

SOME ASPECTS OF THE LIGHT PROTECTION OF POLYMERS

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ABSTRACT

Some aspects of the protection of polymers against light degradation are discussed. (1) It is shown that the actually measured efficiency of light stabilizers depends very markedly on the brands of polymers used, on the preparation of the test sample, and on supplementary additives. (2) Two mechanistic conceptions are discussed on how u.v.-absorbers of the *o*-hydroxyphenyl type can dissipate their excitation energy. (3) As experiments show, the efficiency of u.v.-absorbers in thin samples and/or at low concentration cannot be explained by their filtering effect alone. (4) An empirical model is developed for the classification of the spectroscopic properties of u.v.-absorbers. (5) It is shown that the efficiency of esters of 4-hydroxy-3,5-di-*tert*-butylbenzoic acid as light stabilizers is not related to rate or yield of the photo-Fries-rearrangement of these compounds.

1. INTRODUCTION

The breakdown of the properties of polymeric substrates upon light exposure is a very complex phenomenon. Except for polymers especially designed to be highly photosensitive, direct photolytic cleavage of the backbones seems to be a minor cause of the degradation observed in air. This is evidenced by the well known fact that irradiation is much less harmful in an inert atmosphere than in the presence of oxygen¹. Quite often the light exposure acts merely as a trigger of the oxygen induced ageing, observed even in the dark.

Oxygen is known to have at least two major ways of enhancing photo-degradation. One widely observed mechanism is the autoxidation, i.e. the formation of hydroperoxides, the other mechanism is the quenching, i.e. the formation of singlet oxygen. The latter process is somewhat ambiguous in its consequences insofar as the quenching of excited species by oxygen reduces the chances for start-ups of harmful autoxidative chain reactions. Singlet oxygen so produced is on the other hand very reactive and liable to form hydroperoxides also. However, one excited state produces at most one hydroperoxide by the singlet oxygen route; in the autoxidative reaction mode it is by definition the source of many hydroperoxides. From this several possibilities for the light protection of polymers become obvious:

The filtering of light by u.v.-absorbers which can dissipate the absorbed energy in a perfectly innocuous way. This is, however, only practicable for u.v.-light, as coloured filters substantially alter the aspect of the material to be protected. Other limitations will be discussed later.

The quenching of harmful excited states by quenchers which themselves form harmless, i.e. non-reactive excited states. Since such deactivation mechanisms are very specific and demand highly elaborate and laborious methods of investigation, quenchers have only lately entered the arsenal of commercially useful light protective agents.

The breaking of autoxidative chains by antioxidants, which themselves form radicals unable to start up new chains. Antioxidants are the topic of Prof. Scott's and several other papers and will be dealt with only in respect of the interdependence with light protective agents.

The suppression of the harmful effects of hydroperoxides by: (a) metal deactivators or chelators which lessen the catalytic effect of traces of certain metals, and/or (b) peroxide decomposers or synergists which promote a harmless decomposition of peroxides, either by themselves or through their degradation products such as sulphur dioxide.

2. PROBLEMS IN TESTING LIGHT STABILIZERS

More and more it has become clear that a single member of the cited classes of protective compounds alone provides inadequate protection, be it that too high concentrations are needed, which causes other problems, be it that the desired level of protection cannot be reached at all. Today it is the practice in industry to use complex systems to ensure the kind of protection needed in each major application of a particular polymer. For the producer of stabilizers this poses a very difficult problem. The truly scientific investigation of a compound necessitates work in solution and/or supercooled solvent matrices. However, the thus obtainable thermodynamic and kinetic data have not necessarily any bearing on the actual behaviour of this compound in the complex system comprising the polymer, several stabilizers, processing aids and possibly fillers and pigments. What complicates matters even more is the fact that today many, if not most, polymers themselves consist of at least two distinct phases, be it a so-called crystalline and amorphous phase in the chemically homogeneous crystalline polymers like the nylons or polypropylene, be it two amorphous phases in the chemically inhomogeneous polymers of the high impact strength type like ABS resin.

For the above reasons the testing of stabilizers in our laboratories has been dealt with in a very pragmatic way. Most tests bear some or even a close resemblance to the actual end use exposure of the polymer in question. Obviously some kind of acceleration is called for in the early screening. The results of highly accelerated tests, however, have always to be regarded with great caution.

The primary problem is the preparation of a suitable test specimen. There, the first hurdle to take, is the reproducibility of the mechanical and/or electrical properties of these test specimens. Highly crystalline polymers are particularly trying. This is illustrated by the following example. Fibre grade polypropylene was pressed for six minutes at a temperature well above the crystalline melting point to 0.1 mm thick sheets. These were immediately annealed for 60 minutes at 150°C and then air-quenched to room temperature. *Table 1* gives the properties of the resulting test specimens. Thus, not even

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quite extensive annealing can always be counted upon to correct differences in the previous history of a specimen.

Table 1. Properties of pressed polypropylene sheets

Property	Temperature in press	
	200°C	260°C
Aspect of specimen	translucent large crystals	almost perfectly clear very fine crystals
Tensile strength (kg/cm ²)	299 ± 7	290 ± 19
Elongation at break (%)	25 ± 21	997 ± 60

The next example illustrates (*Table 2*) the known and sometimes very marked effect of the molecular weight of one and the same polymer—albeit from two different producers—upon its light stability.

Table 2. Light stability of 0.1 mm polypropylene specimen

[Stabilizer system: 0.5% 2-(2-hydroxy-3,5-di-tert-pentylphenyl)-benzotriazole; 0.2% octadecyl β-(4-hydroxy-3,5-di-tert-butylphenyl)-propionate]

Indicated is the exposure time in a Xenotest-150 to produce 50 per cent loss of the ultimate elongation.

Melt index	19–22	3.2–3.5	1.3–1.4
hours	840	1400	2100

Another complication is the different composition, particularly with respect to trace impurities, of otherwise identical polymers as produced by different producers. So caution has to be exercised in comparing two different brands of polymers.

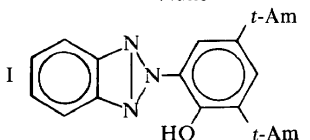
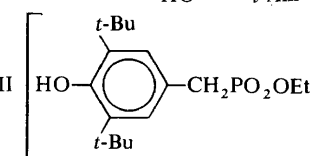
A typical example of what can happen is given in *Table 3*. Otherwise comparable polypropylene samples from two different producers were used in the screening of experimental u.v.-absorbers. Using otherwise identical stabilization, light stabilities in the two polymers were normally identical within the limits of error (Nos. 1–4). In some instances, however, one polymer responded much better to specific light stabilizers (Nos. 5, 6) than the other.

Table 3. Light stability of polypropylene (the time to 50 per cent loss of elongation at break is recorded)

light stabilizer	polymer A h	polymer B h
1	930	855
2	1270	1290
3	1450	1340
4	830	765
5	1400	2100
6	1550	2500

But not only the polymer and the conditions during the preparation of the test specimens are critical. The following example illustrates how important the exact details of the whole testing sequence can be. The light stability of polypropylene containing 0.2 per cent octadecyl β -(4-hydroxy-3,5-di-tert-butylphenyl)-propionate as antioxidant and optionally 0.5 per cent light stabilizer was determined as the time to 50 per cent loss of the ultimate elongation of small probes after light exposure in the Xenotest-150. The tensile-probes were obtained in one of three ways. 0.1 mm thick sheets were pressed for six minutes at 260°C. These sheets were then either quenched to room temperature and the probes were punched out and irradiated (Method A) or else the sheets were annealed for one hour at 150°C. The probes in this case were either punched out directly and irradiated (Method B) or else punched out only after irradiation of the intact sheet (Method C). The results in Table 4 indicate that only method C is useful for the testing of light stabil-

Table 4. Light stability of polypropylene (Conditions see text)

Light stabilizer	Sequence of operations		
	A quenched punched irradiated	B annealed punched irradiated	C annealed irradiated punched
None	200 h	225 h	310 h
I 	260 h	255 h	840 h
II 	Ni 295 h	225 h	830 h

izers. The punching out of the tensile-bars apparently results in surface lesions which lead to failure in the subsequent light exposure independent of the presence of light stabilizers.

3. THE LIGHT STABILITY OF UV-ABSORBERS

Of the known u.v.-filters or u.v.-absorbers the *o*-hydroxybenzophenones and *o*-hydroxyphenylbenzotriazoles are most frequently used in industrial practice. This popularity is based mainly on their extreme light stability in polymeric substrates. Two kinds of explanations have been put forward to explain this striking superiority of the *o*-compounds over their *p*-isomers.

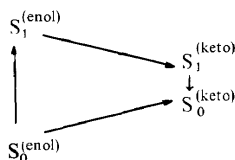
Based upon the observation of an extremely large Stokes-shift of the fluorescence of *o*-hydroxyphenylpyrimidines², Otterstedt attributes the unique

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behaviour of such *o*-hydroxyphenyl systems to the interplay of 'enol'- and 'keto'-forms. In generalized notation they can be formulated as follows:



It is assumed that in the ground state the 'enol' form is energetically preferred, whereas the reverse is true for the first excited singlet. Upon absorption of a photon the following cycle ensues:



Arguments for this viewpoint are the facts that in the excited state phenols become much more acidic, whereas heteroatoms of sp^2 -hybridization become more basic than in the ground state. However, the question remains whether these differences in acidity can account fully for the magnitude of the effect. Also one would expect that the 'keto'-form would be the more preferred, the more basic the heteroatom Y is in the ground state and hence the more light stable is the compound. This extrapolation of the postulated mechanism is, however, at variance with some experimental evidence³.

Furthermore the 'keto'-form—even in the ground state—should be quite vulnerable to attack by a variety of chemicals and since the combined lifetimes of the keto-forms should be appreciable—the establishing of two keto-enol equilibria being involved—the extreme light stability is not self-evident.

In view of the much poorer protective capacity of *o*-hydroxyphenyl-pyrimidines in unsaturated polyester resins as compared to the industrial u.v.-absorbers one critical experiment is missing: nothing is known about the fluorescence of the *o*-hydroxybenzophenones and *o*-hydroxyphenyl-benzotriazoles in the i.r.-region. The observation of such fluorescence would lend much weight to the postulated 'keto-enol'-mechanism.

In another attempt to explain the singularity of the two *o*-hydroxyphenyl classes of u.v.-absorbers it is postulated that the rate of internal conversion from the excited singlet is particularly high⁴. It is speculated that these molecules exist in the ground state in 'perpendicular' and 'coplanar' forms in comparable concentrations. The 'perpendicular' form, i.e. a configuration in which the *o*-hydroxyphenyl group is substantially twisted out of the plane of the benzotriazole nucleus, is favoured sterically and possibly stabilized by the interaction of the lone pair electrons on the 2-nitrogen with the π -system of the hydroxyphenyl group. The 'coplanar' form on the other hand is favoured by resonance between the triazole nucleus and the hydroxyphenyl

group as well as by hydrogen-bonding. Apparently the various effects practically cancel out, so that the *o*-hydroxyphenyl ring can rotate with respect to the triazole ring. Hence a great number of vibrational and rotational levels exist in both the ground and the first excited singlet state which fact accounts for a large Franck-Condon factor. If this picture is right and the further assumption is made that the first absorption band is mostly charge-transfer in nature, the intensity of this first band provides an estimate of the fraction of the 'coplanar' form.

In a preliminary investigation it was found that the integral absorption intensity of the first band of 2-(2-hydroxy-4-methylphenyl)-benzotriazole increases with increasing temperature, whereas the intensities of the second and third band (mainly locally excited transitions of the benzotriazole system) are temperature independent. (All the data were corrected for changes in volume of the solvent.) These changes in intensity of the first band are reversible and are established within the time needed for heating and cooling the samples (for example, five minutes from 80° to 20°C).

The absolute concentration of the 'coplanar' form cannot be determined from the absorption spectrum. But the change in intensity of the first band (six per cent increase from 20° to 80° in isooctane) indicates that the 'perpendicular' form is more stable than the 'coplanar' form by less than 2 kcal/mol. (0.3 kcal/mol is found if the first band is assumed to be a pure charge-transfer transition.)

These results prove that two forms are present in about the same concentration and that the activation energy between them is rather small.

4. SYNERGISM BETWEEN UV-ABSORBERS AND ANTIOXIDANTS

As pointed out earlier, autoxidation is quite often the main contributor to photoinduced degradation of polymers. Interestingly, there exists little correlation between the activity of an antioxidant against pure thermal autoxidation and light injury.

An illustration of this is given in *Figure 1*, the data of which were collected on cold stretched (1:3.5), 5 mil thick polypropylene fibres stabilized with 0.2 per cent antioxidant and 0.5 per cent u.v.-absorber. The irradiated light energy needed to reduce the tensile strength to 75 per cent and 50 per cent of the original value was determined.

While indeed no correlation between the effect of the antioxidants in the oven-ageing and the light stability is found, the ranking of the various antioxidants with two different light stabilizers is, within the limits of error, exactly the same. As the two tests are conducted at widely different temperatures—in polypropylene 147°C is customary for oven tests, while approximately 30°C is common for light stability tests—one contributing factor is the difference in the activation energies of the diffusion coefficients of the various antioxidants. Also different antioxidants might respond to the photogenerated primary radicals differently than to the chain-propagating hydroperoxy radicals.

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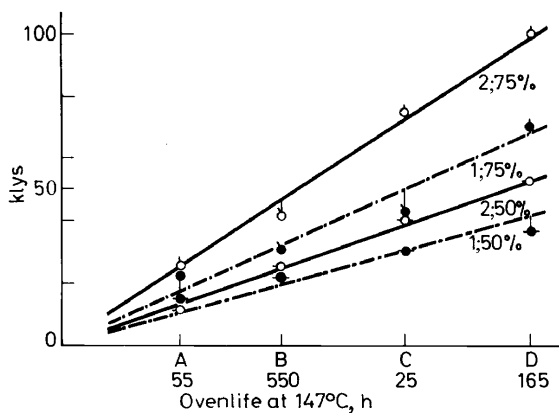
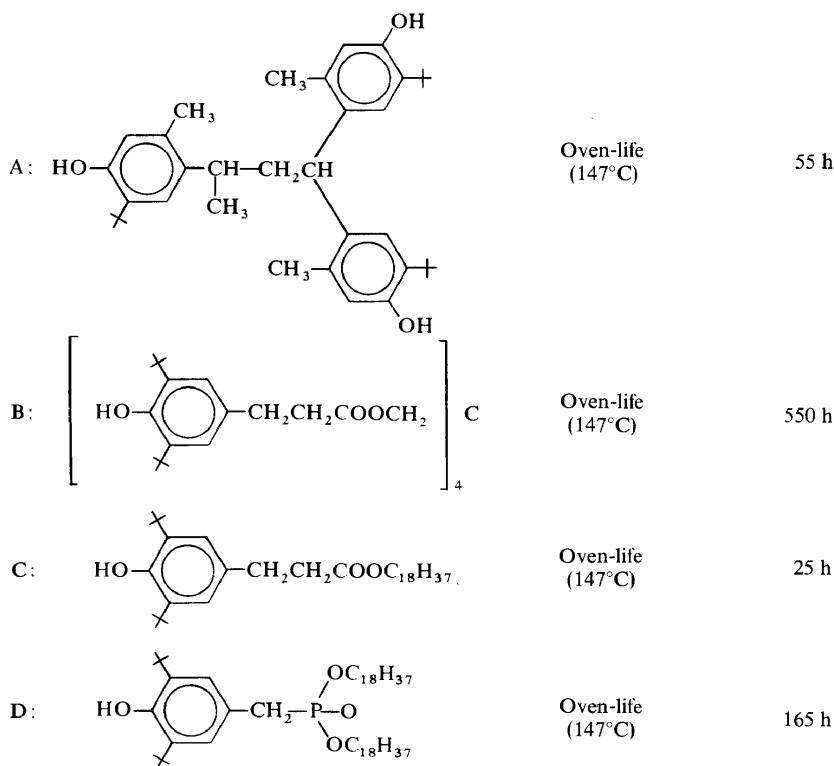


Figure 1. Influence of antioxidants on the light stability of polypropylene monofilaments. Light stabilizers: 1: 2-hydroxy-4-octoxybenzophenone; 2: 2-(2-hydroxy-3,5-di-tert-butyl-phenyl)-5-chlorobenzotriazole.

Antioxidants



(+ denotes a tert-butyl group in these formulae)

For experimental conditions, see text.

5. QUENCHING PROPERTIES OF UV-ABSORBERS

Commercially used u.v.-absorbers can quench the luminescence of carbonyl compounds. This has been demonstrated by Ershov *et al.*⁵ for atactic polypropylene and by Shlyapintokh *et al.*⁶ for chemiluminescent benzophenone in solution.

We have tried to determine the approximate importance of the quenching versus the filtering effect of benzophenones and benzotriazoles under practical conditions. The underlying model is based upon the following assumptions.

- (i) The amount of light absorbed by the substrate to produce a certain effect is independent of the amount of u.v.-absorber present, other variables being kept constant, and
- (ii) The quantum yield of degradation is—within the frequency range of the irradiation source and the absorption of the substrate—independent of the wavelength and the absolute intensity of the incident light.

This leads to the following formula for the protection by a pure filter effect of a light stabilizer :

$$f = \frac{E_F}{E_0} = \frac{D_{\text{tot}} - D_F}{D_{\text{tot}}} \frac{A_{\text{tot}}}{A_0} = \frac{1}{R_s} \quad (1)$$

where f is the protective factor. E is the total light energy (klys) with which the sample is irradiated in order to produce a given mechanical, electrical or optical effect; the subscript F (0) denotes a sample with (without) u.v.-filtering stabilizer. D_{tot} is the optical density of the sample with stabilizer and D_F is the optical density due solely to the stabilizer in the sample. A stands for absorption, $A_{\text{tot}} = 1 - 10^{-D_{\text{tot}}}$ and $A_0 = 1 - 10^{-(D_{\text{tot}} - D_F)}$. This notation has been used to account for possible light absorption of the degradation products.

Obviously E can also stand for a time, if the light source is of constant light intensity or an effect, if the latter is linear with time.

If the optical density of the substrate (or the sensitizer in the substrate) and the one of the degradation products is very small, as compared to D_F , formula 1 can be reduced to⁷:

$$f = \frac{E_F}{E_0} = \frac{A_{\text{tot}}}{D_{\text{tot}}} \log e = 0.4343 \frac{1 - 10^{-D_F}}{D_F} = \frac{1}{L_s} \quad (2)$$

The model according to equations 1 and 2 would be absolute if monochromatic light were used for degradation experiments. In order to produce measurable degradations in technically interesting samples, however, high light intensities are needed, a fact which precludes the use of monochromatic light.

Average D_F and D_{tot} (and the corresponding A -values) have therefore to be determined. They depend upon the light source and the polymer and are calculated from one experimental point, the protective factor (f) of which can be assumed to arise solely or overwhelmingly from a pure filtering effect of the stabilizer. Such experimental points correspond to very high stabilizer concentrations and/or very thick samples.

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If no such point is available, the one with the highest share of filtering effect is chosen, but then only a lower limit of the quenching effect can be estimated.

Two such experiments, both of preliminary character, have been carried out to test the one parametric model. In the first of these experiments the light stability of polypropylene test specimens of varying thickness (fibres, films and plaques) but otherwise identical stabilization and heat history was studied. Three different light stabilizers were used and the average \bar{D}_F -values (\bar{D}_F) were calculated from the thickest plaques. For stabilizer 1 (2-hydroxy-4-octoxybenzophenone) a \bar{D}_F of 1.5 was calculated, which corresponds to an average absorptivity of 10 [whereas the peak absorptivities are 33.3 (327 nm) and 48.2 (289 nm)]. For stabilizer 2 [2-(2-hydroxy-3,5-di-tert-butylphenyl)-5-chlorobenzotriazole] an average optical density \bar{D}_F of 1.9 corresponding to an average absorptivity of 13 was determined. The absorptivities at the maxima are 44.4 (351 nm) and 40.6 (312 nm). For stabilizer 3 (nickel salt of monobutyl-4-hydroxy-3,5-di-tert-butylbenzylphosphonate) no \bar{D}_F was calculated, as this stabilizer absorbs very little in the longwave u.v. and is considered to be a typical quencher. From the above \bar{D}_F values the protective factors expected on the basis of a pure filter effect of stabilizers 1 and 2 were calculated as a function of the sample thickness. These values correspond to the heavy lines in *Figure 2*.

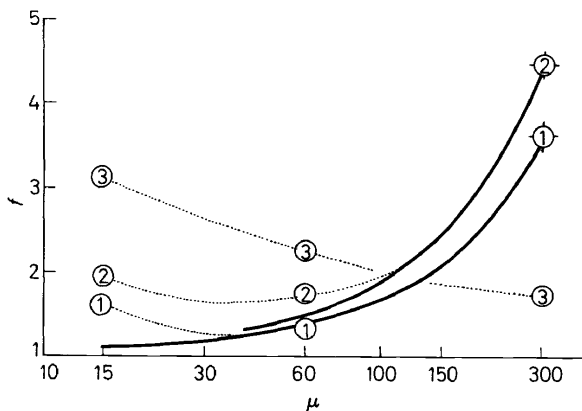


Figure 2. Protective factors in polypropylene as function of the sample thickness (in μ): 1: 2-hydroxy-4-octoxybenzophenone (0.5%); 2: 2-(2-hydroxy-3,5-di-tert-butylphenyl)-5-chlorobenzotriazole (0.5%); 3: Nickel salt of monobutyl 4-hydroxy-3,5-di-tert-butylbenzylphosphonate (0.5%).

The protective factors actually observed are indicated by the numbered circles, which are connected by the thin dotted lines. It is obvious that both stabilizers offer a higher protection in thinner samples than would be expected on the basis of a pure filter effect and it is logical to attribute this effect to the quenching capacity of the benzophenone and benzotriazole u.v.-absorbers.

As it is very difficult to obtain polypropylene samples of different thickness but exactly identical degrees of crystallinity and orientation, the observed effects are only qualitative in nature and cannot be used for quantitative purposes.

The second of these experiments to check for quenching capabilities of u.v.-absorbers in polymeric substrates is based upon the well known yellowing of chlorinated polyester resins. The yellow colour which develops as a consequence of polymer degradation has itself a protective power and retards further degradation. This renders the computations somewhat cumbersome, so the average optical density of the unstabilized polymer (D_p) and of the degradation product (\bar{D}_g) had to be determined from the action spectrum (absorption \times source intensity). It was then assumed that \bar{D}_p was the same in all the samples of the same thickness. \bar{D}_F was calculated from the protective factor of the thickest plaque (6.3 mm) at the highest concentration of u.v.-absorber (0.5 per cent). The self-protecting effect of the degradation products is much smaller in stabilized than in unstabilized samples. So the protective factors were determined and calculated for an irradiation time of 200 hours. In *Table 5* the measured R_s -values (reciprocal of the protective factor) are compared with those calculated by equation 1. This example also indicates the quenching properties of u.v.-absorbers.

Table 5. The measured R_s -values after 200 h of irradiation and those calculated by equation 1. (Measurements on 1.25 mm thick plaques of Polylyte X-133-Z). Stabilizers used:

A = 2-(2-Hydroxy-5-methylphenyl)-benzotriazole;
B = 2-Hydroxy-4-octoxybenzophenone

Stabilizer	Concentration (%)	R_s (meas.)	R_s (calc.)
A	0.1	12 \pm 1	6.5
	0.25	19 \pm 1.5	15
	0.5	31 \pm 2.5	30
B	0.1	5 \pm 1	3.5
	0.25	8.5 \pm 1	8
	0.5	17 \pm 1.5	16

6. THE LONG WAVELENGTH ABSORPTION OF UV-ABSORBERS

Theoretically no simple mathematical description of absorption curves is to be expected. Purely empirical curve-fitting, however, has often been tried. For nearly symmetrical absorption curves the Gaussian normal distribution curve has attained some popularity in the u.v.-field much more so than the Lorentz function. On closer inspection, however, both these two parametric curves fail to describe actual absorption curves. A typical example is the absorption curve of dimethyl *p*-methoxybenzalmalonate as depicted in *Figure 3*.

On account of the asymmetry of the absorption curve the Gaussian curve marked in can only describe a small sector. Such behaviour is quite common and in general the precise mathematical description of whole peaks is very difficult.

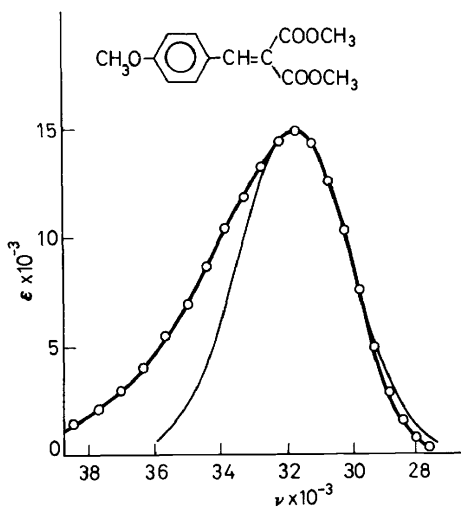


Figure 3. Spectrum of dimethyl *p*-methoxybenzmalonate in chloroform. For explanation, see text.

The long wavelength tail-end of an absorption band, on the other hand, is frequently easy to describe. As illustrated in *Figures 4* and *5* $\log \epsilon$ of the long wavelength branch of the curve approaches a straight line asymptotically. It is further seen that the fit is somewhat better in a plot versus wavelength than versus frequency. That this is not an isolated phenomenon is shown in *Figure 6*, in which the long wavelength part of two commercial u.v.-absorbers is shown in a plot of $\log a$ versus λ . The accuracy of the linear relationship is approximately ± 1.5 nm in the range of square densities of 0.25 g/m² to 50 g/m² (square density = concentration \times thickness of layer).

In order to test the applicability of this rule of linearity, a large number of compounds have been investigated. In most cases linearity of $\log a$ versus the wavelength is found between $\log a$ values of about -2 up to close to $+1$. So far we have no measurements taken in the $\log a$ region below -2 as such measurements necessitate high concentrations of u.v.-absorbers and demand a very high degree of purity of compounds. Conversely the deviation from linearity is often a very sensitive method of detecting impurities.

In some cases, however, broken lines are obtained, indicating the presence of a rest-absorption, possibly some weak $n \rightarrow \pi^*$ -transition normally hidden under a dominating $\pi \rightarrow \pi^*$ -absorption.

An illustration of the variety is given in *Figure 7*. The difference between the short wavelength absorbing u.v.-filters for cosmetic purposes (Nos. 1, 2, 3) and the long wavelength absorbing industrial u.v.-filters (Nos. 4 to 10 inclusive) is seen clearly.

In practical usage only this very tail-end of the absorption curve, which is linear in its logarithmic form, determines the optical quality and the filtering capacity of an u.v.-absorber. This is illustrated by the transmission curves of *Figure 8*, of which the logarithmic plot appears in *Figure 6* below. Absorber

1 which is characterized by a straight line of a lower gradient in *Figure 6* produces distinctly yellow solutions at a square density of 100 g/m^2 . In *Figure 8* this is visualized with the help of the circle (86 per cent transmission at 420 nm). If a steep monotopic rise of the transmission curve is presumed, an object is the more yellow the further below this circle its transmission curve passes. Absorber 2, with a steeper gradient in *Figure 6* and whose transmission curve passes through the circle in *Figure 8* yields practically colourless solutions at a square density of 100 g/m^2 .

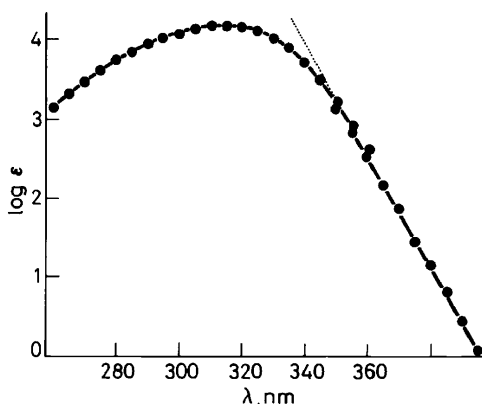


Figure 4. $\log \epsilon$ of dimethyl *p*-methoxybenzalmalonate (Solvent: chloroform).

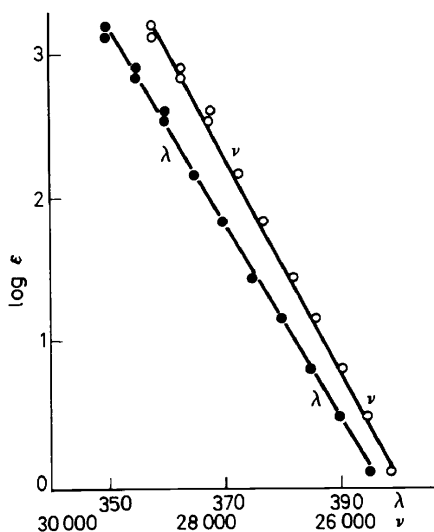


Figure 5. $\log \epsilon$ of dimethyl *p*-methoxybenzalmalonate versus wavelength and frequency. (Solvent: chloroform).

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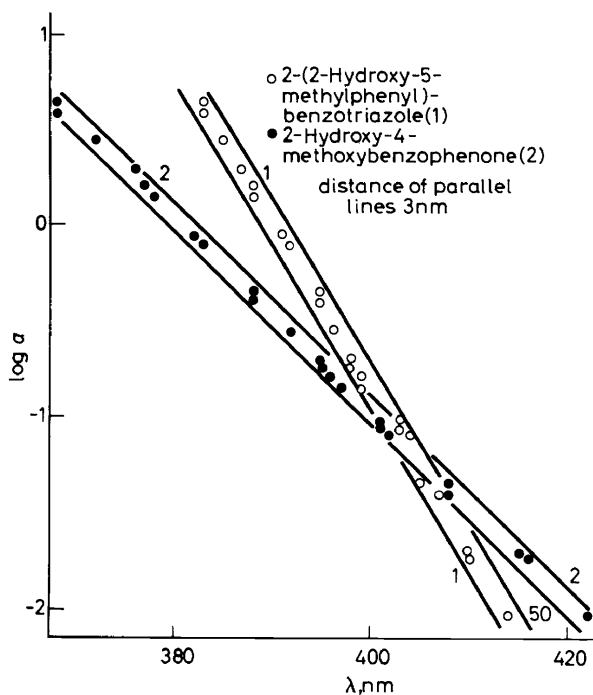


Figure 6. Long wavelength absorption in chloroform of 2-hydroxy-4-methoxybenzophenone (2) and 2-(2-hydroxy-5-methylphenyl)-benzotriazole (1).

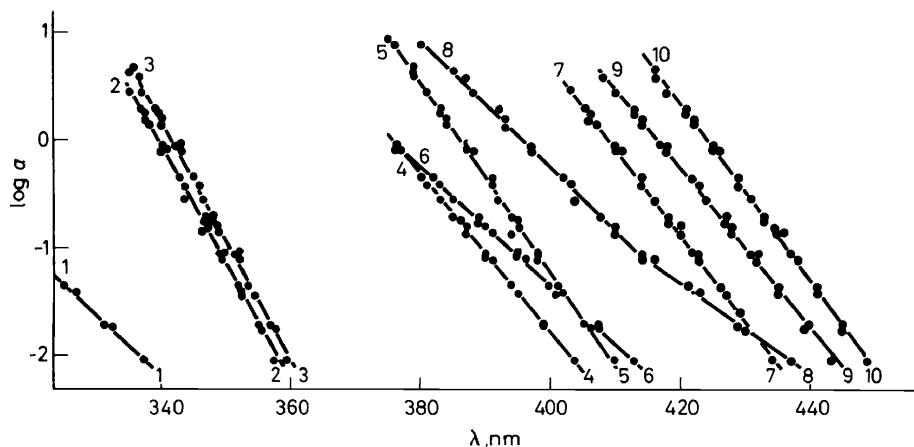


Figure 7. Log α values of various classes of u.v.-filters. Benzoates (1). Salicylates (2,3). α -Cyanocinnamates (4, 6). 2-(2-hydroxyphenyl)-benzotriazoles (5, 7, 9). 2,4-bis-(2-hydroxyphenyl)-s-triazines (8). Azocompounds (10). All values were measured in chloroform.

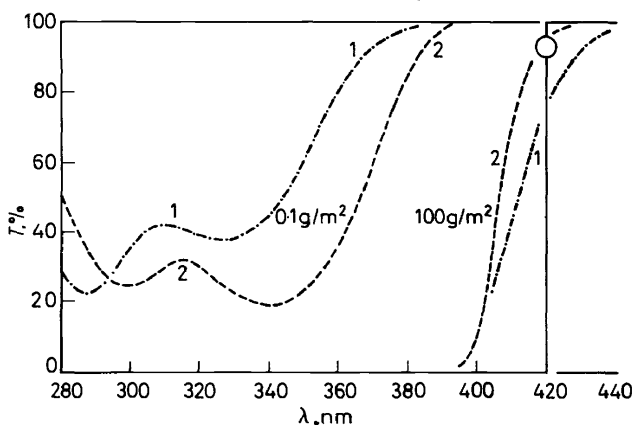


Figure 8. The transmission-curves of 2-hydroxy-4-methoxy-benzophenone (1) and 2-(2-hydroxy-5-methylphenyl)-benzotriazole (2). (Solvent: chloroform).

At low square densities, however, absorber 1 is a distinctly poorer u.v.-filter than absorber 2, its transmission curve being shifted to much shorter wavelengths.

From this the general conclusion can be drawn that an u.v.-absorber is the better a filter the steeper is the gradient of the straight line of the logarithmic plot of the long wavelength tail-end of its absorption curve. This can be quantified easily:

$$\log a = (g - \lambda)/s - 1 \quad (3)$$

a denoting the absorptivity, s the 'steepness'* and g the 'applicational limit of absorption'. The latter is defined arbitrarily as the wavelength at which a is 0.1 which corresponds in practice to the utmost limit at which an absorber is useful.

Combination of equation 3 with the law of Beer-Lambert yields

$$T = 10^{-10^{-\frac{1}{s}(\lambda + s - g) - \log \delta}} \quad (4)$$

wherein δ stands for the square density. Differentiation yields

$$dT/d\lambda = -(\ln 10/s)T \ln T \quad (5)$$

This expression depends explicitly only on the 'steepness' and the transmission itself. Accordingly, for one compound, i.e. for constant s , all transmission curves have to be parallel at high square densities for which the linearity of $\log a$ holds.

As illustrated in Figure 9, this is really the case. At long wavelengths the transmission curves are equidistant and a change in the square density by a factor of ten produces a shift of the curve by the exact amount of the 'steepness' s .

* The steepness in this definition is reciprocal to the gradient discussed above. Hence the smaller s is, the more favourable is the u.v.-absorber for filtering purposes.

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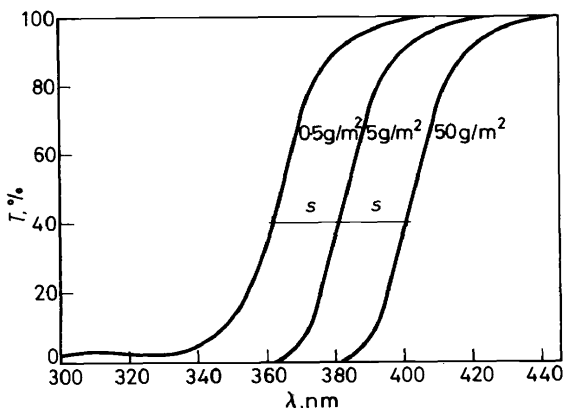


Figure 9. The transmission-curves of 2-hydroxy-4-octoxy-benzophenone at different concentrations (Solvent: chloroform).

Thus the ‘steepness’ s and the ‘applicational absorption limit’ g are essential characteristics of an u.v.-absorber coming close in practical importance to the value of the maxima.

In order to be able to determine these characteristics in a simple manner from transmission curves, a normalization is indicated.

With
$$\bar{\lambda} = (\lambda + s - g)/s - \log \delta \tag{6}$$

the normalized transmission curve is obtained

$$T = 10^{-10^{-\bar{\lambda}}} \tag{7}$$

which is graphically represented in Figure 10. A table of $\bar{\lambda}$ as a function of

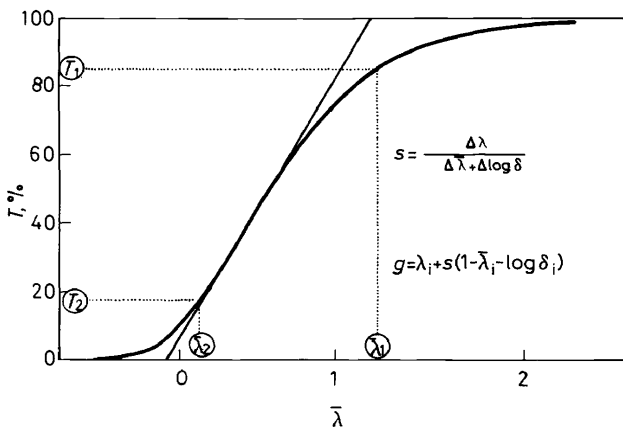


Figure 10. The normalized transmission curve.

T (in per cent) is given in the appendix. The practical use of this concept is simple. For two convenient transmission values the wavelengths on two transmission curves are determined.

Using the $\bar{\lambda}$ values according to *Figure 10* or the table in the appendix, s and g are then calculated from the expressions:

$$s = \frac{\lambda_1 - \lambda_2}{\bar{\lambda}_1 - \bar{\lambda}_2 + \log \delta_1 - \log \delta_2} \quad (8a)$$

$$g = \lambda_i + s(1 - \bar{\lambda}_i - \log \delta_i) \quad (8b)$$

An example is found in the appendix.

The 'steepness' s and the 'applicational limit of absorption' g of some u.v.-absorbers are given in *Figure 11*. It is seen that the two spectral characteristics of one class of compounds are markedly influenced by substituents; however, the differences between the various classes of compounds clearly surpass these variations.

The substituted cinnamates offer applicational limits of absorption at the shortest wavelengths. Correspondingly, these compounds are only used in special applications in which absolute insensitivity towards base and metal ions is required.

The two most popular u.v.-absorber systems—the *o*-hydroxybenzophenones and *o*-hydroxyphenylbenzotriazoles—exhibit applicational limits of absorption in the middle range, i.e. approximately from 400 to 430 nm. On average, the benzotriazoles show a much smaller, i.e. more favourable, 'steepness' s than the benzophenones. The absorption of the latter compounds is much more sensitive to the square density, i.e. to changes in concentration and/or thickness of layer.

The *s*-triazines and particularly the hydroxy-xanthenes and azo compounds derived from activated methylene compounds have their applicational limit of absorption at very long wavelengths. Generally they are suitable in substrates which are very sensitive in the long wavelength region of the u.v.-spectrum. Accordingly they provoke in thicker layers a distinct yellow discoloration.

In the benzotriazole series, for which most data are available, we find quite reproducible substituent effects. The replacement of a hydrogen by a chlorine in the 5-position results in a shift of the applicational limit of absorption to longer wavelengths by about 7 to 8 nm while the steepness is hardly affected. The kind of alkyl group in the 5'-position is relatively unimportant; changing from a methyl- to a tert-butyl-group lowers the applicational limit of absorption by 1 to 2 nm, and the steepness is again unchanged within the limit of error. On the other hand the two spectral characteristics are very sensitive to changes in substitution in the 3'-position, e.g. the replacement of hydrogen by a tert-butyl group results in an increase of the applicational limit of absorption by 11–12 nm and of the steepness by 1 to 2 nm. It is quite interesting to note that the effects—chlorine in 5-position and *t*-butyl group in 3'-position—are additive within the limits of error.

In view of these regularities and particularly the possibilities to classify u.v.-absorbers with respect to their filtering properties in the long wavelength

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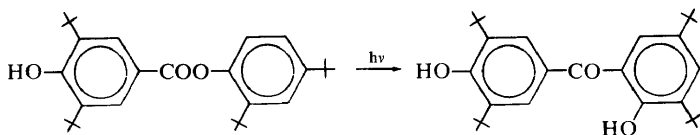
R_p R_m	Cl	Me	Me	Me	t -Bu	t -Bu	t -Bu	t -Am	Me
	H	H	Me	Me	H	H	H	H	H
R_o	H	H	t -Bu					t -Am	$CH_2N \begin{matrix} \diagup \\ \diagdown \end{matrix} \begin{matrix} CO \\ R \end{matrix}$
X	H	H	SO ₂ Et	H	H	Cl	COOH	H	H
g	397	402	430	413	400	407	430	414	405
s	11.5	11.5	14.2	13.3	11.9	11.8	13.7	13.1	13.0
R_1	H	H	H	Cl	OH	OH	OMe		
R_2	H	H	H	Cl	Cl	Cl	Me		
R_3	Me	Me	Oct	Me	Me	Me	Oct		
g	400	400	398	391	426	426	424		
s	19.5	19.5	19.5	17.3	17.2	17.2	17.3		
	R	H	H	Cl	X	X	COOMe	CN	
g	g	430	444		g	g	394	389	
s	s	20.0	22.0		s	s	18.4	13.6	
	g	436			R	R	H	Me	
s	s	15.0			g	s	422	428	
							18.7	18.3	

Figure 11. 'Applicational limit of absorption' and 'steepness'.

region the notations of 'steepness' and 'applicational limit of absorption' are considered to be of value as spectral characteristics of a compound.

7. *p*-HYDROXYBENZOATES AS LIGHT STABILIZERS

Esters of 4-hydroxy-3,5-di-*tert*-butylbenzoic acid are effective light stabilizers for polyolefins. The ester with 2,4-di-*tert*-butylphenol has received the widest attention of this class in the literature⁸. On the basis of its filtering capacity this compound should make a poor stabilizer. In practice, however, it exhibits a good efficiency. It has been speculated, therefore, that the observed photo-Fries-rearrangement leading to an *o*-hydroxybenzophenone



could be the source of the efficiency. However, it is hard to see how the protection of a polymer by an u.v.-filter slowly produced during the irradiation could be so effective. Dr H. Lind in our laboratories has recently found convincing evidence that the photo-Fries-rearrangement is not the basis of the effectiveness of the 2,4-di-*tert*-butylphenyl 4-hydroxy-3,5-di-*tert*-butylbenzoate. First, the rearrangement product has been isolated in sufficient amounts to allow a separate test of its efficiency as a light stabilizer. The 2,4'-dihydroxy-3,3',5,5'-tetra-*tert*-butylbenzophenone is distinctly less effective in polypropylene than its precursor when tested in exactly the same way. Secondly, esters of 2,4,6-trialkylphenols with 4-hydroxy-3,5-di-*tert*-butylbenzoic acid are light stabilizers with an effectiveness comparable to 2,4-di-*tert*-butylphenyl 4-hydroxy-3,5-di-*tert*-butylbenzoate, in spite of the fact that they undergo rearrangement at a much slower rate (*Figure 12*). Hence the

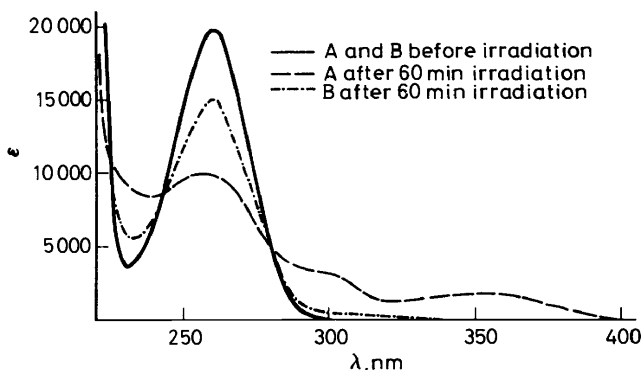


Figure 12. The u.v.-spectra of 2,4-di-*tert*-butylphenyl 4-hydroxy-3,5-di-*tert*-butylbenzoate (A) and of 2-methyl-4,6-di-*tert*-butylphenyl 4-hydroxy-3,5-di-*tert*-butylbenzoate (B) before and after 60 min irradiation with a mercury medium pressure arc filtered by a 1 mm Pyrex glass. Solvent: cyclohexane.

Fries-rearrangement is not the cause of the efficiency of these compounds; at best it is a coincidental consequence of a protective mechanism not known as yet. As the photo-rearrangement of the 2,4-di-tert-butylphenyl 4-hydroxy-3,5-di-tert-butylbenzoate does not constitute the basis of its efficiency as light stabilizer the simultaneous use of u.v.-absorbers is not precluded. In fact mixtures of 2,4-di-tert-butylphenyl 4-hydroxy-3,5-di-tert-butylbenzoate and *o*-hydroxyphenylbenzotriazoles give excellent results in the light stabilization of polyolefins. This is yet another step in the direction of more complex stabilizer systems as outlined earlier.

ACKNOWLEDGEMENT

We wish to acknowledge with gratitude the supply of applicational data by our colleagues from product development under the supervision of Dr H. Gysling.

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NOTE: Appendix follows on pages 164, 165.

APPENDIX. The 'normalized transmission' curve (equation 7)

	0	1	2	3	4
0	—	-0.30103	-0.23019	-0.18267	-0.14549
10	0.00000	0.01836	0.03583	0.05254	0.06861
20	0.15554	0.16891	0.18205	0.19499	0.20776
30	0.28160	0.29359	0.30553	0.31742	0.32927
40	0.40018	0.41205	0.42395	0.43589	0.44788
50	0.52139	0.53398	0.54669	0.55953	0.57250
60	0.65394	0.66823	0.68276	0.69754	0.71260
70	0.80994	0.82757	0.84567	0.86430	0.88350
80	1.01363	1.03851	1.06456	1.09193	1.12079
90	1.33954	1.38765	1.44115	1.50145	1.57070

Example of use of the table

Given the two points

(1) $\delta = 5 \text{ mg/cm}^2$; 90 per cent transmission at 424 nm(2) $\delta = 2.5 \text{ mg/cm}^2$; 20 per cent transmission at 405 nm $\bar{\lambda}_1 = 1.340$ and $\bar{\lambda}_2 = 0.156$ are read from the table and hence

$$s = \frac{424 - 405}{1.340 - 0.156 + 0.699 - 0.398} = \frac{19}{1.485} = 12.8$$

$$g = 414.5 + 12.8 (1 - 0.748 - 0.548) = 414.5 - 3.8 = 410.7$$

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5	6	7	8	9
-0.11429	-0.08702	-0.06255	-0.04017	-0.01943
0.08412	0.09915	0.11376	0.12800	0.14192
0.22036	0.23282	0.24517	0.25740	0.26954
0.34110	0.35291	0.36472	0.37653	0.38835
0.45994	0.47206	0.48426	0.49654	0.50891
0.58563	0.59892	0.61239	0.62604	0.63988
0.72796	0.74363	0.75964	0.77601	0.79277
0.90330	0.92377	0.94497	0.96696	0.98981
1.15131	1.18375	1.21838	1.25557	1.29576
1.65216	1.75132	1.87850	2.05681	2.36004