

# Light Stabilisers

David Leppard\*, Pascal Hayoz, Thomas Schäfer, Thomas Vogel, and Frédérique Wendeborn

**Abstract:** The degradation pathways for polymeric materials and coatings under the influence of light and oxygen are presented and the consequent need for light-protecting agents (light stabilisers) is discussed. The mechanisms of action of hindered amine light stabilisers and certain UV-absorbers are explained. The use of light stabilisers in photographic-, automotive- and wood-coatings as well as cosmetic applications is described.

**Keywords:** Coatings · Degradation · Hindered amine light stabilisers · Light stabilisers · Quenchers · UV-absorbers

## 1. Introduction

The continuous radiation from the sun (approximately between 1 to 3000 nm) reaching the earth's surface has, after passing the atmospheric layers, an energy spectrum between 290 and 750 nm. The ultra-violet (UV) wavelength part between 290 and 400 nm in combination with the air's oxygen initiates the photo-degradation of exposed natural and synthetic substrates.

Some natural living species have learnt how to deal with this harmful irradiation. The *cyclops abyssorum tatricus* fish, which lives in high mountain lakes and is therefore exposed to an extraordinary high amount of UV-irradiation, protects itself by consuming UV-absorbers present in shinorine plankton [1]. Certain corals, on the other hand, produce their own UV-absorber protecting agents [2].

In synthetic materials the most visible results of photo-oxidative degradation are the deterioration of the exposed material's appearance such as surface crazes, gloss reduction, chalking on the surface, loss of colour or the variation of colour under exposure. Changes in physical-mechanical properties such as loss of

elongation, tensile strength or impact strength also occur. The use of synthetic resins for construction and household applications rose extraordinarily in the sixties and seventies, and the limitations of their technical performance became more visible to the public.

This was the driving force for the industries involved to investigate the different pathways of degradation of polymer products such as polyolefins, engineering plastics and coatings. The knowledge gained in these investigations led to the development of stabilisers, in particular UV-absorbers, free radical scavengers, quenchers and peroxide decomposers.

## 2. Degradation Pathways

Theoretically, pure fully saturated hydrocarbons such as polyolefins do not absorb light in the UV region, and for that reason such polymers should be photostable. In reality, such technical polymers are light sensitive due to photoactive residues, such as trapped polymerisation catalysts.

Such residues act as chromophores (Ch), which absorb UV- and visible-light and are therefore promoted into an excited state (Ch\*). It is usually these excited chromophores which are responsible for photo-degradation of polymers and coatings. They have four different possibilities for energy dissipation (Scheme 1):

- They can return directly to the ground state by fluorescence or radiationless deactivation (heat)

- They can decompose into radicals (R·) which can react with the polymer matrix (P-H) or oxygen (<sup>3</sup>O<sub>2</sub>)
- They can form radicals by hydrogen abstraction from the polymer matrix (P-H)
- They can transfer excited state energy to other molecules (*e.g.* formation of singlet oxygen (<sup>1</sup>O<sub>2</sub>) from ground state oxygen).

## 3. Degradation Prevention

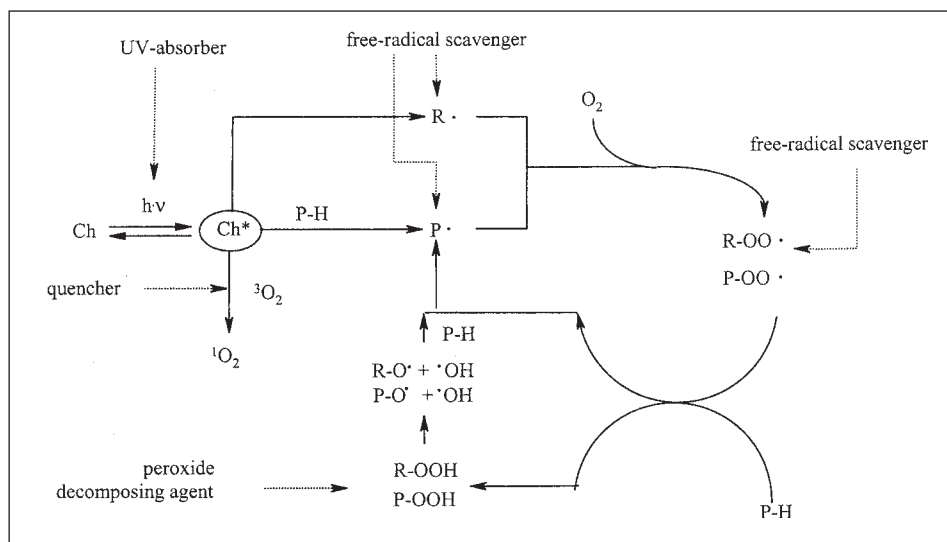
The first approach to prevent degradation is to attempt to filter off the harmful irradiation with suitable absorbers before it can form excited chromophores (Ch\*). If this is not 100% efficient, however, some excited chromophores will nevertheless be formed. Energy acceptor molecules, usually called quenchers (Q), can be used to deactivate these excited species.

If, in spite of these two prevention procedures, carbon-centred radicals are formed, they may be trapped by free radical scavengers.

Free radical scavengers can also destroy peroxide radicals formed in a radical chain mechanism involving ground-state oxygen (see Scheme 1). Peroxide radicals not decomposed by radical scavengers will abstract a hydrogen atom from the polymer or coating matrix to give hydroperoxides. These can be destroyed using peroxide decomposing agents.

The technical properties of these light degradation prevention agents, normally

\*Correspondence: Dr. D. Leppard  
R-1059.6.11  
Ciba Specialty Chemicals Inc.  
Schwarzwaldallee 215  
CH-4002 Basel  
Tel.: +41 61/636 2331  
Fax: +41 61/636 2332  
E-Mail: david.leppard@cibasc.com



Scheme 1. Photo-oxidative polymer degradation and possible protection mechanisms [5]. (Ch: chromophore; P: polymer; .....> protection pathways)

referred to as light stabilisers, are very demanding. They should normally be colourless, light stable, chemically inert towards substrates, thermally stable at high temperatures, non-migrating and efficient for the life-time of the exposed article. They must obviously also have sufficient solubility in certain application media such as coatings systems. Light stabilisers are normally used in concentrations of 0.05–2% of the total mass of the exposed coating or plastic material.

### 3.1. UV-absorbers

The purpose of a UV-absorber is to absorb harmful UV light (250–400 nm) and quickly transform it into harmless heat. When UV-absorbers absorb UV light, they are transformed into an excited state which, by a rapid intramolecular process, is deactivated and returns to its original state accompanied by harmless heat formation. Normally, UV-absorbers should have a high absorption and they should also be very light stable, since they would otherwise be degraded too fast. In general, the preferred absorption band lies, depending on the substrate, between 300 and 400 nm. Additionally, for

most applications, there should be no absorption above 400 nm, since this will lead to a yellowing of the substrate.

#### 3.1.1. UV-absorbers Containing Hydrogen Bridges

The four most common commercial classes of UV-absorbers are oxalanilides (OA), hydroxy-benzophenones (HBP), hydroxyphenyl-benzotriazoles (HBZ) and hydroxyphenyl-s-triazines (HPT) (Fig. 1).

The hydrogen bridge(s) present in all these compound classes has been shown to be responsible for their inherent light

stability. In the case of the oxalanilides this is, however, not unequivocally proven. The absorption spectrum of these four classes can be modified by varying the substituents. The absorption maximum [ $\lambda_{\max}$  (nm)] and extinction coefficient [ $\epsilon$  ( $1 \text{ mol}^{-1} \text{ cm}^{-1}$ )] for some commercial products are given in Fig. 2.

The photophysics of the three 'phenolic' classes will be presented later.

The spectra of these four compounds are shown in Fig. 3.

The hydroxyphenyl-s-triazines have two advantages over the above-men-

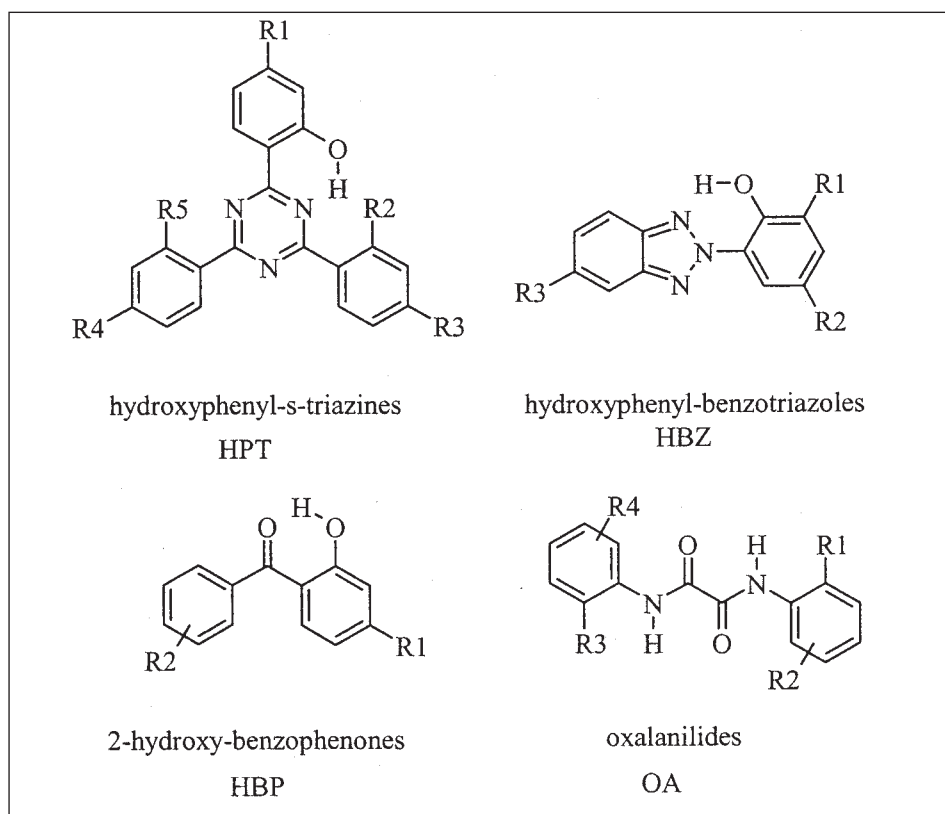


Fig. 1. Common commercial UV-absorber classes

tioned classes. They are generally more light stable and their UV-absorption spectra can be more easily tailored by varying the substituents (and hence electron density) on the aryl groups. For example, by increasing the number of resorcinyl groups on the triazine nucleus, the spectrum can be shifted to longer wavelength. At the same time the extinction coefficient is raised considerably. The spectral characteristics of mono- bis- and tris-resorcinyl-s-triazines are compared in Fig. 4 and 5.

### 3.1.2. Deactivation Mechanism

The intramolecular hydrogen bridge is responsible for the light stability of phenol-substituted UV-absorbers [3]. The mechanism of conversion of the light energy into heat is given for hydroxyphenyl-s-triazines as an example for all the hydrogen-bridged UV-absorbers. During the absorption of UV-light, the hydroxyphenyl-s-triazine is promoted from its first ground state ( $S_0$ ) to its first excited state ( $S_1$ ). In the  $S_1$  state, an intramolecular proton transfer from the phenolic oxygen to the triazine nitrogen takes place. This leads to a new first excited state ( $S_1^{PT}$ ) with a lower energy. The  $S_1^{PT}$  excited state can be written in two mesomeric forms. After a radiationless deactivation the hydroxyphenyl-s-triazine reaches its ground state ( $S_1^{PT_0}$ ). This deactivation is more likely to occur than the  $S_1 \rightarrow S_0$  deactivation, because of the lower energy gap between  $S_1^{PT_1}$  and  $S_1^{PT_0}$ . A proton back transfer from the nitrogen to the oxygen regenerates the triazine UV absorber in its  $S_0$  ground state.

This deactivation mechanism is depicted in Fig. 6.

### 3.1.3. UV-absorbers without Hydrogen Bridges

UV-absorbers without hydrogen bridges are generally compounds which are inherently less light stable but, because of a high absorption per weight, they have found interest in various applications. For example, the requirement of a UV-absorber for colour photographic negative films is to absorb all the UV-light passing through a camera lens during the very short shutter opening. To meet these demands a very high extinction coefficient and absorption as close to 400 nm as possible is mandatory. Compounds such as UV-1 in Fig. 7 are not inherently light stable compared with hydroxy-benzotriazoles *etc.* but they are sufficiently stable for the duration of their short exposure to light, as well as providing an efficient UV-light filter ef-

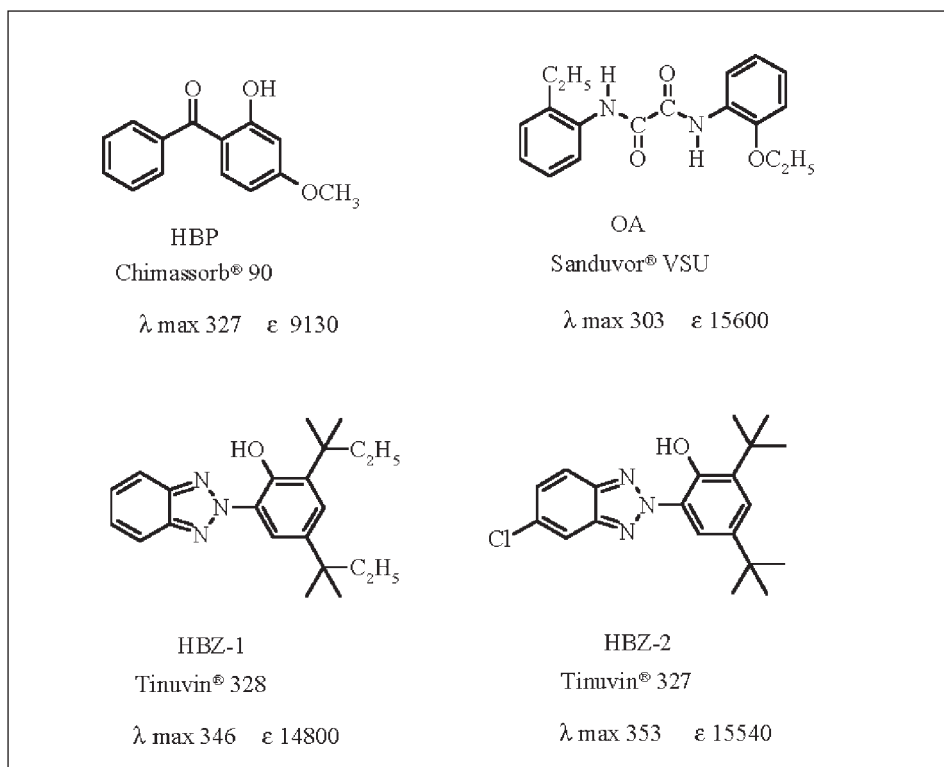


Fig. 2. Spectral characterisation for some commercial products [ $\lambda_{\max}$ ] = nm, [ $\epsilon$ ] = l.mol<sup>-1</sup> cm<sup>-1</sup>

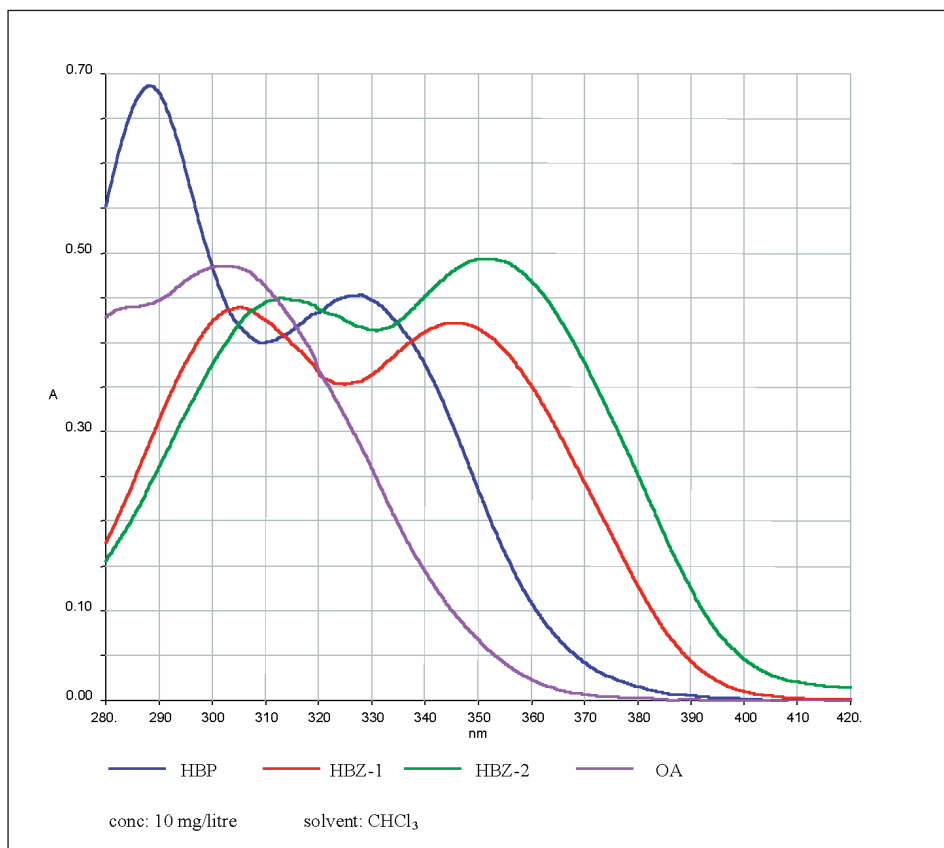


Fig. 3. Absorption spectra of HBP, OAN, HBZ-1, HBZ-2

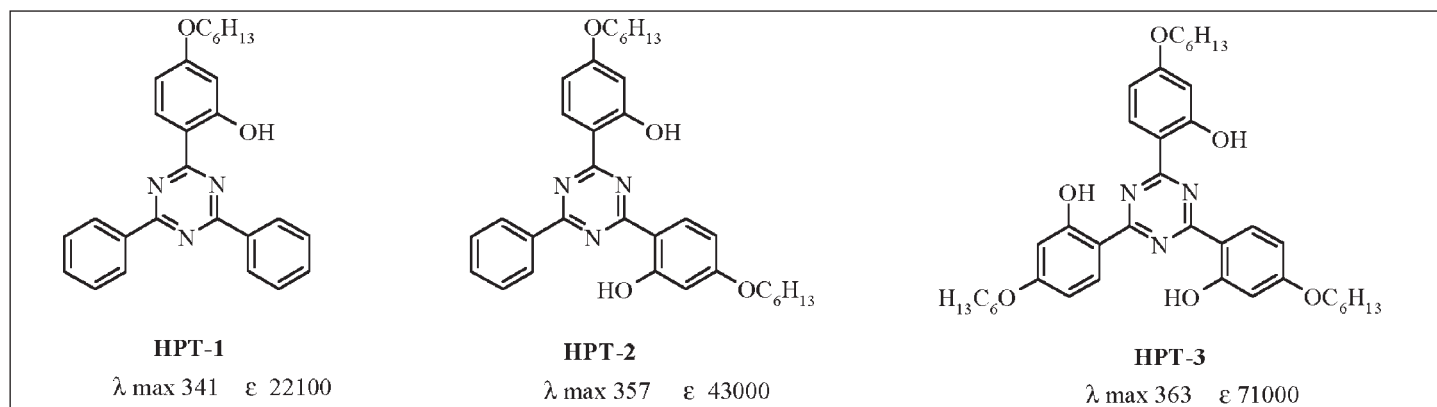


Fig. 4. Comparison of  $\lambda_{\text{max}}$  and  $\epsilon$  for mono-, bis- and tris-resorciny triazines, [ $\lambda_{\text{max}}$ ] = nm, [ $\epsilon$ ] =  $\text{l}\cdot\text{mol}^{-1}\text{cm}^{-1}$

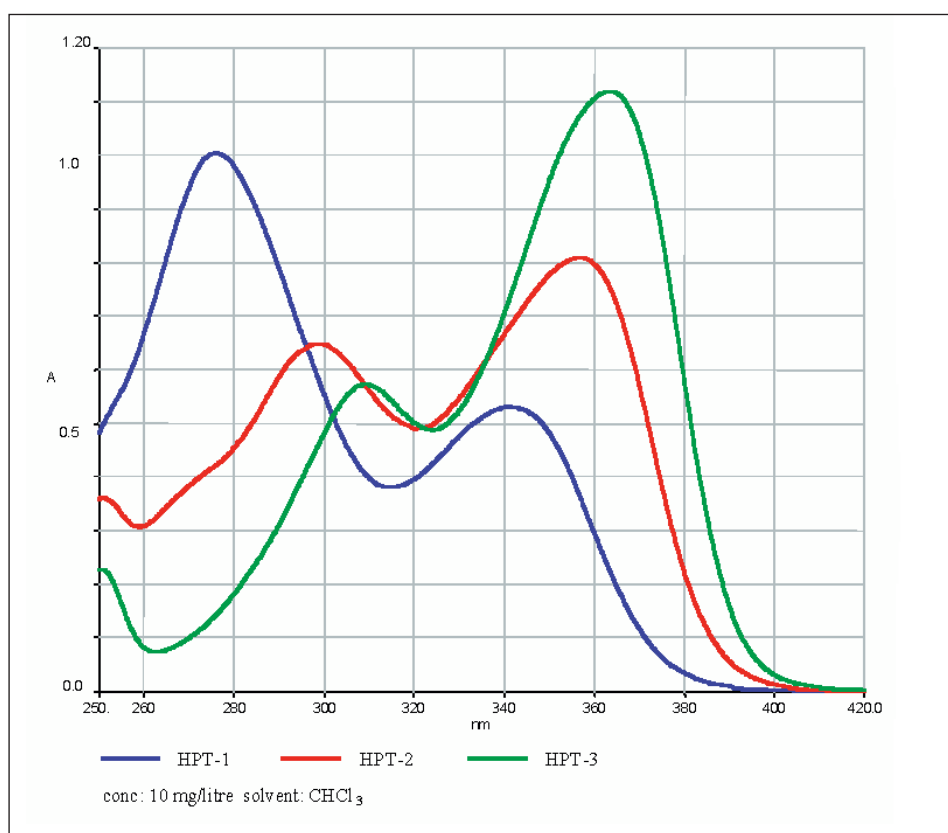


Fig. 5. Absorption spectra of mono- bis- and tris-resorciny-s-triazines

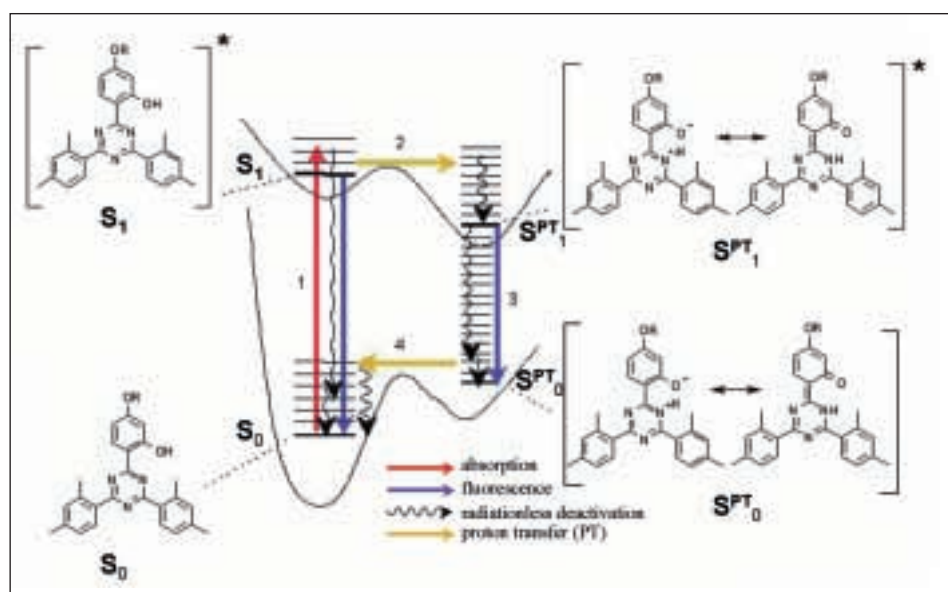


Fig. 6. Deactivation pathways according to Otterstedt [4]

fect. Likewise the four commercial compounds, UV-2, UV-3, UV-4, and UV-5, have also found utility in various applications:

The UV-absorption spectra for the five above-mentioned UV-absorbers are shown in Fig. 8.

### 3.2. HALS

Sterically hindered amines have been used since the early seventies to stabilise resins on a commercial scale. The substances are almost exclusively derivatives of 2,2,6,6-tetramethylpiperidine and are generally referred to as HALS, which is an acronym for *hindered amine light stabilizers*. In working applications HALS are normally used together with UV-absorbers.

The technical requirements of the various HALS classes are very demanding. They should have high exudation-thermal- and photo-stability and very good compatibility with the applications media. Under photo-oxidative exposure conditions HALS are transformed into their corresponding red-coloured active nitroxyl radical. The cyclic mechanism (the Denisov cycle) of HALS radical scavengers is shown below in Scheme 2.

Nitroxyl radicals are only light stable if they have no active hydrogen atoms in the alpha position to the nitroxyl function.

The application requirements determine the basicity of the HALS being used. HALS structures with N-H or N-alkyl groups have basic properties ( $pK_a$  ca. 9) and cannot be used for acid-catalysed cross-linking resin systems. For these systems acylated HALS derivatives and alkoxy substituted (NOR) HALS have been developed. Important commercial examples of HALS are shown in Fig. 9.

### 3.3. Other Quenchers

By absorbing light of appropriate frequency molecules are promoted from their electronic ground state ( $S_0$ ) into their first ( $S_1$ ) or even higher excited states ( $S_n$ ). These deactivate very fast by radiationless decay ( $10^{-13}$ s) to the lowest vibrational ground state of the first excited state ( $S_1$ ). In this state there are at least three deactivation pathways.

- The first pathway, internal conversion, is a radiationless process (emission of heat) bringing the molecule back to  $S_0$ . This deactivation process is harmless to the substrate.
- The second deactivation pathway involves the loss of energy by fluorescence, whereby the molecule returns

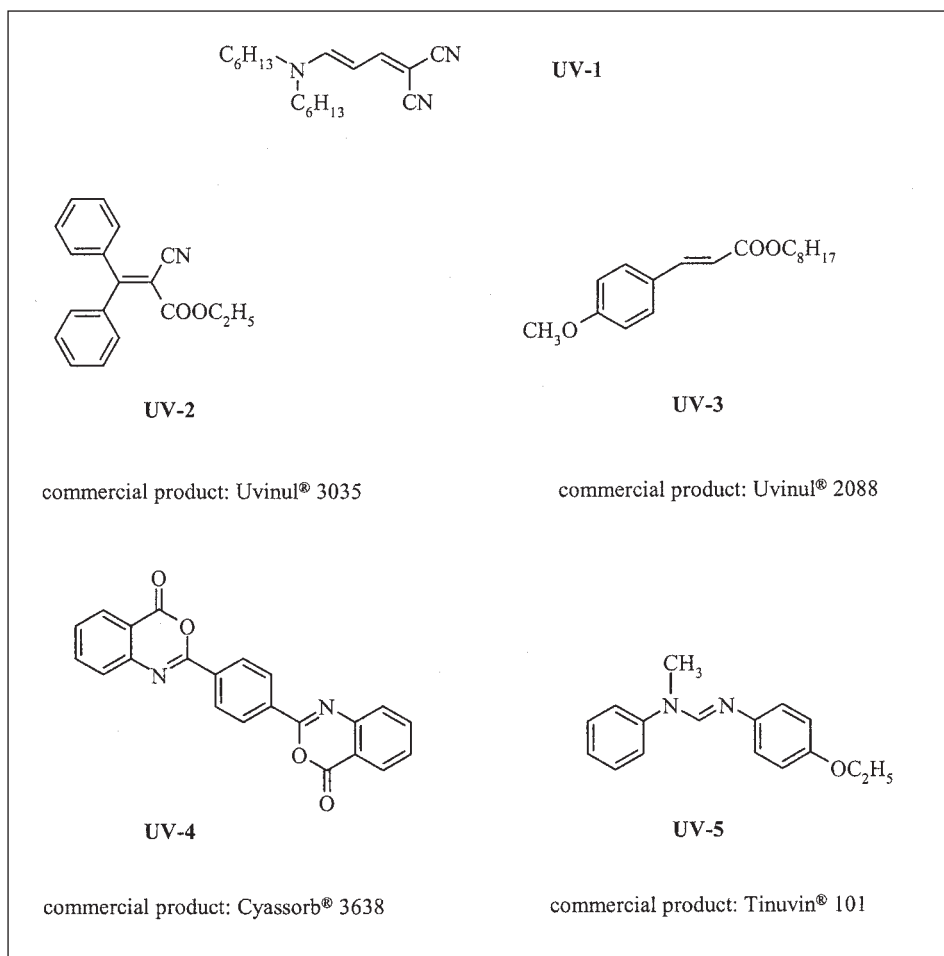


Fig. 7. UV-absorbers containing no H-bridges

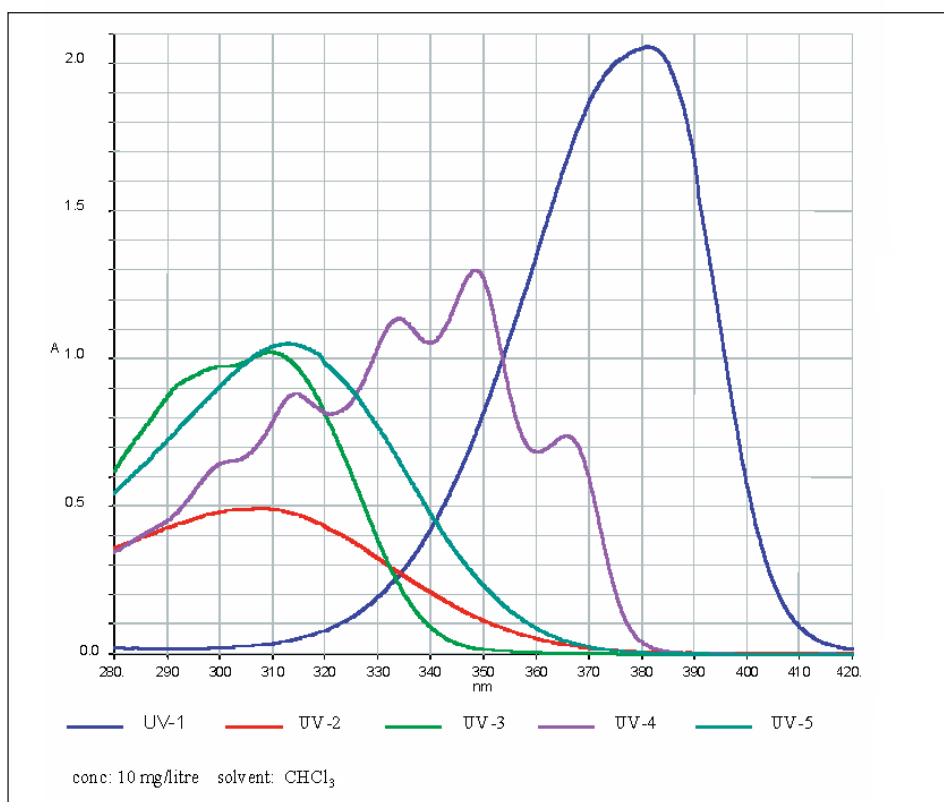


Fig. 8. Absorption spectra of UV-absorbers without H-bridges



to its ground state. This process does not harm the emitting molecule itself, but if the sphere of surrounding molecules absorb this energy, further photochemistry of the new excited molecule may occur.

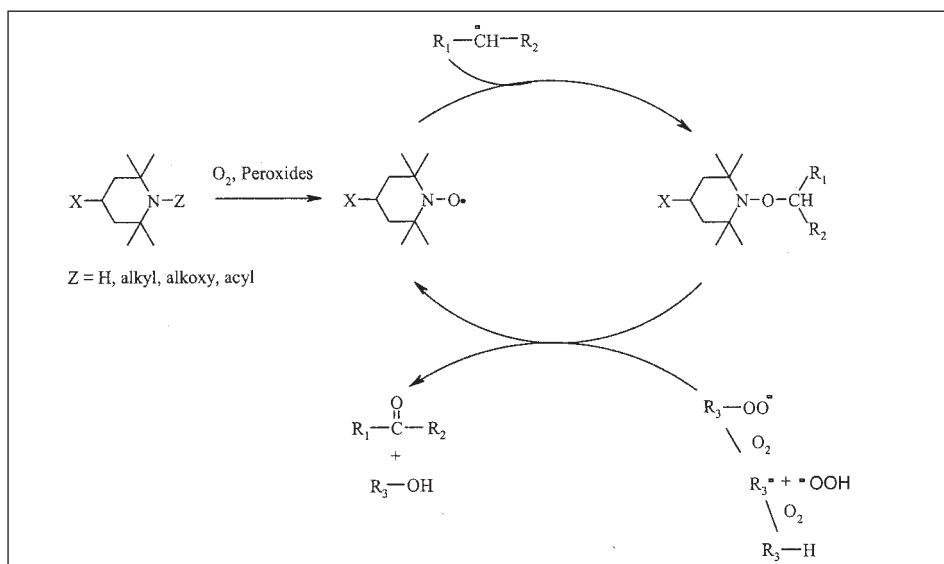
- If the fluorescence quantum yield is less than 100% a third possibility arises.  $S_1$  can either undergo an intersystem crossing into a triplet state or, if a high enough concentration of reaction partner is available, make a chemical reaction. Once the molecule is in its triplet state the life-time, due to spin forbidden conversion processes, is much higher ( $10^{-6}$  to 1s) allowing it to undergo manifold photochemical reactions. An important reaction is the spin-allowed (and therefore very fast) reaction with molecular oxygen in its triplet ground state converting the molecule itself into  $S_0$  and promoting the oxygen into its excited singlet state. The long lifetime of this very reactive singlet oxygen enables it to diffuse to its surrounding molecular sphere where it can undergo oxidation reactions.

### 3.3.1. Singlet Oxygen Quenchers

Singlet oxygen can be deactivated by energy transfer (physical quenching) or by chemical reaction (chemical quenching). To the first class belong DABCO (2,2,2-bicyclo-octane-diamine), heavy metal complexes (*e.g.* nickel-dithio-carbamate) and HALS in their nitroxyl form. Examples of chemical quenchers are furane substituted in the two-position with a diethylaminomethyl substituent, 1,3-diphenylisobenzofurane, polyenes (*e.g.* carotinoids, 2,3-dimethyl-butadiene) and nicotine.

### 3.3.2. Triplet Quenchers

A triplet quencher molecule possesses an energetically lower lying  $T_1$  niveau than that of the excited chromophore ( $Ch^*$ ). For that reason an exothermal radiationless energy transfer from the energetically higher lying  $T_1$  niveau to the  $T_1$  niveau of the quenching molecule can take place. The quenching process is most efficient if the quencher molecule is very close to the excited molecule or is even molecularly linked to it by a short linking unit such as a methylene group. Common triplet quencher molecules are stilbene derivatives, cyclooctatetraene or heavy metal ions (*e.g.* nickel complexes).



Scheme 2. The modified Denisov cycle for HALS radical scavengers

<p><b>NH-HALS:</b></p> <p><b>HALS-1</b></p> <p>Plastics applications</p> <p>Commercial compound:</p> <p>TINUVIN® 770</p>	
<p><b>N-methyl HALS:</b></p> <p><b>HALS-2</b></p> <p>Thermosetting</p> <p>Automotive coating applications</p> <p>Commercial compound:</p> <p>TINUVIN® 292</p>	
<p><b>N-Acyl HALS:</b></p> <p><b>HALS-3</b></p> <p>Thermosetting</p> <p>Automotive coating applications</p> <p>Commercial compound:</p> <p>Sanduvor® 3058 or</p> <p>Cyasorb® UV 3668</p>	
<p><b>NOR-HALS:</b></p> <p><b>HALS-4</b></p> <p>Particularly for acid catalysed thermosetting automotive and coil coating applications</p> <p>Commercial compound:</p> <p>TINUVIN® 123</p>	<p>Ⓢ = isomer mixture</p>

Fig. 9. Important HALS derivatives

## 4. Applications

### 4.1. Photographic Dye Light Stabilisers

A class of light stabilisers, not previously mentioned, find their utility in stabilising the dyes of photographic colour paper. A colour photo is made up of many gelatine layers and is depicted in simplified form in Fig. 10.

Images in colour photographs are made up of combinations of the three dyes, magenta, yellow and cyan. Unfortunately the rate of light fading of these dyes is not the same and this leads to a colour imbalance or distortion. The magenta dye usually fades faster than the other two. The yellow dye is the second weakest and therefore photos will look greenish-blue after exposure to light. In

order to minimise the colour distortion by fading certain electron-rich aromatic ether stabilisers are therefore added to the magenta layer [6]. Others may be added to the yellow. Examples of magenta dye light stabilisers are shown in Fig. 11.

UV-absorbers are incorporated into the protection layer and filter off much of the harmful UV-light. Often a UV-absorber may be added to the cyan layer or even below the cyan layer in the first interlayer.

### 4.2. Automotive Coatings

A typical car surface is represented schematically in Fig. 12.

The clear coat stabilisation against atmospheric influences such as UV-light, moisture, pollutants, *etc.* is achieved by

using a combination of UV-absorber and HALS. The HALS (*e.g.* HALS-2) prevents UV-induced polymer degradation, which otherwise would cause cracking of the clear coat. Non-basic HALS are required, (*e.g.* HALS-4), however, when acid-catalysed systems are applied. The UV-absorber is mainly responsible for the colour retention of the base coat. Examples of the most commonly used UV-absorbers hydroxyphenyl-benzotriazoles (*e.g.* HBZ-3) or hydroxyphenyl-s-triazines (*e.g.* HPT-4) are shown in Fig. 13. The effect of clear-coat stabilisation is shown on model cars in Fig. 14. The non-stabilised car surface shows the typical degradation effect such as loss of gloss and adhesion as well as crazing of the coating surface.

Fig. 10. Simplified cross-section of a colour photograph. The colour blocks depict where dye formation has been developed in the specific layer

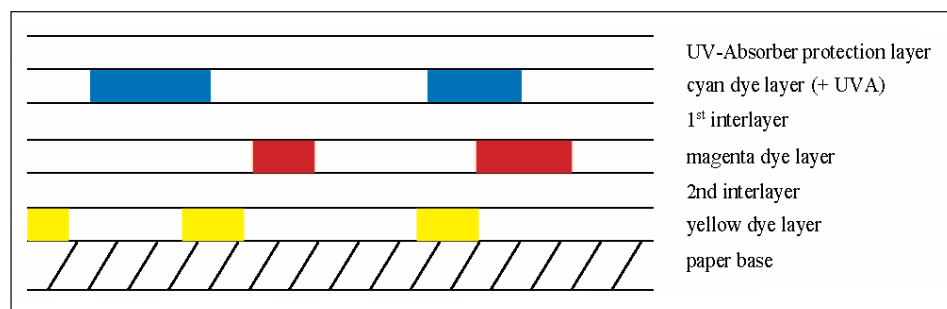


Fig. 11. Examples of light stabilisers for photographic magenta dyes

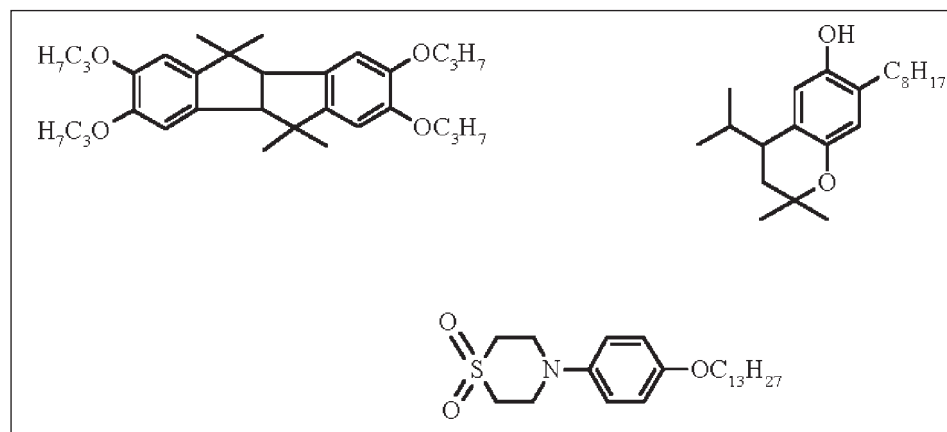
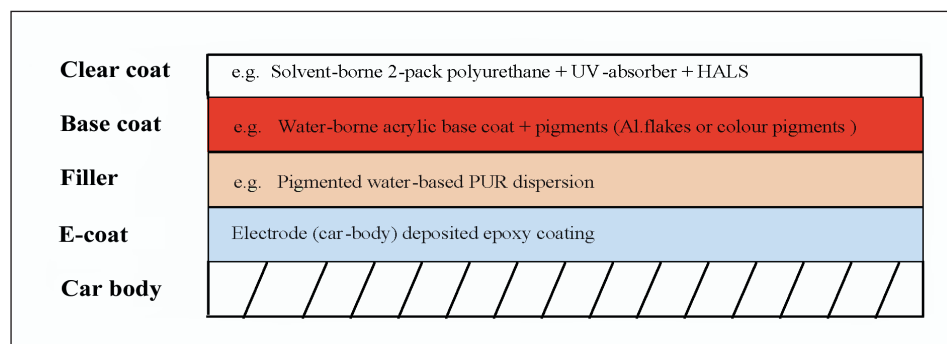


Fig. 12. Example of a cross-section of a car surface



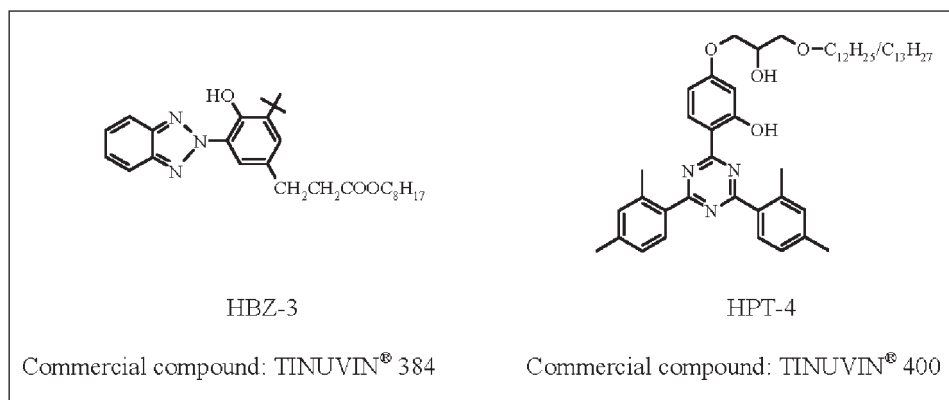


Fig. 13. UV-absorbers used for automotive coatings

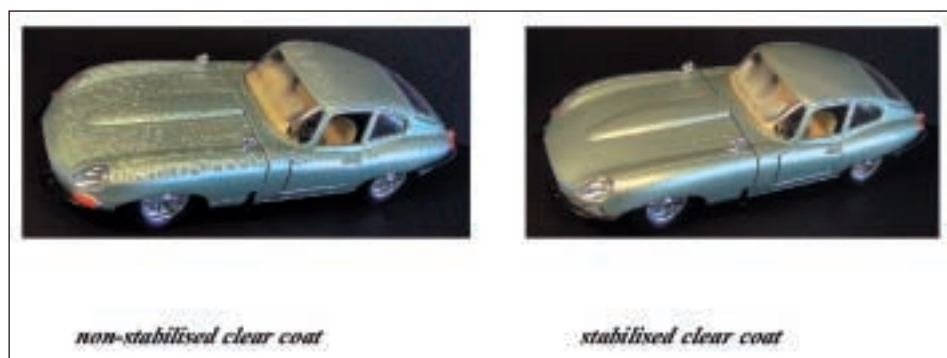


Fig. 14. Model cars demonstrating non-stabilised and stabilised surfaces

### 4.3. Wood Protection

The extreme sensitivity of certain wood components, particularly lignin, to UV-light degradation is the main reason for the rapid colour change of pale wood. The use of UV absorbers reduces the yellowing of the wood significantly and provides long-term stability to transparent and pigmented wood coatings by filtering off the harmful UV light. The addition of a HALS light stabiliser improves surface properties such as gloss and colour retention, as well as protecting the whole paint film against brittleness and loss of adhesion by trapping any free radicals.

The effect of light stabilisers can be seen below in Fig. 15. A clear alkyd var-

nish without and with hydroxy-benzotriazole/HALS, applied on pre-treated pine, was exposed for 24 months in Sydney (45° North) sunlight.

### 4.4. Cosmetic Sun Creams

Of the UV light arriving at the earth's surface it is the short wavelength (high energy) radiation (290–320 nm/UV-B; 5–10% of the entire UV intensity), which is more likely to induce photo-chemical reactions, whereas the long-wave radiations (320–400nm/UV-A; 90–95% of the entire UV intensity) being less reflected by matter, will penetrate deeper into the skin. UV-radiation below 290 nm (UV-C) is removed by the ozone layer. This

wavelength of light/penetration relationship is schematically depicted in Fig. 16.

The deeper penetrating UV-A light stimulates tanning and pigmentation but is also responsible for skin ageing and skin cancers such as melanoma. UV-B radiation stimulates the production of vitamin D, which controls the calcium and phosphorus metabolism. It also affects the epidermal layer of the skin, causing sun-burn (erytherma). Frequent and intense exposure to UV-B light induces lesions in the DNA and suppresses the immune response of the skin. This in turn enhances the risk of mutations, eventually leading to skin cancer and reduces the chance that a malignantly transformed

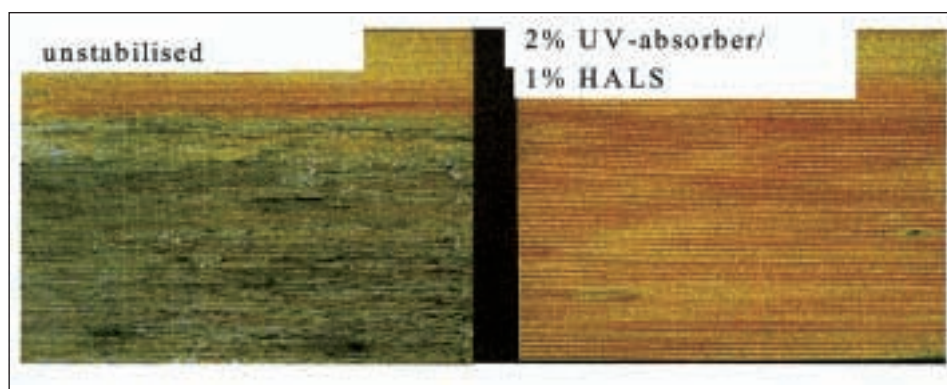


Fig. 15. Unstabilised and stabilised wood surfaces



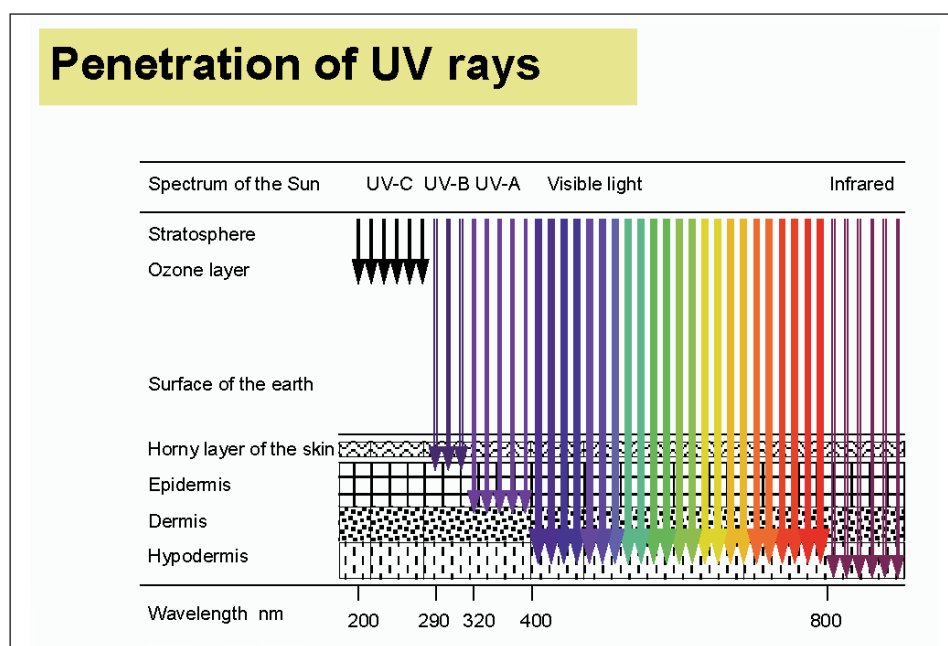


Fig. 16. Penetration of skin by light of various wavelengths

cell is recognised and destroyed. There are three major reasons for the general increase of skin damage occurrence:

- Pale-skinned northern Europeans are migrating into areas (*e.g.* Australia) where there is a greater intensity of UV-light.
- People working indoors (pale skin) are encouraged to participate more and more in outdoor leisure/holiday activities.
- Depletion of the ozone layer.

Sun creams are becoming correspondingly more and more important for skin protection [7]. They contain, among other ingredients, UV-absorbers such as octyl methoxycinnamate, butyl methoxydibenzoyl methane, titanium dioxide, zinc oxide, methylene bis-benzotriazolyl-tetramethylbutylphenol and very recently the triazine UV-absorber, HPT-5 (see Fig. 17).

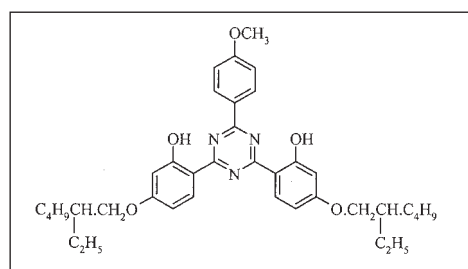


Fig. 17. The first hydroxyphenyl-s-triazine (HPT-5) used in sun cream

## 5. Conclusion

The demand for protection against harmful solar irradiation in coatings, plastics, textiles and cosmetics is very high. The importance of light stabilisers in everyday life is exemplified in various applications, *e.g.* sun creams, photographic-, automotive- and wood-coatings applications. The article 'Additives for Plastic Applications' [8] augments the application areas where light stabilisers are used in industry. The search for new light stabilisers, as well as for new areas of application, is actively ongoing.

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