Defended from the sun

Optimised use of UV absorbers and HALS in the weathering protection of wood substrates.

A major drawback in the use of wood materials for construction and decorative applications is its sensitivity to light. Coatings are usually used to prevent deterioration of the wood surface. The protection effect depends strongly on the opacity of the coatings, and is particularly difficult for coatings of low opacity, which transmit most radiation. However, optimised use of UV absorbers and HALS both in the coating system and also in a direct wood impregnation step can improve the light stability considerably.

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The popularity of natural wood as an exterior design and construction material would be even greater if significant improvements could be achieved in extending its durability with reduced maintenance work. But under outdoor conditions, weathering causes deterioration of the surface, due to a complex set of reactions induced by factors such as solar radiation, water, temperature and oxygen.

How light degrades wood

Many researchers have shown that ultraviolet (UV) and elements of the visible (VIS) spectrum of solar radiation cause most of the chemical modification and mechanical breakdown of exposed wood. To understand these effects, it is important to understand wood biology and the related mechanisms of photo-oxidation and degradation.

Chemically, wood is a complex biopolymer composed of structural polysaccharides, essentially cellulose as a structural substance, hemicelluloses as a kind of glue and lignin as strength provider. Lignin contains chromophores with aromatic conjugated bond systems and carbonyl groups, and this is why its interaction with light (UV/VIS) in the presence of oxygen is the main cause of wood photo-oxidation.

The lignin undergoes chemical modifications resulting in radical formation and finally decomposition, producing coloured and hydrophilic by-products. The resulting surface property changes lead to discoloration and increased water sensitivity followed by hydrolysis, leaching of the chromophores, and finally erosion and greying of the wood. Today the photo-oxidation of lignin is well understood and at least four degradation pathways have been identified [1].

The key to increasing the service life of wood with film-forming finishes is the optimisation of light protection of the wood surface and the coating. Since the early 1970s it has therefore been common practice to combine UV absorbers (UVA) with hindered amine light stabilizers (HALS).

The chemistry of HALS and UVA

HALS are mainly derivatives of 2,2,6,6-tetramethylpiperidine and help to prevent surface defects such as gloss loss, chalking in pigmented systems and cracking in clear coats. Figure 1 shows the chemical structures of some commercial UVA and HALS products.

The most important HALS compounds are difunctional piperidine derivatives, as shown in Figure 1. Here the substituent on the nitrogen atom determines the properties of the HALS due to basicity. For instance, HALS-1 with R = CH 3 is basic (pK a ~ 5) and interferes with acid catalysed and some air-drying alkyd systems. Therefore, the non-basic aminoether function N-OR, e.g. HALS-2 with R = OC 8 H 17 (its pK a of ~ 10 denotes a much weaker base) has gained wide acceptance in the paint industry, as it has the major advantage of non-interaction with biocides, acidic media and the drying process of acid-catalysed or air-drying systems.

In contrast to HALS, which trap radicals at the surface, UVA filter out the harmful wavelengths of the light spectrum before photochemical reactions can take place, and therefore reduce the rate of radical generation [2]. Today, UVA based on 2-(2-hydroxy-phenyl)-benzotriazole (BTZ) chemistry are considered to be the most important class for stabilisation of clear coats. Commonly used UVA are BTZ-1 for solventborne and BTZ-2 for waterborne applications.

Some limitations of benzotriazole-based UVA have pushed the paint industry to adopt a new UVA class based on 2-hydroxyphenyl-s-triazine (HPT) chemistry [3]. This new class of UVA can be fine-tuned by selective choice of substituent, allowing tailor-made additives to be created for powder [4], high performance automotive, industrial and wood coating applications [5].

For wood, a UVA based on substituted tris-resorcinol triazine (Figure 1, HPT-1) with exceptional photo-permanence and a more pronounced red-shifted absorption was introduced for UV curable systems [6], high performance solventborne [7, 8] and, in encapsulated form, for waterborne wood coating applications [9, 10].

Direct wood pretreatment based on special HALS

As both UV and visible light up to 500 nm causes lignin degradation [11], wood has to be protected from parts of the visible light spectrum. Therefore a new two-step protection strategy was introduced, in which a lignin stabiliser is applied as a dilute pre-treatment solution or in an existing primer formulation directly onto wood and selected UVA (for indoor applications) or UVA/HALS (for outdoors) are used either in the same treatment stage (internal UV filter effect) or preferably in a subsequently applied top coat (external filter effect).

Such lignin stabilising treatments, which improve colour stability in interior applications and long term durability in low opacity exterior wood coatings [12] are based on a special HALS. This traps the radicals formed by visible light at the wood surface, which have not been screened by organic UVA (> 400 nm) [13, 14]. This approach finally allows the use of clear or low-pigmented coatings even in high performance, high durability outdoor applications, e.g. wooden window frames.

Today most of the paints used are semi-transparent finishes, where the pigments may act as partial VIS light protectors. This protection can be increased by combination with organic UVA for substrate protection and HALS for coating protection as well as the lignin stabiliser. It is well known that such combinations of organic and inorganic UV/VIS light screeners show good performance in certain ratios.

The knowledge of how to use this two-step protection strategy is still limited and has to be improved to obtain efficient and economic use of light stabilisers for film-forming wood coating systems according to the shade of the coating, i.e. the degree of pigmentation. It is evident that clear, semi-transparent and opaque coatings behave differently during weathering and therefore require different light stabiliser packages.
Experimental

The effectiveness of various light-protective treatments was evaluated using the following conditions:

Wood samples

Pine (pinus radiata) 200 x 90 x 10 mm with back and end grain sealing with an automotive 2K-PUR clear coat.

Paint system

Linseed long oil alkyd (LOA) with different amounts of transparent black, red and yellow iron oxides plus a white pigmented system (2 x 120 g/m² applied by brush)

Stabilisers

HPT-1 as UVA, HALS-2 (decanedioic acid, bis(2,6,6-tetramethyl-1-(octoxy)-4-piperidinyl) ester) and a lignin stabiliser pre-treatment (2% aqueous solution; 1x 80 g/m² brush applied).

Artificial weathering

Atlas "Weather-Ometer Ci-65 A", Xenon light according to the Xe-WOM CAM 7 cycle for exterior applications (inner & outer borosilicate filter) according to DIN EN ISO 11341 A (0.35 W/m² / 340 nm: 102 min light and 18 min light and spray).

Colour difference measurement

Minolta "CM-3600d" device (gloss included) and calculation of L*, a*, b*, C*, h and $\Delta E^*$ with "CGREC" software according to DIN 6174.

Gloss measurement

60° gloss with Byk/Gardner "Micro-Tri-Gloss" equipment according to DIN 67530.

Cracking

Visually according to DIN EN ISO 4628-4.

UV-VIS spectroscopy

Integrated transmission spectra of 20 µm dry film thickness (DFT) on glass 200 to 800 nm with 1 nm resolution (Perkin Elmer "Lambda 900" UV/VIS/NIR spectrophotometer).

Artificial weathering

The integrated transmission spectra (i.e. their light protection capacity) of different test coatings are shown in Figure 2. Based on the transmission value at 500 nm they can be classified as:
- clear: >90% transmission (LOA-1)
- low pigmented: 90% - 60% (LOA-2, -3)
- medium pigmented: 60% - 30% (LOA-4, -5)
- dark pigmented: 30% - 0% (LOA-6, -7) and
- opaque pigmented: 0% (LOA-8).

Organic light stabilisers, i.e. HPT-1 and HALS-2 and lignin stabilisers pre-treatments were compared. The colour deviation of pine with LOA stabilised with UVA/HALS (0.5% and 1.0% / 0.5% on total paint) with and without lignin stabiliser pre-treatment (2% aqueous solution) after 1000 h Xe-WOM CAM 7 exposure is shown in Figure 3.

Adapting UVA use to the opacity

In the clear, low and medium pigmented finishes the use of UVA alone reduces the colour deviation on pale wood species to a certain extent, with better results for a higher UVA concentration. The visible light screening of the pigment evidently also improves performance. In all cases, the lignin stabiliser system has the best performance.

Dark and opaque systems require HALS

However, it is well known that colour retention is not the main problem for dark and opaque pigmented systems. Earlier studies showed that these tend to suffer more from chalking and then complete erosion of the paint and the wooden surface, whereas clear and low pigmented systems primarily show cracking. In this case higher amounts of HALS are necessary to protect the binder against photo-oxidation and avoid surface defects such as gloss loss, chalking and subsequent flaking [15].

Direct lignin stabilisation yields best performance

The effect of the lignin stabiliser on colour and coating protection of pine with a clear UVA containing top coat after 1 year outdoor exposure is shown in Figure 4. Here LOA-1 pigmented system was applied without (A), but with 1% HPT-1 and 0.5% HALS-2 on total paint (B) and the second coating was applied over 2% aqueous solution of the lignin stabiliser (C). System (A) shows gloss loss, cracking, and erosion with greying of the wood surface. The use of HPT-1 and HALS-2 obviously improves the coating properties but some colour deviation with darkening and yellowing can be seen. The lignin stabiliser further improves the colour retention to almost retain the initial colour of the wood. In general, this approach shows excellent results in colour retention as well as mechanical properties of the paint film for all common pale wood species like pine, fir and ash.

Natural weathering tests

The effect of HALS on the 60° gloss of LOA paints with different degrees of pigmentation after 12 months 45° south exposure in Pfeffingen, Switzerland is shown in Figure 5. The initial 60° gloss was around 30 for all paints. After exposure, paints without HALS had a 60° gloss of around 15. The use of UVA shows only slight improvement for all the paints.

HALS are always beneficial

The use of HALS is beneficial, regardless of whether UVA is used. For the low and medium pigmented paints (LOA-3, LOA-5) the higher levels of HALS have little advantage over the 0.5% addition.

For the dark LOA-6 and the opaque LOA-8, obvious improvements in performance are only obtained by using 1.0% or even 2.0% HALS. These results indicate that the use of higher amounts of HALS is necessary with increasing pigmentation in the paint.

There is no single optimal light stabiliser package

These results show the value of light stabilisers in retaining the mechanical and aesthetic properties of outdoor wood coatings. Unfortunately a single light stabiliser package is not equally suitable for all shades from clear to opaque pigmented systems. But it is possible to give rough guidelines based on the transmission profile of the pigmented paints. In general the concentration of UVA can be reduced and the concentration of HALS should be increased with increasing pigmentation.

For clear paints, higher amounts of an optimum UVA (0.5% to 1% on total paint) have to be used to protect the substrate, with HALS added (0.5%) to protect the coating from surface defects. In addition a solution of 1% to 2%
lignin stabiliser, preferably used in aqueous solution or an existing primer formulation helps to retain aesthetic and mechanical properties.

For light and medium pigmented systems the amount of UVA can be reduced to 0.5% as the pigment itself protects against light, but the amount of HALS should be increased (0.5% to 1.0%). The lignin stabiliser again improves results.

In dark and opaque pigmented systems the UVA and lignin stabiliser add no real benefit to the overall performance of the system as long as sufficient amounts of HALS (1% to 2%) are used to avoid surface defects.

This has to be seen as a basic general guideline for starting point formulations. The benefits may differ according to the quality of the binder system, the solids content of the paint, the quantity and type of the pigments used, the final application and the local weather conditions. Ultimately, it is always the real experiment that tells us the final answer.

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REFERENCES

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Figure 1: Chemical structure of some commercial UVA and HALS products.
Figure 2: Integrated transmission spectra of the LOA paints tested.

Figure 3: Colour deviation of pine with LOA with HPT-1/HALS-2 with and without lignin stabiliser after 1000 h Xe-WOM CAM 7 exposure.

Figure 4: Pine with LOA (A: no additive; B: 1% HPT-1 + 0.5% HALS-2; C: 2% lignin stabiliser pre-treatment / 1% HPT-1 + 0.5% HALS-2) after 1 year 45° south open rack exposure in Pfeffingen, Switzerland.
Figure 5: Effect of the HALS-2 concentration on 60° gloss of LOA paints after 12 months 45° south exposure in Pfeffingen.