th>2K-PU</th>
<th>Acrylic - melamine</th>
<th>PU emulsion</th>
<th>Acrylic emulsion</th>
<th>F-copolymer</th>
<th>Alkyd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Architectural</td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
</tr>
<tr>
<td>Wood protection</td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
</tr>
<tr>
<td>Transportation</td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
</tr>
<tr>
<td>Automotive (OEM)</td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
</tr>
<tr>
<td>(Car refinish)</td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
</tr>
</tbody>
</table>
In general, traditional stabilizers used in waterborne systems do not comply with all requirements!

- To protect these waterborne coatings against adverse effects from solar radiations, humidity and weather, it is necessary to add light stabilizers.

- Light stabilizers must fulfill the specific requirements from waterborne systems:
  - Stabilization efficiency
  - Easy incorporation and broad compatibility in binder systems

Liquid UV stabilizer

Powder UV stabilizer
Clariant UV Stabilizer Solutions have been optimized to meet these specific requirements:

- Broader compatibility with binders vs. traditional additives
- Higher concentration for low-dosage performance
- Easier and safer incorporation into the coating
- **Example 1**: on glass plate

  **System**: WB acrylic based clear coat with 2% active ingredient

- **Example 2**: on coated PET film
Standard work flow of paint production

1. **pig.**
2. **bind. sol. add.**
3. **pig.-prep.**

The process involves the addition of binders, solvents, and additives, followed by pigment preparation and mixing. The flowchart illustrates the sequence and components involved in the paint production workflow.
Standard work flow of paint production

- Risks

1. Addition to mill base
   - UV stabilizers get easily adsorbed on the pigment surface and lose partly their efficiency

2. Addition with let down
   - Prolonged stirring may cause intake of air and CO$_2$ and, in extreme, coagulation of binder

3. Addition as dispersion
   - In practice no risks; as a rule the most simple and safe way of incorporation
Clariant UV stabilizer solutions fulfil the requirements from the growing waterborne coatings market

- A comprehensive range to serve all customer’s needs, recently completed by new high performance UV stabilizers:

<table>
<thead>
<tr>
<th>Chemical class</th>
<th>Active content [%]</th>
<th>Main applications</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>30</td>
<td>Wood coatings</td>
<td>+</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>52</td>
<td>OEM, industrial</td>
<td>++</td>
</tr>
<tr>
<td>Hal. benzotriazole</td>
<td>52</td>
<td>Wood coatings</td>
<td>++</td>
</tr>
<tr>
<td>Traditional HALS</td>
<td>52</td>
<td>OEM, industrial, wood</td>
<td>++</td>
</tr>
<tr>
<td>Proprietary solution</td>
<td>52</td>
<td>Wood coatings</td>
<td>++</td>
</tr>
<tr>
<td>Triazine</td>
<td>52</td>
<td>OEM, wood, plastic</td>
<td>+++</td>
</tr>
<tr>
<td>Oligomeric HALS</td>
<td>52</td>
<td>OEM, wood, plastic</td>
<td>+++</td>
</tr>
</tbody>
</table>
Triazines UV Absorbers – General properties

- Triazines are UV Absorbers from the most recent class of UV A developed for coatings with outstanding performances vs. all other existing UV Absorbers:

  - Strong and broad absorptivity with superior extinction coefficient
  - Long term light stability
  - Less interaction with metal ions
  - High thermal stability
Clariant Triazine – Main characteristics

- Very fine grade
- Appearance: slightly yellowish powder
- Purity: > 99.5%
- Density: 1.403
- High photo-permanence and very low volatility:
  - DSC: melting point at 243°C
  - TGA: decomposition at 370°C (10% loss)
- Broad absorption spectrum:
  - 2 peaks in UV-B and UV-A areas
  - High extinction coefficient

\[ \varepsilon (280 \text{ nm}) = 51400 \]
\[ \varepsilon (340 \text{ nm}) = 10400 \]

Solvent: Cyclohexane
Cell: 1.0 cm
Concentration: 10 mg/L
Clariant Triazine –
Highlights and properties

- Triazine UV spectrum: comparison with other available UV Absorbers (BZP, OXA, BZT)
Clariant Triazine –
Low interactions with transition metal ions

– Initial color of the UV absorber solutions without metal ions
  Dichloromethane solution: 1% UV absorber
  1. Triazine
  2. LMW benzotriazole
  3. HMW benzotriazole
  4. Benzophenone

– Color formation in the presence of 200 ppm Ni-acetate
Clariant Triazine solution – Key features

- High loading dispersion form (52% active substance)
- Milky appearance, slightly yellowish
- Very fine and stable dispersion: $D_{90} < 5 \, \mu m$
- Storage stability > 3 years
- Free of any VOC compounds

![Particle Size Distribution Graph]

$\text{d}(10\%) = 0.619 \, \mu m \quad \text{d}(50\%) = 1.431 \, \mu m \quad \text{d}(90\%) = 3.634 \, \mu m$
Clariant Oligomeric HALS solution – Key features

- High loading dispersion form (52% active substance)
- Milky appearance
- Very fine and stable dispersion: $D_{90} < 5 \mu m$
- Storage stability > 3 years
- Free of any VOC compounds

![Particle Size Distribution Graph]

- $d(10\%) = 0.868 \mu m$
- $d(50\%) = 1.905 \mu m$
- $d(90\%) = 4.867 \mu m$
4. Comparative test results and recommendations
Test results in truck coating

- Comparison of different UV stabilizer packages:
  - waterborne 2K-PU acrylic
  - pigmentation: lead-free, bordeaux-red, semi-opaque

Stabilization 1

BZT 1

Stabilization 2

BZT 2

LMW HALS

HMW HALS
Test results in truck coating

- Comparison of different UV stabilizer packages
  - Absorption at same concentration

![Graph showing absorption vs. wavelength]

**Stabilization 1**
- 0.7 % BZT 1
- 0.4 % LMW HALS

**Stabilization 2**
- 0.5 % BZT 2
- 0.6 % HMW HALS
Test results in truck coating

- Comparison of different UV stabilizer packages
  - WOM exposure according to SAE J 1960
Test results in truck coating

- Comparison of different UV stabilizer packages
  - WOM exposure according to SAE J 1960

![Graph showing ΔE (Colour change) vs. Exposure time [hrs] for different stabilizer packages.](image)
HALS selection is a key criteria for optimized compatibility with binders

- Change of viscosity of a 2K-PU acrylic system, stabilized by different HALS

**LMW HALS:**
- methylated type
- 100 % liquid

**HMW HALS:**
- oligomeric type, non-interacting
- 52 % aqueous dispersion

![Graph showing viscosity changes with days at 50°C for white and black pigmentation with and without HALS](image)
Superior performances in water-based coatings with our optimized solutions

- **Case 1**: comparison of UV stabilization packages for exterior wood protection
  - waterborne 2K-PU
  - clear coat applied on pinewood with 80 microns DFT

**Stabilization 1:**
- 1.2 % BZT 1
- 0.6 % LMW HALS

**Stabilization 2:**
- 1.2 % BZT 3
- 0.6 % LMW HALS 2

**Stabilization 3:**
- 1.2 % Clariant HPT
- 0.6 % HMW HALS
Superior performances in water-based coatings with our optimized solutions

– **Case 1**: comparison of UV stabilization packages in a 2K-PU wood clear coat

<table>
<thead>
<tr>
<th>Stabilization</th>
<th>Initial</th>
<th>After 500 h</th>
<th>After 1000 h</th>
<th>After 1500 h</th>
<th>After 2000 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>No stabilization</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
</tr>
<tr>
<td>Stabilization 1: 1.2% BZT 1, 0.6% LMW HALS</td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
</tr>
<tr>
<td>Stabilization 2: 1.2% BZT 3, 0.6% LMW HALS 2</td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
</tr>
<tr>
<td>Stabilization 3: 1.2% Clariant HPT, 0.6% HMW HALS</td>
<td><img src="image16.png" alt="Image" /></td>
<td><img src="image17.png" alt="Image" /></td>
<td><img src="image18.png" alt="Image" /></td>
<td><img src="image19.png" alt="Image" /></td>
<td><img src="image20.png" alt="Image" /></td>
</tr>
</tbody>
</table>

- WOM exposure according to ISO 4892-2 wet (previously ISO 11 341-A)
- Dosage is % of active ingredient on solid resin
Superior performances in water-based coatings with our optimized solutions

- **Case 2**: comparison of UV stabilization packages in automotive OEM coatings
  - waterborne 2K-PU topcoat
  - stoving system (cured at 140 °C for 30 min.)

<table>
<thead>
<tr>
<th>Stabilization 1:</th>
<th>Stabilization 2:</th>
<th>Stabilization 3:</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,0 % BZT 1</td>
<td>2,0 % Comp. HPT</td>
<td>2,0 % Clariant HPT</td>
</tr>
<tr>
<td>1,0 % LMW HALS</td>
<td>1,0 % LMW HALS</td>
<td>1,0 % HMW HALS</td>
</tr>
</tbody>
</table>

**Stabilization 1:**
- BZT 1
- LMW HALS

**Stabilization 2:**
- Comp. HPT
- LMW HALS

**Stabilization 3:**
- Clariant HPT
- HMW HALS

Proprietary structure

**HPT**

**LMW HALS**

**HMW HALS**
Superior performances in water-based coatings with our optimized solutions

- **Case 2**: comparison of UV stabilization packages in a stoving 2K-PU automotive OEM top coat

Comparison Clariant triazine with current UVA+HALS stabilization packages: gloss retention WOM exposure according to ISO 4892-2 wet (previously ISO 11 341-A)
Superior performances in water-based coatings with our optimized solutions

- **Case 2**: comparison of UV stabilization packages in a stoving 2K-PU automotive OEM top coat

![Graph showing gloss retention and cracking against exposure time for different stabilization packages.](graph.png)

Comparison Clariant triazine with current UVA+HALS stabilization packages: colour change (ΔE) WOM exposure according to ISO 4892-2 wet (previously ISO 11 341-A)
Recommendations in water-based wood coatings

- UV Absorber: Clariant Triazine [HPT] (1-3%)
  - lower dosage / highly concentrated
  - better compatibility, free of any VOC compounds
  - easy to incorporate

- HALS: Clariant non-migrating HALS [HMW HALS] (1-2%)
  - low volatility, non-migrating
  - neutral HALS (non-interacting)
  - higher thermal stability
  - better compatibility, free of any VOC compounds
  - excellent “toxicological” profile vs. traditional HALS → no labelling required
5. Conclusion
High performance Clariant UV stabilizer solutions offer definite benefits for customer’s formulations

- Tailor made solutions to fit to the needs of high demanding coating markets
- Cost effective formulations with high loading of active ingredients
- Improved gloss retention and reduced colour change
- Broad compatibilities in a variety of binders
- Synergistic combinations based on our Triazine UV-A and non-migrating HALS are recommended for optimized protection of exterior waterborne coatings.
Thank you for listening!
Any question?

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