

SOME ASPECTS OF STABILIZATION OF POLYMERS AGAINST LIGHT

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ABSTRACT

Different mechanisms for the protection of polymers against photodegradation are discussed. (1) The u.v.-absorbers of the 2-(2-hydroxyphenyl)-benzotriazole and the *o*-hydroxybenzophenone type have rates of internal conversion much higher than the rate of intersystem crossing and of fluorescence decay. Evidence is presented that this rapid non-radiative deactivation cannot be explained very satisfactorily by a simple 'enol-keto'-equilibrium in the first excited singlet state only.

(2) At the concentrations used in practice the quenching rate of light stabilizers is so low that quenching cannot compete successfully with other deactivation processes of triplet states, while excited singlet states of primary sensitizers can be quenched efficiently only by additives with extinction coefficients of more than 5000 to 10000.

(3) The derivatives of 2,2,6,6-tetramethyl-piperidines of the structures I to IV cannot quench excited singlet states in the apolar solvent heptane. The corresponding *N*-oxyls inhibit the Norrish reaction of aralkylketones. Specific *N*-oxyl- and *N*-methyl-2,2,6,6-tetramethyl-piperidines as well as certain nickel chelates decelerate the singlet oxygen induced photo-oxygenation of rubrene and 9,10-dimethoxy anthracene.

1. INTRODUCTION

The effect of light on today's bulk polymers such as the commercially available polyolefins, aliphatic polyamides, linear polyesters, polystyrene, PVC and unsaturated polyester resins is highly complex. At least in their non-light stabilized form these polymers are degraded upon light exposure much less by chainbreaks due to direct photon impact than by normal autoxidation induced photochemically. First of all high energy u.v. light below 280 to 290 nm is completely missing from daylight. Consequently a large proportion of known photodissociations of polymers with aliphatic backbones cannot take place under normal ageing conditions. Secondly, the absorbance of these polymers in the near u.v.-region is rather low due to the lack or low concentration of chromophores of high absorptivity. The photochemistry of everyday polymers depends, therefore, on low intensity chromophore transitions, the chemical nature of which is very hard to define. All chromophores in bulk polymers are introduced either as impurities, including residual monomer, from thermal processes undergone in the preparation or work-up of the polymer or, most commonly, in the shape-

giving processing of polymers. The best known photoactive species thermally produced in a polymer with an aliphatic backbone are carbonyl groups and particularly hydroperoxides. The latter groups are particularly important, as simple carbonyl groups are of little consequence in the photodegradation of purely aliphatic polymers such as polyolefins. The formation of these primary photoactive species in polymers is still a fertile ground for speculation and, for the purpose of this paper, we shall simply accept their presence in minute amounts as a given reality[†].

A completely different behaviour, however, is expected from polymers which contain recurring units showing high absorption in the near u.v., such as polyphenylene oxides, the polyamides of aromatic diamines and polyvinyl carbazole or anthracene. The degradation of such polymers does not depend upon minute amounts of primary sensitizers and hence stabilization requires a different approach than that used in today's bulk polymers. However, in what follows, we will not deal with aromatic polymers of such high u.v.-absorption.

Let us now follow the course of events when a processed and shaped polymer is exposed to light.

The first step required in starting any photodegradation is of course the absorption of a photon by a primary sensitizer. The resulting excited singlet has the following possibilities: (i) it dissipates the accumulated energy by fluorescence and possibly internal conversion, (ii) it dissociates into hot fragments, (iii) it reacts with a partner to form hot reaction products, or (iv) it changes its multiplicity by intersystem crossing, whereby a large part of the energy absorbed still remains in the triplet formed. Of these possibilities the first is generally not harmful to the polymer and is therefore the preferred path of energy dissipation. Unfortunately, however, quantum yields in the second and third processes are, in most cases, small but significant. The further fate of the formed hot reaction products is important in

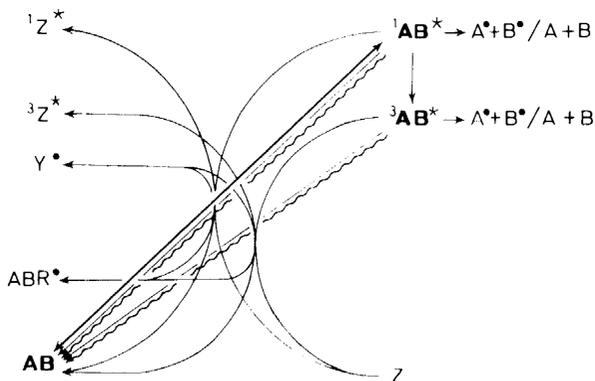


Figure 1. Reaction scheme for the first excited singlet and triplet states of the molecule AB.

[†] In the following sections we will call such chromophores originally present in polymers primary sensitizers. This is, however, without any implication to their actual mechanistic behaviour.

the photodegradation of polymers. If, upon dissociation of the excited singlet or by reaction with a partner, radicals are formed, normal autoxidation of aliphatic compounds—be they monomeric or polymeric in nature—ensues. All these reactions are so fast as to leave the excited singlet a mean lifetime of around 1 to 10 ns.

Intersystem crossing back to the ground state and phosphorescence of triplets is usually slow and gives a mean lifetime of around 10 to 1000 μ s, i.e. triplets outlive singlets by a factor of 10^3 to 10^5 . During their long life triplets have, of course, a good chance to enter chemical reactions. Again radical formation is particularly harmful, be it by dissociation (again the Norrish type I reaction in the case of excited carbonyl compounds) or by photoreductions involving a hydrogen-transfer. A schematic outline of these possibilities is given in *Figure 1*.

As pointed out before, autoxidation of the polymer induced by photolytically generated radicals is a major contributor to the observed overall degradation of the polymer. Any integral light protection of polymers must take this aspect into consideration. Accordingly, the following possibilities for light stabilization exist. They are listed in order of their action during the sequence of events in photodegradation: (i) u.v.-absorption, (ii) quenching of excited states, (iii) scavenging of photolytically produced radicals and (iv) prevention of radical formation by peroxide decomposition. The agents used to perform these actions are summarized in *Figure 2*.

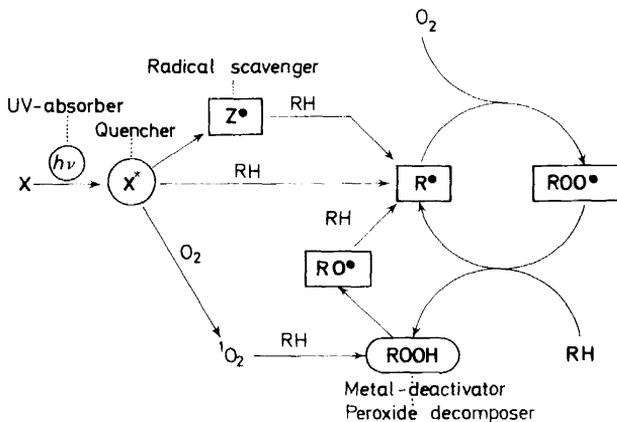


Figure 2. Schematic representation of the reactions involved in the light induced degradation of polymers with aliphatic backbones and name of the additives providing protection against the indicated reaction or chemical intermediate.

2. UV ABSORBERS

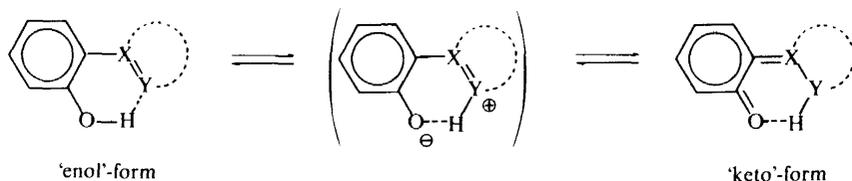
A large number of different chemical classes have been suggested as u.v.-screeners, mostly in the patent literature. However, only a few groups of compounds have found substantial use in industrial practice. They are the *o*-hydroxybenzophenones, 2-(2-hydroxyphenyl)-benzotriazoles and to a

lesser extent salicylates and α -cyanocinnamic acid derivatives. Of the newer classes, the substituted oxanilides seem to be the most interesting ones¹. However, their u.v.-absorption particularly in the long wavelength region is rather poor when compared to that of benzophenones and benzotriazoles. Their claimed effectiveness as light stabilizers seems therefore not entirely dependent upon u.v.-absorbing capacity. Due to the lack of thorough scientific investigation, detailed modes of action for such compounds are not yet clear.

A good u.v.-absorber must dissipate absorbed energy in a manner innocuous to the substrate. This means that dissipation of excitation energy should proceed at a faster rate than side reactions. Spectral data indicate that in 2-(2-hydroxyphenyl)-benzotriazoles and in *o*-hydroxy-benzophenones this energy dissipation process occurs solely in the singlet manifold. 2,4-Dihydroxy-benzophenone shows neither phosphorescence nor triplet-triplet absorption². The phosphorescence of 2-(2-hydroxy-5-methylphenyl)-benzotriazole and of 2-hydroxy-5-methoxy-benzophenone is very weak, while 2-(2-hydroxy-3-tert.-butyl-5-methylphenyl)-5-chlor-benzotriazole does not phosphoresce at all³. Thus, intersystem crossing from the lowest excited singlet state S_1 to the lowest triplet state T_1 must be an unimportant deactivation process for S_1 . Furthermore, the above mentioned compounds do not fluoresce at room temperature, while at 77 K only 2-(2-hydroxy-5-methylphenyl)-benzotriazole shows a very weak fluorescence³. Therefore, these molecules dissipate their excitation energy by a non-radiative singlet process, the rate of which must be significantly higher than natural fluorescence decay and the intersystem crossing rate of the lowest excited singlet state. The natural fluorescence lifetime of a molecule with an extinction coefficient of 20000 is about 5 to 10 ns, consequently the non-radiative decay rate must exceed $\cdot 10^9 \text{ s}^{-1}$ considerably.

The nature of this rapid decay process is, in our opinion, still open to discussion. So far, two mechanisms have been proposed to explain the given facts:

- (A) The participation of an 'enol-keto-tautomerism' in the excited singlet state



It is assumed that, in the excited state, the 'keto'-form is more stable than the 'enol'-form, while in the ground state the 'enol' is more stable⁴.

- (B) The rotation of the hydroxyphenyl group. Thus the Franck-Condon factor between the excited singlet state and the ground state is enhanced (loose bolt effect) leading to a particularly high rate⁵ for the—normally very slow—internal conversion from $S_1 \rightarrow S_0$.

The 'enol-keto-mechanism' is based on the observation of a very large Stokes shift of the fluorescence of *o*-hydroxyphenyl-pyrimidines⁴. Furthermore a number of examples are known in the literature which show that such proton-transfer reactions in the excited singlet state are indeed very rapid processes, with rates comparable or even much higher than the rate of the 'enol'-form fluorescence decay. Examples are derivatives of salicylic acid⁶ or salicylidene anilines and 2-(2-hydroxyphenyl)-benzothiazole⁷. The 'keto'-fluorescence can be recognized by a red shift of about 4000 to 5000 cm^{-1} with respect to the 'enol'-fluorescence and in any case by a Stokes shift of about 10000 cm^{-1} . Our own investigations show that 'keto'-fluorescences are also formed in 2-(2-hydroxyphenyl)-benzoxazole and -imidazole. In polar solvents the imidazole derivative shows even in the ground state a small amount of 'keto'-form. In both compounds the ratio of the intensity of the 'enol' to 'keto'-fluorescence increases with increasing solvent polarity. For such equilibria which are shifted markedly by changing solvent polarity it has been established⁸ that the enthalpy difference in the species taking part in such equilibria generally does not exceed 5 kcal/mol. Hence the energy difference between the excited 'enol'- and 'keto'-forms of these molecules also should not exceed this value of 5 kcal/mol. In fact Weller found⁶ an enthalpy difference of 1 kcal/mol between the excited 'enol'- and 'keto'-forms of methylsalicylate.

One measure for this energy difference between the 'enol' and 'keto'-forms is certainly the difference between the acidity of the proton donor-part—the hydroxy group—and the basicity of the proton acceptor atom in these molecules. So the pK values for some of the interesting systems were determined. Direct measurements yielded values for the ground state while either the Förster-cycle method or fluorescence titration were used for the first excited singlet (pK^*). The results in *Table 1* show that ground-state 'enol-keto'-equilibria can be observed if the difference between donor acidity and acceptor basicity is seven pH units or less. It is well known that in the first excited singlet state the acidity of phenolic hydroxyl groups is raised by about six units and the basicity of the carbonyl-oxygens or the ring-nitrogens functioning as proton acceptors is also raised by four to eight units. Therefore proton transfer in the excited state is much more probable than in the ground state.

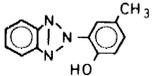
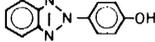
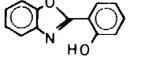
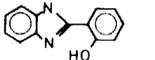
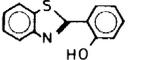
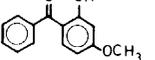
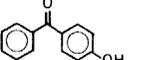
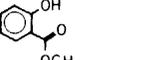
The energy difference between the 'enol' and the 'keto'-forms in the ground state of methyl salicylate can be estimated from measurements by Weller⁶ to be around 15 kcal/mol[†]. The difference in pK values between proton donor and acceptor in this molecule is estimated at 16 to 18 units¹⁰. This coincides very closely with the corresponding values for benzophenone and benzotriazole u.v.-absorbers (cf. *Table 1*). On the assumption that this equality in pK difference implies a similar difference in energy between the 'enol'- and 'keto'-forms in the ground state, i.e. 15 kcal/mol, an estimate of the energy difference of the excited 'enol' and 'keto'-forms can be made. Careful luminescence measurements reveal no 'keto'-fluorescence of the

† 15 kcal/mol \approx 80 kcal/mol ('enol'-fluorescence at 352 nm)
 - 64 kcal/mol ('keto'-fluorescence at 443 nm)
 - 1 kcal/mol (enthalpy difference between excited 'enol'- and 'keto'-forms)

benzophenones and benzotriazoles of *Table 1* up to 800 nm \ddagger . This means that if these *o*-hydroxybenzophenones and *o*-hydroxyphenylbenzotriazoles were to yield excited 'keto'-forms, their excitation energies would be at most 35 kcal/mol. This value is substantiated by the estimate that the rate of internal conversion ($S_1 \rightarrow S_0$) for rigid systems, which the 'keto'-forms are, will become comparable to the fluorescence decay only at higher wavelengths

Table 1. Properties of various u.v.-absorbing phenolic compounds.

The formulac of the compounds, the corresponding pK values in the ground state (pK), their difference (Δ pK) and the ones in the first excited singlet state (pK*) as well as the qualitatively spectroscopically determined presence of 'keto'-forms in the ground state (S_0 keto) and of 'keto'- and 'enol'-forms in the first excited singlet state (fluorescence enol, keto) are given in the columns from left to right.

	pK ₁	pK ₂	Δ pK	pK ₁ [*]	pK ₂ [*]	in ethanol		
						S ₀ keto	Fluorescence enol	keto
	-4.9	9.2	14	-0.5	(3)	—	+ ¹	—
	-4.6	8.9		0	2	—	+	—
	0.9	9.7	9	4	4	—	+	+
	5.3	9.3	4	11	3	+	+	+
	<3 ²	≈8.5 ²				+ ³	+ ³	+ ³
	-6.5	9.4	16	(1)	(3)	—	—	—
	-6.3	7.8		(-1)	(3)	—	—	—
	-6.5 ²	10 ²	16			—	+ ⁴	+ ⁴
¹ see text	² ref. 10	³ ref. 7	⁴ ref. 6					

\ddagger The low temperature fluorescence of 2-(2-hydroxy-5-methylphenyl)-benzotriazole at 396 nm and the very weak room-temperature fluorescence of 2-(2-hydroxyphenyl)-5-methoxy-6-methylbenzotriazole at 385 nm (in ethanol) are certainly 'enol'-fluorescences.

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of the luminescence, i.e. at around 700 to 800 nm⁹ which again corresponds to 35 to 41 kcal/mol. As the 'enol'-fluorescence of the hydroxybenzophenones and *o*-hydroxyphenylbenzotriazoles is around 400 nm or less (≈ 70 kcal/mol) the hypothetical excited 'keto'-form would have to be more stable than the excited 'enol'-form by at least 20 kcal/mol. This—when compared to the

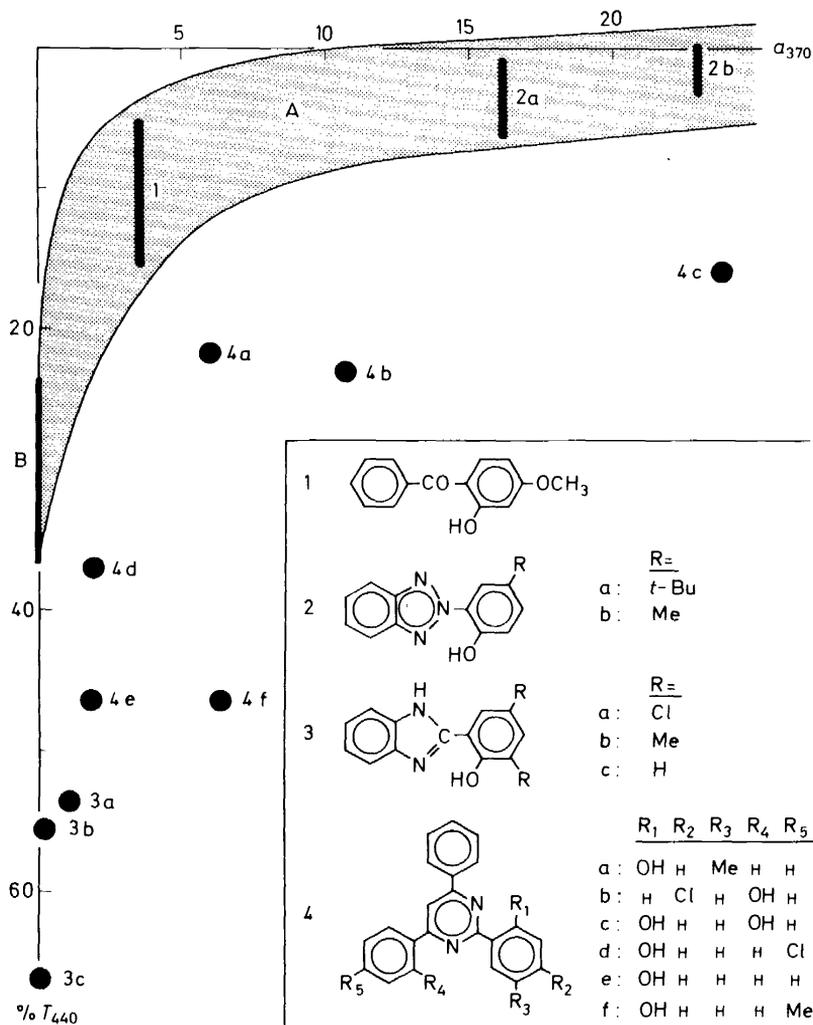


Figure 3. Action of various additives upon the light ageing of polyester resin. Plotted is the loss in transmission (at 440 nm) of 2 mm thick polyester plates versus the absorptivity of the u.v.-absorbing additive at 370 nm. (This latter value represents the empirically determined maximum of a wavelength dependent factor. This is the product of the sensitivity of polymer, its absorbance and output of the Fadeometer® arc). The vertical bar (B) on the ordinate indicates the range of loss in transmission of additive free polyester plates. The shaded area (A) represents the loss area encountered with the best commercial and experimental u.v.-absorbers.

1 kcal/mol difference in the case of methyl salicylate—is a very unlikely value, particularly in view of the fact that the basicity of the proton acceptor in the benzophenones and benzotriazoles in question is very close to the one in methyl salicylate. From an energy point of view it is therefore very doubtful that 'keto'-forms exist during the deactivation process in these u.v.-absorbers and hence their contribution to energy dissipation seems highly questionable.

The existence of excited 'keto'-forms does not in itself make a compound a light-stabilizing u.v.-absorber. This is proved by the fact that *o*-hydroxyphenyl-pyrimidines and *o*-hydroxyphenylbenzimidazoles have low light-stabilizing efficiency or even accelerate the discoloration of polyester resin as shown in *Figure 3*.

It is difficult to judge whether the rotation mechanisms can really explain the rapid dissipation of energy. The fact that 2-(2-hydroxy-5-methylphenyl)-benzotriazole does fluoresce weakly at 77 K but not at room-temperature indicates that the non-radiative deactivation process—whatever it is—must have an energy barrier; however, its activation energy is probably rather small. This finding is not in contradiction with a rotation which—in order to be operative—would require an activation energy of less than about 5 kcal/mol. Unfortunately no direct measurements are available today. Another indication in favour of the rotation mechanism is the fact that 2-hydroxy-4,6-di-*tert*-butyl-benzophenone shows a strong phosphorescence¹¹. In this molecule in which rotation is strongly inhibited by steric hindrance, the dominant first excited singlet state deactivation process is obviously intersystem crossing to T_1 .

While we favour the rotation mechanism for normal *o*-hydroxybenzophenones and 2-(2-hydroxyphenyl)-benzotriazoles, it should not be overlooked that other mechanisms can and must be operative in other systems. The high efficiency of 1-hydroxyxanthenes as light stabilizers obviously requires a deactivation mode totally different from the loose bolt mechanism.

The predominance of a rapid and harmless deactivation process for the first excited singlet state—which process in our experience should be non-radiative—is, however, not the only pre-requisite of a technically useful u.v.-absorber. In addition to the spectral characteristics which have been discussed elsewhere¹², a truly monomolecular dispersion of the screener in the polymeric substrate is necessary. If this pre-requisite is not fulfilled, the activity of a specific compound is lower than expected from its behaviour in solution. This fact allows easy determination of u.v.-absorber 'functional compatibility', in contrast to the commonly used 'visual compatibility', i.e. the lack of an observable formation of an additional stabilizer phase in the polymer. In order to assess 'functional compatibility' the experimentally determined absorbance of a film or plaque containing u.v.-absorber is compared to the one calculated from the spectral data of the u.v.-absorber in a solvent with characteristics comparable to the polymeric substrate. In this general procedure the use of a series of homologous compounds—all containing the same chromophore—is particularly recommendable. *Figure 4* presents data obtained with *o*-hydroxyphenyl-benzotriazoles into which alkyl sidechains of varying length and/or branching were introduced by means of an ester group. The absorbance of approximately 0.1 mm thick low density polyethylene films containing 0.2 per cent

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Compatibility in polyethylene

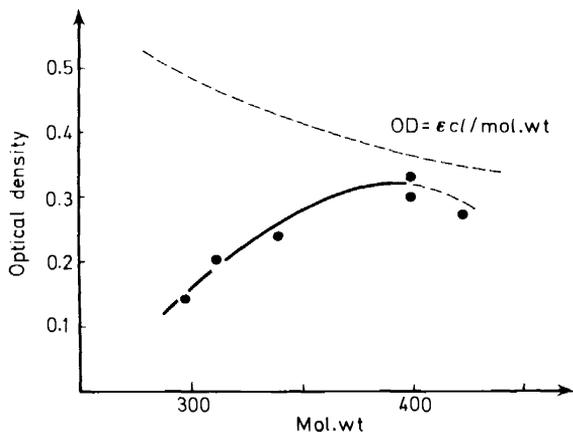


Figure 4

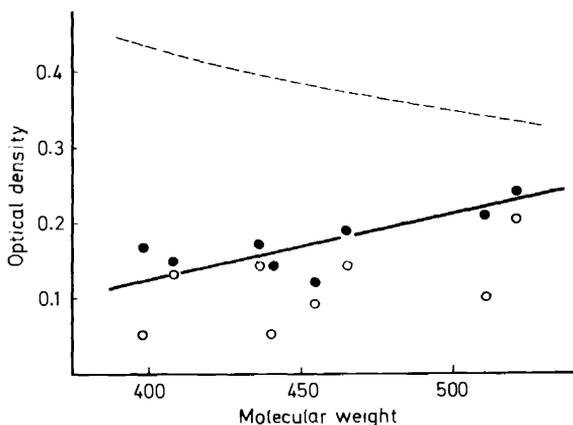


Figure 5

Figures 4 and 5. Absorbance of polyethylene films versus the molecular weight of u.v.-absorber.
Formulae of absorbers:

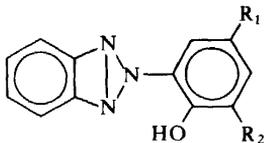


Figure	R_1	R_2
4	$-\text{CH}_2\text{CH}_2\text{COOR}$	$-\text{H}$
5	$-\text{CH}_3$	$-\text{CH}_2\text{NHCOR}$

(R standing for alkyl rests)

Concentration of u.v.-absorber 0.2 per cent. The dashed line represents the calculated absorbance.
Further explanations appear in the text.

u.v.-absorber is plotted versus the molecular weight of the absorber used. 'Visual compatibility' was obtained with all compounds of this series having a molecular weight larger than 300. It is evident on the other hand that 'functional compatibility' is restricted to compounds of a molecular weight 400 ± 20 corresponding to octyl esters. For such compounds the observed absorbance equals the expected absorbance within the limits of error.

Figure 5 gives similar results for *o*-hydroxybenzotriazoles containing an amide linkage in a sidechain (●). 'Visual compatibility' extended over the whole range while true 'functional compatibility' is not reached with any compound of this series. Of interest is the effect of light on these films. An exposure of 100 hours in a Fadeometer® () produces a significant loss in absorbance of these specific compounds in low density polyethylene, while the same exposure in other polymeric substrates, such as cellulose acetate films and polystyrene plaques, does not lead to any measurable changes after exposure. The cause of this absorbance loss is not photolysis of the chromophores but a slow agglomeration or even crystallization of the u.v.-absorber in the polyethylene substrate. In some extreme cases this is evidenced by visual appearance of turbidity. In such cases of borderline compatibility, the excitation energy can be used to yield the activation energy of separation of these rather larger molecules from their submicroscopic agglomerates or the activation energy of diffusion. Thus larger aggregates are formed or even crystallites which eventually become visible to the naked eye.

3. QUENCHERS

A number of commercially available light-protecting additives for polymers are called quenchers. The most important and, by now, established group of these are the nickel chelates. The main feature of all these substances is their light-protecting effect despite their low absorptivity in the region of 300 to 400 nm \dagger . But are these compounds in the true sense of the word quenchers, i.e. do they accept energy from the excited primary sensitizers?

Phenomenologically two different kinds of quenching can be distinguished in photochemistry. (i) One is long-range energy-transfer. This process is normally observed in the quenching of excited singlet states. It is found to operate only when distances between sensitizer and quencher (R_Q) \ddagger are 50 Å or greater. (ii) The other types are contact transfers. These are mechanisms of a different nature, but all of which are effective when the distance between quencher and sensitizer is 15 Å or less. The quenching process is successful only if the quencher is or gets within quenching distance of the excited sensitizer within the latter's lifetime. High diffusion constants in a substrate, i.e. good mobility of quencher and quenchee, and long lifetime of the excited sensitizer may therefore enlarge the apparent action sphere of

\dagger Obviously the normal u.v.-absorbers can act as potential quenchers, but since their activity depends on a high molar extinction coefficient in the near u.v., they are normally not termed quenchers.

\ddagger In the following R_Q stands for the mean distance between sensitizer and quencher at the moment of the energy transfer act. R_{SQ} , however, is meant to indicate the distance between sensitizer and quencher, calculated from concentration.

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the quencher or in other words lower the concentration of quencher necessary to observe a certain effect. Obviously this can be accurately calculated for each specific case. In order to get an overall impression of the general situation *Figure 6* is presented. The assumptions underlying this

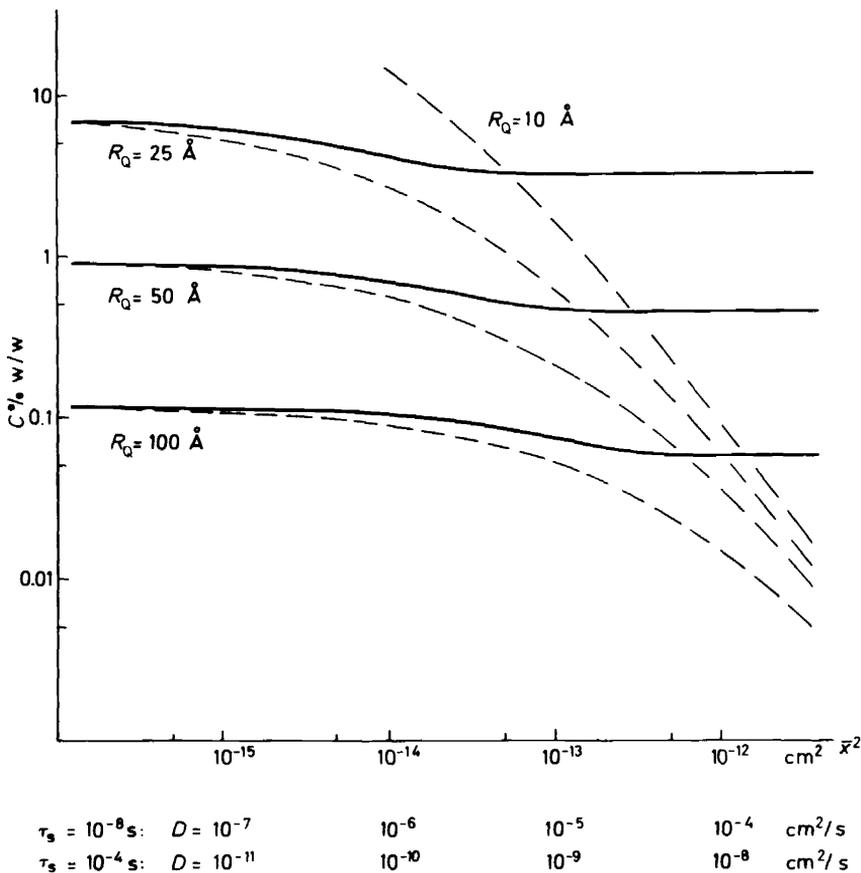


Figure 6. Concentration of quencher versus mean square displacement. For explanation, see text.

figure are (i) a freely diffusing quencher of molecular weight 500 and (ii) a fixed sensitizer with an active site diameter of 5 \AA †.

In this graph, the quencher concentration is plotted as a function of the mean square displacement (\bar{x}^2), i.e. the concentration needed to allow quenching within the lifetime τ_q in a substrate characterized by a diffusion

† Such fixed sensitizers would correspond to sensitizing moieties attached to the polymer chains in polymeric substrates.

constant D . Each curve represents a specific distance (R_Q) at which the energy transfer becomes operative.

The dashed lines give the best possible case (unit probability), i.e. the biggest enlargement of quencher action sphere, which results if each quencher is surrounded by sensitizers. Under these circumstances any movement of the quencher, independently of direction, would lead to a successful encounter. The full lines reflect a situation in which sensitizer concentration is equal to or even lower than quencher concentration. In this case the direction of quencher diffusional movement—toward or away from the sensitizer—starts to play a role. The figure was constructed on the basis of a 20 per cent probability of success in diffusional movement. It is seen that under these conditions the mean square displacement, i.e. the product of half-lifetime and diffusion coefficient, has little influence on the concentrations needed to effect quenching.

The concentrations presented in *Figure 6* should be considered from the point of view of light stabilizer concentrations actually used in practice, which range from 0.1 to 0.5 per cent weight by weight. *Figure 6* demonstrates that based on the above assumptions and at practical additive levels only quenchers with an operational mode effective at or above 50 Å can be expected to deactivate excited states efficiently. In other words, only long-range energy transfer can be expected to contribute to excited-state deactivation with the usual half-life of singlets and triplets. This means that quenching of excited triplets, which is usually ascribed to contact transfers, plays a minor role in light stabilization by the so-called quenchers. The same conclusion has been arrived at by B. Felder and R. Schumacher in our laboratories¹³. Let us therefore have a closer look at long-range energy transfer. From the theory of dipole-dipole interactions the following expression for the quenching rate k_Q has been deduced¹⁴

$$k_Q = 3.7 \times 10^{22} \times (\Phi_s/\tau_s R_Q^6) \int_0^\infty f_s(\nu) \epsilon_Q(\nu) d\nu/\nu^4$$

In this formula Φ_s is the fluorescence yield of the sensitizer, τ_s its lifetime, R_Q the mean distance of sensitizer and quencher in Å, f_s is the normalized spectral distribution of the fluorescence of the sensitizer, ϵ_Q is the spectral distribution of the extinction coefficient of the quencher and ν is the wave-number in cm^{-1} . Assuming the spectral distribution of fluorescence f_s and the absorption ϵ_Q to be of Gaussian type with maxima at 345 nm and half-width of 4000 cm^{-1} † and considering that the ratio of Φ_s/τ_s is equal to the fluorescence decay rate k_f , one finds the following proportionality between the rate of quenching and the rate of fluorescence decay

$$k_Q = 3.7 \times 10^4 \times \epsilon_{Q\text{max}} \times k_f/R_Q^6$$

A quencher concentration of 0.02 mol/l., say, one per cent at a molecular weight of 500, corresponds to $R_{SQ} \approx 40$ Å. Experience shows that the quench-radii calculated by the theoretical model are about a factor of two

† These are reasonable assumptions for aliphatic ketones as sensitizers and nickel chelates or u.v.-absorbers as energy acceptors.

lower than those determined from the concentration. Thus

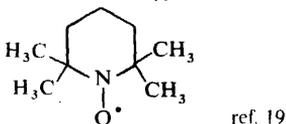
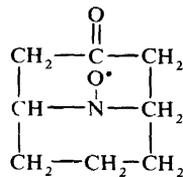
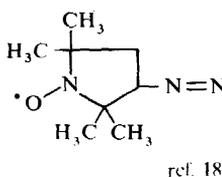
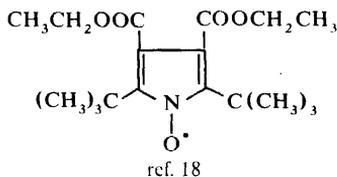
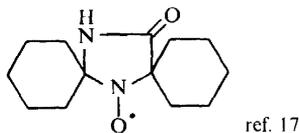
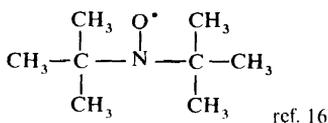
$$k_Q = 5 \times 10^{-4} \times \epsilon_{Q_{\max}} \times k_f$$

This expression leads to the conclusion that additives with extinction coefficients of 2000 and higher can quench excited singlet states with rates equal to or higher than the fluorescence decay rate[†]. However, the very low fluorescence yields of primary sensitizers, such as ketones and peroxides (e.g. diethylketone $\Phi_f = 0.01^{15}$), mean that non-radiative deactivation processes of the excited singlet state are faster and more important than the fluorescence. Hence k_Q must be much larger than k_f if quenching is to compete with these non-radiative deactivation processes of the sensitizer. Thus a compound acting as a long-range quencher must have an $\epsilon_{Q_{\max}}$ in excess of 10000 around 340 to 350 nm. Such compounds, however, are the typical u.v.-absorbers known to the trade.

To conclude this section, we would like to stress that at the additive levels usually employed in polymeric substrates, the quenching of excited triplet states by contact transfer does not appear to be a major factor in the light stabilization of polymers with aliphatic backbones. Quenching of excited singlet states by dipole-dipole interaction, however, can be a major factor in the stabilization process. An entirely different situation may exist in polymers with strongly luminescing moieties in the backbone or as pendant sidechains.

4. AMINE STABILIZERS

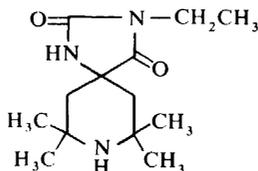
In the scientific literature as well as in patents, specifically substituted derivatives of heterocyclic amines have been suggested as polymer additives. Early publications have concentrated on *N*-oxyl free radicals such as:



[†] The work of Chien and Conner¹⁵ provides evidence that the singlet state of diethylketone can be quenched by the nickel chelate of 2,2'-thiobis-[4(1,1,3,3-tetramethylbutyl)-phenol], which has an ϵ_Q (313 nm) of 4000. However, the concentration (0.5 mol/l.) of diethylketone (mol. wt 128.22) used is so high as to prove little for practical conditions in actual polymers.

Excellent review articles on nitroxyls have been published by K. Murayama²⁰ and E. G. Rosantzev *et al.*²¹. The latter has contributed significantly to the general knowledge of the nitroxyl free radicals. These compounds are very useful spin probes for polymers²¹. The application of nitroxyl radicals in the stabilization of polymers was originally considered on the basis of their capability to trap the free radicals essential in the degradation of polymers²². Accordingly the simple nitroxyls were thought to be good antioxidants. However, their efficiency in preventing thermal oxidative degradation is not sufficient to allow commercial usage for this purpose. Later on the usefulness of these additives in polymer light stabilization, particularly polyolefins, was discovered²³. Their efficiency in suppressing photodegradation of polyolefins can—depending upon the specific substitution—be quite remarkable. In this respect our own experiments confirm²⁴ statements made in and the claims of various patents. However, the colour of nitroxyl radicals—yellow to red—effectively prevents usage as commercial plastic additives in the concentration range normally utilized, e.g. around 0.5 per cent based on the polymer.

A big step forward was the surprising finding by chemists of Sankyo Company Limited that not only the free radicals described, but also specific free amines, e.g.



are effective light stabilizers²⁵. As these compounds do not absorb appreciably above 280–290 nm—the short wavelength limit of daylight—the question arises as to how such compounds function as light stabilizers. In spite of the aforementioned conclusions concerning quenching in polymers, it was felt that investigation of the quenching properties of these specific amines and the nitroxyl radicals derived therefrom was worthwhile; particularly in view of the known capacity of aliphatic and aromatic amines for efficient quenching—especially in polar solvents—of excited singlet states of aromatic hydrocarbons²⁶ as well as singlet and triplet states of ketones and oxygen²⁷. As the excited states of the aliphatic amines lie higher than those of the sensitizer, normal quenching mechanisms cannot explain the efficiency of these compounds. Weller²⁶ showed that the singlet deactivation mechanism of the amines proceeds by an excited charge-transfer complex between amine and sensitizer. Thus for a given sensitizer in a given solvent the quenching rate k_Q is proportional to the ionization potential of the amine. In order to determine whether tetramethyl-piperidine derivatives of the patent literature could deactivate singlets in polymers and what factors affect their quenching efficiency, ionization potentials and quenching constants for a series of amines were measured. The ionization potentials were determined by ground state charge-transfer complexes with iodine

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as an electron acceptor. The quenching constants presently reported are the gradients $k_Q \tau_s$ of Stern-Vollmer plots using fluorenone as a sensitizer in acetonitrile.

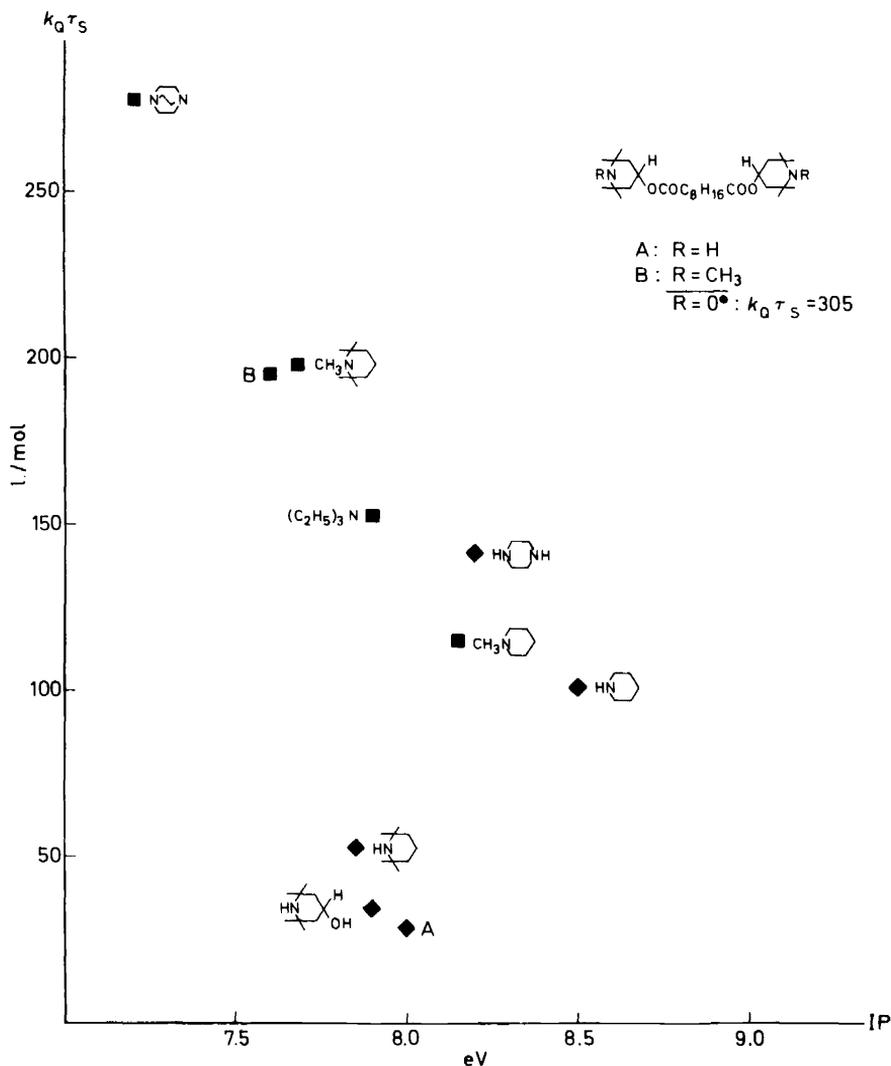


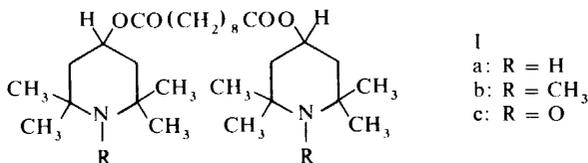
Figure 7. Quenching efficiency ($k_Q \tau_s$) for fluorenone versus ionization potential (IP) of various amines. For explanation, see text.

Figure 7 shows that 2,2,6,6-tetramethylpiperidines—independent of the substituent in position 4—have ionization potentials similar to triethylamine, namely 7.85 to 8.0 eV. The corresponding *N*-methyl derivatives have lower ionization potentials by about 0.2 eV or 5 kcal/mol. The nitroxyl

radicals did not form measurable amounts of iodine complexes; consequently their ionization potential could not be determined. *Figure 7* shows, furthermore, that the ionization potential is not the only factor affecting the quenching constant. Apparently the steric hindrance of the lone pair on the nitrogen by the α -position substituents lowers the probability of a successful sensitizer quencher encounter. *N*-Methylation increases the quenching constants remarkably (4- to 6-fold). The reason for this enhancement in spite of further steric hindrance of the nitrogen is not clear at the moment. One could speculate that the exciplex encounter distance increases with decreasing ionization potential.

The reciprocal of the quenching constant gives the quencher concentration needed to deactivate one half of the excited sensitizers before they fluoresce. In apolar solvents the quenching constants are about 50 times smaller than in acetonitrile (heptane: triethylamine $k_Q\tau_s = 3$ l./mol, 1,2,2,6,6-pentamethylpiperidine $k_Q\tau_s \approx 1$ l./mol). Thus it is not possible for even the most efficient of these amines to act as quencher of excited singlets of primary sensitizers in polyolefins, considering the normal stabilizer concentration.

This conclusion is borne out by the experiments of H. Lind²⁸ in our laboratory. The initial rate of disappearance of 1-phenyl-decanon-(1) as well as the formation of the photolysis products acetophenone and octene-(1)[†] in *n*-heptane using a high pressure mercury lamp was not changed by the addition of compounds Ia and Ib in the concentration range of 4×10^{-3} to 1.3×10^{-1} .



This proves that the free amines Ia and Ib, under the experimental conditions used, have no quenching ability on the first excited singlet state of carbonyl compounds. In addition they cannot quench the triplet states.

The nitroxyl Ic, however, completely suppresses the Norrish photolysis of 1-phenyl-decanone-(1) under the same conditions. This means that nitroxyls can effectively quench excited states of araliphatic ketones. The most probable process is triplet state quenching as singlet quenching in polar solvents is not great enough to be efficient in solvents of low polarity (cf. *Figure 7*, Ic: $k_Q\tau_s = 305$).

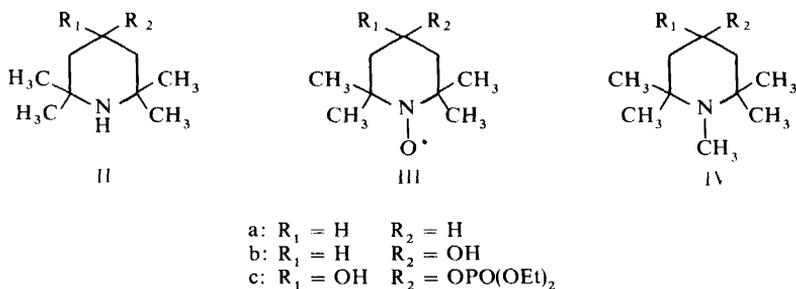
From these experiments it can be concluded that in the photodegradation of polymers such as polyolefins the quenching of excited carbonyls as primary sensitizers is not a very important process. This is further supported

[†] The reaction in degassed solution was followed by VPC up to ten per cent conversion of the starting ketone which had an initial concentration of 2.5×10^{-3} .

by the fact that the addition of low volatility aliphatic ketones[†] does not significantly change the photodegradation rates of polypropylene stabilized only with the amount of antioxidant necessary to ensure reproducibility of the films pressed²⁸.

What other possibilities exist then which contribute to the light induced breakdown of polymers with aliphatic backbones? One agent which has been mentioned frequently in the last few years is singlet oxygen. Consequently Felder and Schumacher¹³ and Belluš, Lind and Wyatt²⁹ have investigated the ability of various types of compounds to quench singlet oxygen, produced either photochemically, i.e. by rose bengal and methylene blue, or chemically, i.e. by the hydrogen peroxide/hypochlorite reaction. For this purpose the disappearance of various singlet oxygen scavengers such as rubrene was followed.

Ia as well as some other secondary amines IIa, b and c did not show



significant quenching of singlet oxygen while the corresponding nitroxyls Ic as well as III a, b, c had a marked effect on the deactivation of the photo-induced oxygen addition of the indicators used. The *N*-methyl compounds IIb and IVa, b, c also slowed down the disappearance rate of the singlet oxygen indicators; however, it could be shown that oxidative demethylation of the tertiary amines by singlet oxygen occurred under these conditions²⁹. This renders the detection and quantification of any quenching effect impossible.

In Figure 8 the ratio of rubrene concentration in samples with and without additive after irradiation for ten minutes is given for various classes of compounds. As indicated before, the apparent high efficiency of *N*-methyl-2,2,6,6-tetramethylpiperidines is at least partly, if not wholly, due to chemical consumption of singlet oxygen. The next most effective class are the nickel chelates followed by the tetramethylpiperidine-*N*-oxyls. The secondary amines of the tetramethylpiperidine series as well as antioxidants of the sterically hindered phenol class have little or no quenching effect at the additive concentration (5×10^{-2} mol/l. in ethanol/benzene 1:1) used.

[†] 0.2 per cent each of nonadecanone-(2), nonadecanone-(9) and stearone corresponding to a carbonyl value (absorbance at 1718 cm^{-1}) in 0.1 mm films of 0.035, 0.035 and 0.02 respectively. A control film of the same composition and thickness but without added ketones shows a complete loss of mechanical properties at carbonyl values of 0.1 to 0.2.

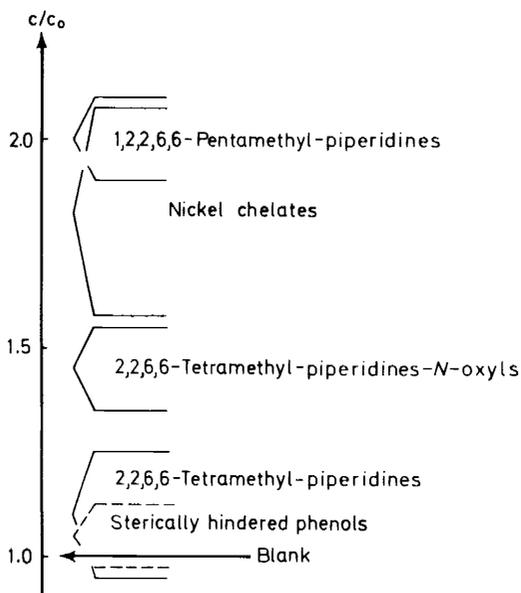
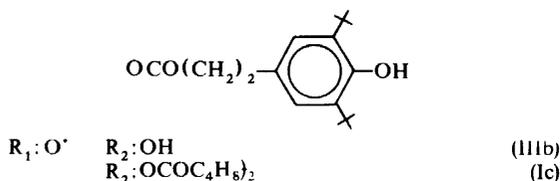
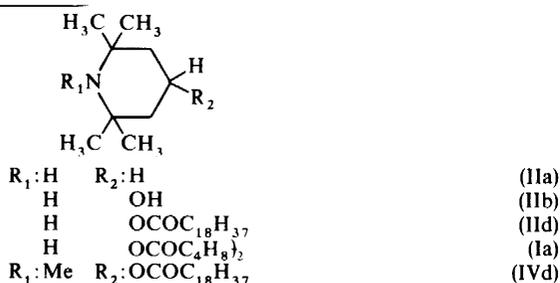
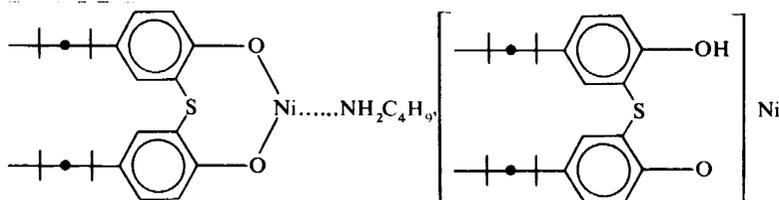


Figure 8. Singlet oxygen quenching efficiency of various classes of compounds. Further explanation is given in the text. The figure is constructed with results from the following compounds (from ref. 13):

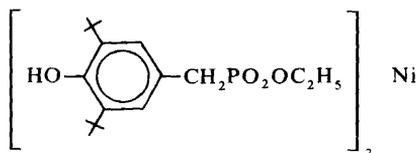
(i) 2,2,6,6-Tetramethyl-piperidines:



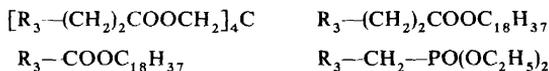
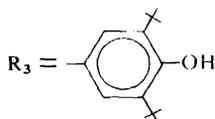
(ii) Nickel chelates



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(iii) Sterically hindered phenols



This allows the following conclusions:

- The quenching of primary sensitizers is not necessarily very important in antioxidant containing substrates, as has been pointed out above in the case of carbonyls.
- The deleterious effect of singlet oxygen is either not very important or its consequences can be healed in subsequent stabilization steps.
- The secondary and tertiary amines act by mechanisms of stabilization other than u.v.-absorption and quenching.

EXPERIMENTAL SECTION

The ground state pK-values were determined spectroscopically in buffer solutions or sulphuric acid with 20 per cent ethanol. The H_0 -values are based on the acidity function of Dolman and Stewart³⁰ (calibrated with diphenyl amines). The gradients of the logarithmic titration curves were 0.85 to 0.95 for benzotriazoles and 1.02 to 1.08 for benzophenones.

The pK*-values were calculated by the 'Förster cycle'³¹ with the O—O transitions as averages of the maxima of the fluorescence and the absorption bands. For 2-(4-hydroxyphenyl)-benzotriazole and for 2-(2-hydroxyphenyl)-benzoxazole this value corresponded within ± 0.5 unit with the one from fluorescence titration. For the non-fluorescent benzophenones the pK* had to be determined from the absorption spectra of acid and base alone. These values are inaccurate and are therefore given in brackets in *Table 1*.

The ionization potentials were calculated from the absorption maxima of the charge-transfer-spectra of the amines with iodine as the electron acceptor in heptane. These relative values were calibrated with absolute data obtained by photoelectron spectroscopy in the gas phase³² (four calibration points, adiabatic ionization potentials). The quenching constants

were obtained from the gradients of 'Stern-Vollmer plots' with fluorenone as sensitizer in acetonitrile:

$$\Phi_0/\Phi_Q = 1 + k_Q\tau_s[Q]$$

Φ_0 is the fluorescence intensity of the sensitizer without quencher and τ_s the lifetime of the first excited singlet state of the sensitizer. Φ_Q is the fluorescence intensity in the presence of a quencher in the concentration $[Q]$. k_Q is the quenching rate constant. In heptane, only triethylamine and 1,2,2,6,6-pentamethyl-piperidine were soluble enough to produce a measurable decrease of the fluorescence of fluorenone.

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