Efficient stabiliser packages in waterborne transparent wood coatings.

Conventional light stabilisers based on iron oxide provide good protection for wood, but change its colour. However, products now exist that do the job without affecting the natural colour of the substrate. The right combination of organic and inorganic variants together with radical scavengers proves to be the solution.

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If coated wood is not sufficiently protected against weathering, the resulting damage follows a typical pattern. It progressively darkens, the gloss reduces and the coating yellows. This is followed by chalking, blistering, and cracking. The coating becomes brittle and delamination takes place with the subsequent decomposition of the wood. The damage is mainly caused by UV-A and UV-B radiation and to a lesser extent by the visible portion of the spectrum. The wood turns grey as the decomposition of lignin and the subsequent washout make the whitish-grey cellulose visible. The surface becomes fibrous and ribbed.

The most effective light stabilisers are coatings pigmented with transparent iron oxides. However, these yellowish-red pigments change the colour of the wood. The aim of the work presented here was to develop products which give effective protection of wood coatings over a long period, whilst avoiding colour change and achieving maximum transparency.

Physical light protection by organic and inorganic absorbers

UV absorbers give protection by absorbing the high-energy radiation in sunlight. According to the Lambert-Beer law, the light absorption of a medium depends largely on the concentration of the UV absorber and the distance that light rays penetrate into the medium. The deeper penetration of the UV radiation, the more effective the absorption, thus increasing the effect of the UV absorbers. The physical-chemical reaction caused by organic absorbers is shown for a 2-hydroxy phenyl benzotriazole in Figure 1. The process, called keto-enol tautomerism, is a continuously repetitive proton transfer which leads to an energy transfer in the form of thermal energy.

Halogenated benzotriazoles are particularly suited for the protection of photosensitive wood. Less energy is required to move the electrons into the excited state. The absorption maximum reaches the area of the visible sunlight ("bathochromic shift"), thus protecting the lignin more efficiently from the damaging effect of this type of radiation.

Special grades of titanium dioxide (TiO₂) may also be used as UV absorbers for transparent coatings. The ability of a pigment to cause scattering not only depends on the refractive index and the wavelength of the light, but also the particle size. Ultra-fine titanium dioxide particles do not scatter visible light, making them suitable for transparent coatings.

The way inorganic UV absorbers work is similar to their organic variants. Energy absorption releases two mobile charged particles, "excitons": the negatively charged electrons in the conduction band, and the positive charge in the valence band. As described for the organic UV absorbers, the UV radiation is absorbed and transformed into thermal energy. However, the chemically inert titanium dioxide does not decompose, thus increasing the long-term stability of the entire system.

It is important to reduce the photo-activity of titanium dioxide, a property which may lead to radical formation. The required photo-stability is achieved by crystal lattice doping of the TiO₂ core with foreign ions (Figure 2). In addition, the surface of the pigment is encapsulated with an inorganic coating consisting of aluminium oxide (Al₂O₃) and/or silica (SiO₂). This makes it possible to modify not only the photo-activity, but also the optical and colloidal properties of the white pigment. Good dispersion of the ultra-fine pigments is achieved by treatment with an additional organic substance.

Experimental

The optimal light stabilisation formula was determined using a waterborne clearcoat based on a styrene-free acrylic emulsion, in which different light stabilisers were dispersed. Table 1 lists its ingredients. The test materials used were all proven products from various manufacturers (Table 2).

UV absorbers

A typical organic UV absorber, o-hydroxyphenyl benzotriazole was tested in two variants: a Cl-substituted crystalline type and an unsubstituted product in liquid form. The crystalline variant was applied as an aqueous emulsion, in which different light stabilisers were dispersed. The two inorganic UV absorbers used were ultra-fine titanium oxides in the rutile modification (both containing more than 99% rutile). They differed mainly in their primary crystal size and doping: Mikronutile 10 nm and Mikronutile 15 nm.

HALS

All of the radical scavengers tested were sterically hindered amines. HALS 1 was at 100% as a liquid; a second product consisted of an 80%-solution HALS 2 in N-methyl-2-pyrrolidone (NMP) and a third, HALS 3, which was photo-reactive was used as an aqueous dispersion. A total of 76 different combinations of these light stabilisers were investigated. Inorganic and organic UV absorbers and HALS were tested individually and in double and triple combinations. An exception was made for HALS compounds, as experience has shown that they do not yield...
sufficient results if they are not combined with an UV absorber. The stabiliser concentration in the coating mixture ranged from 0.5 to 2% wt. of the total formula, with the total amount of stabilisers never exceeding 4%.

Substrates
In order to test different properties, such as elasticity, hardness, transparency and UV absorption, various substrates such as polypropylene, aluminium and glass were coated. Polypropylene was used to measure the UV absorption, transparency, and elasticity of the coating. The aluminium substrate was used for the film thickness and elasticity according to ASTM D522, and DIN 53455 (tensile strength), respectively, and a glass substrate allowed the measurement of hardness according to EN ISO 1522.

Weathering tests
For the weathering tests, pieces of North European pine with the dimensions 7 x 28 cm were coated with products differing stabiliser additives. After drying, the coated panels (dry coating thickness around 40 µm) were exposed to artificial and outdoor weathering.

A “Weather-O-Meter Ci 35” A was used for artificial weathering test according to ISO 11341. The exposure duration was 2,000 hours. The samples were examined every 200 hours. The parameters tested included gloss (20°, 60°), transparency, yellowing (ΔE*), loss of brightness (ΔL*), and reddening (Δa*), as well as an evaluation of the general stability of the coatings.

For outdoor weathering tests, samples were exposed at a weather station 50 km north of Düsseldorf in Germany. Exposures of 9 and 15-months were tested. The above parameters were measured every six weeks. In addition, the wood panels were screened for fouling.

Stabilisers affect the coating viscosity and conductivity
The basic chemical structure of the light stabiliser used can alter the properties of the wet coating. Due to their basic amine function, HALS increase the pH value, thus prompting the resin in the product to behave more like a solution than a dispersion. Consequently, the viscosity of the coating increases, as it is strongly influenced by the molecular weight of the resin.

The addition of both inorganic UV absorbers and dispersed organic stabilisers also cause a viscosity increase. However, this is significantly lower, but still measurable. In both cases, this happens after adding a small amount of finely distributed solids to a liquid.

HALS and dispersed light stabilisers can also increase the specific conductivity, thus modifying the electric resistance of the coating. This can be of crucial importance when coatings are electrostatically sprayed (ESTA).

Mechanical properties are hardly affected
The nature of the inorganic absorber and also the concentration of titanium dioxide have a major influence on the transparency of the coating: the lower the concentration and the smaller the particles, the more transparent the clearcoat. A film thickness of 40 µm and a concentration of roughly 0.75%, Mikro rutile 10 nm does not reduce the transparency of the coating. For Mikrotule 15 nm, the limit is at a lower concentration of 0.5%.

Coatings with organic stabilisers show exceptionally good transparency. This makes them suitable even for the most sophisticated applications.

As expected, when adding crystalline particles, such as ultra-fine titanium dioxide, the coatings become harder and slightly less elastic. HALS or organic UV absorbers lead to a slightly lower hardness, but they do not affect the elasticity of the coating. To sum up, adding light stabilisers barely affects the mechanical properties of the coatings.

Best light stability with inorganic plus organic absorber
The results obtained through artificial and natural weathering were comparable and lead to similar conclusions. Already at a pigment concentration of 0.5%, titanium dioxide shows very good protection. Higher concentrations are more effective, but are less transparent. The direct comparison shows that Mikrotule 10 nm provides a slightly better UV protection and is more transparent than Mikrotule 15 nm, which has a visibly higher brightness due to residual scattering. The optimal concentration to give permanent protection while maintaining optimal transparency is 0.75%.

Figure 3 shows the weathering results after 1,000 hours W0M. The tests revealed that Mikrotule 10 nm is not only more transparent than Mikrotule 15 nm but also has a superior stabilising effect.

The combination of ultra-fine titanium dioxide with a HALS lead neither to visible synergies nor significant improvements of the light stabilisation. Thus, light stabilisation is mainly provided by the inorganic absorber. However, a suitable alternative is the use of inorganic and organic UV absorbers together. This combination offers very good UV protection. Again, Mikrotule 10 nm was evaluated as the best option.

Additional HALS to prevent yellowing
The organic UV absorbers tested create coatings with high transparency, which are not affected by long-term radiation. However, when clearcoats are only stabilised with organic UV absorbers, they show a tendency to yellowing. This can be reduced by adding a HALS - the addition of radical scavengers substantially increases the stability of the coatings. The photos of various samples as shown in Figure 4 confirm this. Additional tests showed that the optimal concentration is at approx. 2 wt.% UV absorber, and 1 to 2 wt.% HALS (on the total formulation and 40 µm thickness of the dry film).

The best results are obtained with a combination of three colourless light stabilisers. Figure 5 shows the permanent stability of the coating. Even after 15 months of outdoor exposure, it remains colourless and transparent. The positive effect of the triple combination comes from the use of the following light stabilisers: ultra-fine TiO2, which by itself provides excellent and permanent UV protection, together with organic UV absorbers and HALS, to give outstanding transparency and colourlessness. This synergy effect is confirmed by the measurement of the yellowing and brightness in relation to the length of the weathering test. Figure 6 shows how the total colour value Δ E changes with ongoing artificial weathering. Based on the current findings, the best light stabilisation for water-based clearcoats is a combination of 0.5% ultra-fine titanium dioxide Mikrotule 10 nm, 1% dispersed HALS, and 1% organic UV absorber in dispersion form (based on the total formulation and 40 µm thickness of the dry film).

Results at a glance
- When coated wood is not sufficiently protected against weathering, considerable damage to it can occur. Inorganic and organic UV absorbers provide effective protection.
- Inorganic UV absorbers can be viewed as most appropriate for exterior use, because they offer the most effective long-term UV protection and do not decompose even under continuous weathering.
- Organic UV absorbers in combination with HALS are the first choice for situations that require utmost transparency.
and brilliance, for example in the furniture industry.
- The highest transparency and brilliance in combination with long-term stabilisation are obtained by using the triple combination of the different light stabilisers. Clearcoats containing these additives are suitable for sophisticated applications and offer UV protection over a long period.
- It is not only solar UV radiation that leads to the decomposition of wood. The radiation of the visible range, which passes through colourless clearcoats, also has a destructive effect on the material, although at a slower pace.
- The addition of light stabilisers cannot completely prevent the photocatalytic decomposition of wood, but it can delay it considerably.

The authors:
-> Angela Classen, Dipl. Ing. (FH) graduated in chemistry from the University of Applied Sciences Niederrhein in Krefeld, Germany. 13 years of experience in the medium-size coatings industry. Joined the Sachtleben Chemie research and development department in 2000, with responsibility for application technology.
-> Dr. Thomas Rentschler studied chemistry at the University of Tübingen, Germany and California Polytechnic State University San Luis Obispo, USA. He received a Ph. D. in 1992. Since 1996 Thomas Rentschler has been working for Sachtleben Chemie GmbH, Since October 2005 he has been working in the business unit functional additives as sales and technical manager in coatings.
-> Karl Bechtold studied synthetic organic chemistry at the Universities of Freiburg (Breisgau) and Würzburg, Germany. He joined Sandoz Huningue S.A. (now Clariant Huningue) in 1990. He runs the coatings application laboratory, with a focus on light stabilisers and "Colourants for wood applications." Since July 2005 he has also been responsible for technical marketing in Japan, Greater China, and some European countries.
-> Gerd Faoro obtained his graduated from University of Applied Sciences Niederrhein in Krefeld, Germany in 1978. He joined Sandoz AG (now Clariant Huningue) in 1991. He is head of application technology of light stabilisers in coatings.
Figure 1: Physical-chemical reactions of UV absorption in organic light stabilisers, shown for 2-hydroxy phenyl benzotriazole
Figure 2: Ultra-fine titanium dioxide is being modified for UV absorption without photocatalytic activity: doping, inorganic and organic coatings. UV absorption triggers the transfer of an electron from the valence band to the conduction band. The absorbed energy is released as harmless radiant heat.
Figure 3: Short-term weathering results after 1000 h WOM, using 0.75 % Mikrorutile 10 nm, or 15 nm, respectively.
Figure 4: Short-term weathering results after 1000 h WOM, using a 1-% organic UV absorber with and without 1-% HALS.
Figure 5: The combination of inorganic, organic UV absorbers with HALS provides optimal protection and transparency, here shown after 15 months of weathering.
Figure 6: Modification of the change of the total colour value $\Delta E$ with extended weathering - the triple combination in direct comparison with artificial weathering of up to 1000 hours WOM.
### Table 1: Basic formulation for a waterborne wood coating, with subsequent addition of light stabilisers

<table>
<thead>
<tr>
<th>Product</th>
<th>Product name</th>
<th>Manufacturer</th>
<th>Amount (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymer dispersion</td>
<td>“Acronal LR 8960”</td>
<td>BASF</td>
<td>67.00</td>
</tr>
<tr>
<td>In-can preservative</td>
<td>“Actizide MBS”</td>
<td>Thor Chemie</td>
<td>0.50</td>
</tr>
<tr>
<td>Silicone tenside</td>
<td>“Byk 346”</td>
<td>Byk Chemie</td>
<td>0.10</td>
</tr>
<tr>
<td>Defoamer</td>
<td>“Tego Foamex 810”</td>
<td>degussa/Tego</td>
<td>0.20</td>
</tr>
<tr>
<td>Neutralizer</td>
<td>“AMP 90”</td>
<td>Dow (Angus Chemie)</td>
<td>0.30</td>
</tr>
<tr>
<td>Associative thickener</td>
<td>“Coatex BR 100P 50%”</td>
<td>Dimed Lackrohstoffe</td>
<td>0.25</td>
</tr>
<tr>
<td>Various solvents</td>
<td>(deionized water, solvent naphtha, butyl diglycol, propylene glycol)</td>
<td></td>
<td>17.10</td>
</tr>
<tr>
<td>Demineralized water for viscosity adjustment</td>
<td></td>
<td></td>
<td>14.55</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>
Inorganic UV absorbers: titanium dioxide (TiO₂)

<table>
<thead>
<tr>
<th>Crystal size</th>
<th>TiO₂ content</th>
<th>Rutile content</th>
<th>Specific surface</th>
<th>Product name</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>~15 nm</td>
<td>~87%</td>
<td>~99%</td>
<td>~70 m²/g</td>
<td>&quot;Hombitec RM 300&quot;</td>
<td>Sachtlieden</td>
</tr>
<tr>
<td>~10 nm</td>
<td>~78%</td>
<td>~99%</td>
<td>~110 m²/g</td>
<td>&quot;Hombitec RM 400&quot;</td>
<td>Sachtlieden</td>
</tr>
</tbody>
</table>

**Organic UV absorbers**

- **Benzotriazole, liquid**
  - Example of product used:
    - "Sanduvor 3311" (Clariant)

- **Benzotriazole, halogenated, crystalline applied as a dispersion**
  - Example of product used:
    - "Sanduvor 3326 disp. XP" (Clariant)

- **Radical scavenger (HALS)**
  - 100% HALS, liquid, organic
    - Example of product used:
      - "Sanduvor 3065 liquid" (Clariant)
  - 80% solution HALS in NMP
    - Example of product used:
      - "Sanduvor 3065 liquid" (Clariant)
  - Photo-reactive HALS, crystalline, applied as a dispersion
    - Example of product used:
      - "Sanduvor PR:31 disp. XP" (Clariant)