The Mechanism of Photoprotection of Wool by UV Absorbers of the 2-Hydroxybenzophenone Class

IAN H. LEAVER, *CSIRO, Division of Protein Chemistry, Parkville 3052, Australia*

Synopsis

The mechanism by which sulfonated 2-hydroxybenzophenone ultraviolet (UV) absorbers protect wool fabric against photoyellowing has been studied. The absorption and luminescence properties of two 2-hydroxybenzophenone-5-sulfonates and four 2-hydroxybenzophenone-2'-sulfonates are compared. The 2-hydroxy-benzophenones are nonfluorescent in wool, but they all show phosphorescence at room temperature. The phosphorescence is attributed to the phenolate anion produced by ionization of the hydroxyl group. The nature of substituents in the 3-position and 4-position of the phenolic ring is important in controlling the formation of luminescent species which may initiate unwanted photochemical reactions in wool. The protective screening effect of each absorber in wool fabric has been determined theoretically, using a method of analysis based on diffuse reflectance spectroscopy; the results are compared with the values determined experimentally by measuring the changes in yellowness that result when treated and untreated fabrics are exposed to fluorescent sunlamps (maximum energy at 310 nm). In all cases, UV screening was shown to be the important mode of photostabilization. The levels of photoprotection were much higher than those reported previously for treated fabrics that were exposed for long periods to simulated sunlight, behind glass. Possible reasons for the poor long-term performance of the 2-hydroxybenzophenones in wool are discussed.
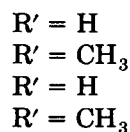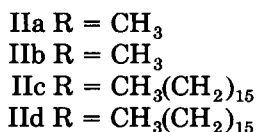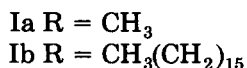
INTRODUCTION

Wool, in common with many textile fibers, is prone to photooxidation in sunlight. Prolonged exposure to sunlight affects the color, strength, and abrasion resistance of wool. Photoyellowing and phototendering are problems of considerable commercial importance, particularly in automotive upholstery fabrics which must have good durability to extremely harsh conditions of sunlight exposure and heat.[1]

Several approaches to the photostabilization of wool have been tried,[2,3] but the simple method of incorporating an ultraviolet (UV) absorber into the fiber to filter out the harmful radiation appears to be the most promising one.[1] Many sulfonated absorbers of the 2-hydroxyphenylbenzotriazole,[4,5] 2-hydroxybenzophenone,[6-9] and 2-hydroxyphenyl-s-triazine classes[10,11] have been synthesized and tested as photoprotective agents for wool. All three types of UV absorber have a phenolic group which is capable of forming an intramolecular hydrogen bond with an adjacent oxygen or nitrogen atom. The photoprotective effectiveness of these absorbers is highly dependent on the nature and the location of substituents in the 2-hydroxyphenyl ring.[4-11] In general, the protection that these compounds give to wool is much less than would be expected on the basis of the UV screening effect.[1,12,13] The poor performance

of some 2-hydroxyphenylbenzotriazole sulfonates in wool has been attributed[13-15] to hydrogen bonding interactions, involving the protein substrate, which disrupt the intramolecular hydrogen bond that is essential for photostability. The recent discovery[4,5] of highly effective benzotriazole photostabilizers in which the phenolic group is flanked by a bulky alkyl or aralkyl group shows that it is important to hinder the formation of intermolecular hydrogen bonds between the absorber molecules and the surrounding medium.

This paper reports on the absorption properties and photoprotective effects of sulfonated UV absorbers based on the 2-hydroxybenzophenone structure. The following compounds were selected from a wide range of structurally modified 2-hydroxybenzophenones that have previously[8,9] been synthesized and tested as photoprotective agents for wool.

Ia R = CH_3
Ib R = $CH_3(CH_2)_{15}$

IIa R = CH_3 R' = H
IIb R = CH_3 R' = CH_3
IIc R = $CH_3(CH_2)_{15}$ R' = H
IId R = $CH_3(CH_2)_{15}$ R' = CH_3

Two variations in structure that lead to an improvement in performance are (a) the introduction of a methyl group adjacent to the hydroxyl group (compounds IIb and IId)[9] and (b) an increase in the chain length of the 4-alkoxy substituent (compounds Ib, IIc and IId).[8,9] The aim of this work is to compare the absorption behavior of the various compounds in wool, and to investigate the manner in which structural modifications to the 2-hydroxybenzophenone molecule bring about changes in its photoprotective effectiveness.

EXPERIMENTAL

Materials

The plain-weave fabric was made from 20 μm Merino wool, and had a density of 140 gm^{-2}. The sulfonated 2-hydroxybenzophenone absorbers were kindly provided by Dr. B. Milligan. The sytheses of the absorbers, and the methods for applying them to wool, are described elsewhere.[8,9] The absorbers were usually applied from aqueous solution at pH 2 (using 4% owf sulfuric acid). In some cases the application was carried out at pH 4 (using 2% owf acetic acid). Absorber concentrations in wool refer to the amount of material actually applied to the fabric.

SPECTRAL MEASUREMENTS

Two types of reflectometer were used to measure the diffuse reflectance of wool fabrics. Point-by-point measurements of reflectance were made using a Perkin Elmer MPF-3L spectrofluorimeter that was fitted with a sample holder having an optical geometry of normal incidence and near-normal viewing of

the reflected radiation.[12,16] Reflectance spectra were obtained with a Perkin-Elmer 575 spectrophotometer, fitted with an integrating sphere accessory. Fluorescence quenching data were obtained with the Perkin Elmer MPF-3L spectrofluorimeter, using the same front-surface sample holder that was used for the reflectance measurements. Phosphorescence spectra were obtained using the phosphoroscope accessory supplied with the spectrofluorimeter. Details of the apparatus and procedures are given elsewhere.[12,14,16]

EXPOSURES

The photoprotective effectiveness of the 2-hydroxybenzophenones was assessed by their ability to retard the photoyellowing of wool fabric during exposure to UV radiation. Treated and untreated fabric samples were exposed, for either 20 h or 40 h, to the unfiltered output (maximum energy at 310 nm) from two fluorescent erythemal sunlamps (Toshiba FL 20E/E). Details of the irradiator have been described previously.[12,17] Yellowness indexes (ASTM-D 1925-70) were measured with a Gardner Spectrogard Color System.

RESULTS AND DISCUSSION

Absorption Properties

Diffuse reflectance spectra of wool fabrics containing different amounts of sodium 2-hydroxy-4-methoxybenzophenone-5-sulfonate (Ia, Cyasorb UV 284) are shown in Figure 1. Fabrics treated with the hexadecyloxy compound (Ib) gave similar spectra. The absorption of both compounds is very strong in the 300–350 nm region, and the fabric reflectance decreases sharply with increasing concentration of absorber, reaching a limiting value of 0.03 at an absorber concentration of 2%. Increasing the concentration of the absorber gives no further change in reflectance.
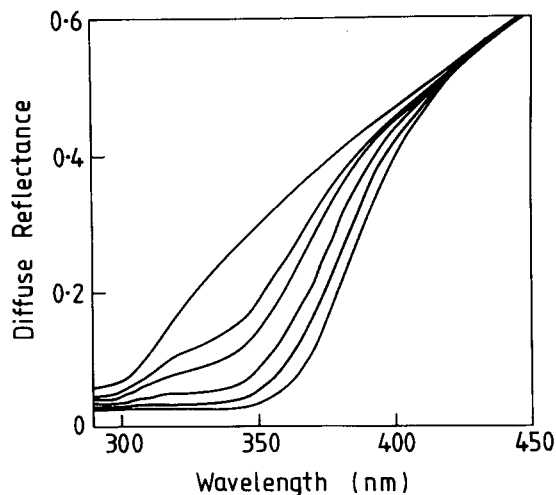

Fig. 1.   Diffuse reflectance spectra of wool fabrics containing different amounts of absorber Ia. Absorber concentrations (from top to bottom): 0, 0.10, 0.19, 0.49, 0.98, 1.94%.

This small residual reflectance actually stems from fluorescent, rather than reflected radiation. The weak, natural fluorescence of wool can be a source of serious error[12] when making reflectance measurements on fabrics that absorb strongly in the UV region of the spectrum. For this reason, the analyses that follow are based on reflectances obtained using a dual monochromator spectrofluorimeter, fitted with a specially constructed front-surface sample holder;[12,16] this technique yields reflectance values which are more accurate than those taken directly from the recorded spectra.

The absorption spectra of the 2-hydroxybenzophenones in wool were calculated from the reflectances of treated and untreated fabrics using a method of analysis[12] based on the Kubelka-Munk[18] remission function, which relates the reflectance R to the absorption coefficient K and scattering coefficient S of the material,

$$K/S = (1 - R)^2/2R \qquad (1)$$

The difference ($\Delta K/S$) between the K/S value of the absorber-treated fabric and that of the untreated fabric gives the absorption coefficient increment contributed by the absorber,[12]

$$\Delta K/S = k_{uv} \cdot c/S \qquad (2)$$

where k_{uv} is the coefficient of absorption per unit concentration of absorber, and c is the absorber concentration. The relative absorption coefficient (k_{uv}/S) of the absorber at a given wavelength is obtained[12] from a plot of the Kubelka-Munk remission function against the absorber concentration. Four layers of fabric were sufficient to give a sample that could be considered as "infinitely thick," as required by the Kubelka-Munk treatment.

The calculated absorption spectra of the 4-methoxy and 4-hexadecyloxy-substituted 2-hydroxybenzophenones in wool fabric are shown in Figures 2A and 2B, respectively. The spectra of the 2-hydroxybenzophenone-2′-sulfonates (compounds IIa and c) show a small hypsochromic shift relative to the spectra of the 2-hydroxybenzophenone-5-sulfonates (compounds Ia and b). This shift is greatly enhanced by the introduction of a 3-methyl group (compounds IIb and d). The presence of a long 4-alkoxy group can have a significant chromophoric effect, depending on the position of the sulfonate group. A comparison of the spectra of compounds Ib and IIc (Fig. 2B) shows that the absorption is much more intense when the sulfonate group is adjacent to the 4-hexadecyloxy substituent (filled circles) than when it is situated in the adjoining ring (open circles). The same compounds show little difference in absorptivity in water (ϵ_{321} = 9,630 M$^{-1} \cdot$ cm^{-1} for Ib[8], ϵ_{318} = 9,470 M$^{-1} \cdot$ cm^{-1} for IIc[9]).

Figure 3 illustrates the linearity that is attained when the Kubelka-Munk reflectance function is plotted against the absorber concentration. The calibration plots usually show good linearity up to an absorber concentration of 2%. However, to avoid errors arising from nonlinear behavior in the high concentration region, particularly at wavelengths below 320 nm where the fabric itself absorbs quite strongly, the absorber concentration range was restricted to 0–1% between 320 nm and 380 nm and to 0–0.5% at 300 nm.
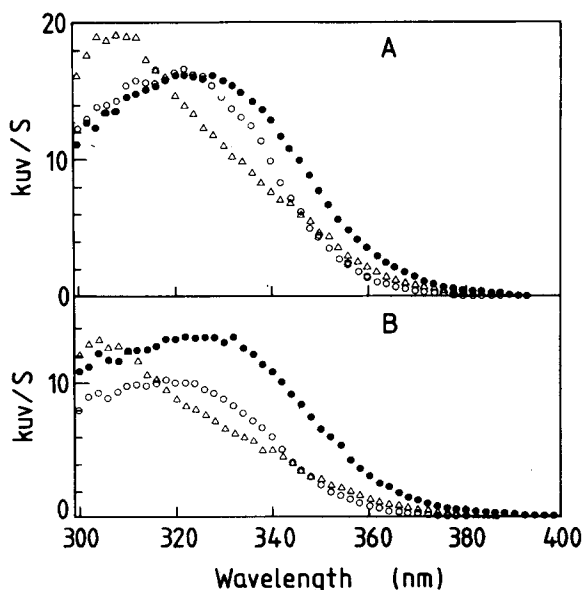
Fig. 2. Relative absorption coefficients of 4-methoxy-substituted (A) and 4-hexadecyloxy-substituted (B) 2-hydroxybenzophenone sulfonates in wool fabric. A: R = CH$_3$, (●) Ia, (○) IIa (R′ = H), (△) IIb (R′ = CH$_3$). B: R = CH$_3$(CH$_2$)$_{15}$, (●) Ib, (○) IIc (R′ = H), (△) IId (R′ = CH$_3$).

An interesting feature of these plots is the marked variation in the degree of scatter of the K/S ratios, depending on whether the absorber has a long or a short side chain. The scatter in the values obtained for Ib (solid symbols in Fig. 3) was typical of that observed with fabrics that had been treated with hexadecyloxy substituted 2-hydroxybenzophenones, suggesting that absorbers with a long alkoxy side-chain are not taken up evenly by the fabric during application. The effect is more pronounced at high concentrations than at low concentrations.
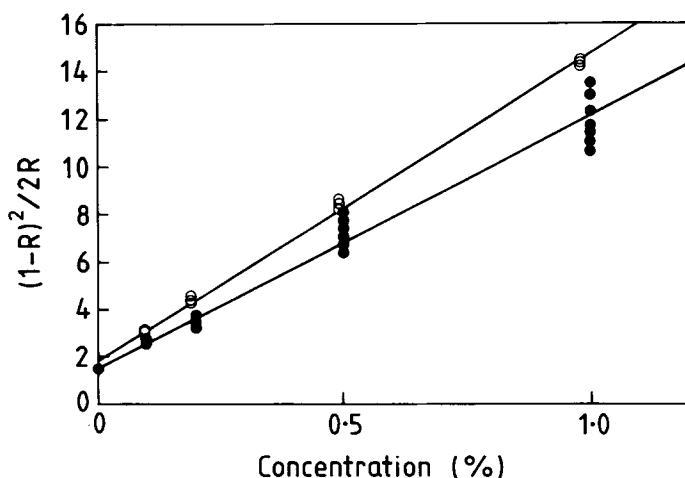

Fig. 3. Dependence of the Kubelka-Munk function on absorber concentration: (○) 4-methoxy derivative (Ia) and (●) 4-hexadecyloxy derivative (Ib) of 2-hydroxybenzophenone-5-sulfonate.

UV absorber	Substituents		Improvement factor (r^{-1})				
	R	R'	300	320	340	360	380 nm
Ia	CH_3	—	2	5	7	4	1–2
Ib	$CH_3(CH_2)_{15}$	—	2	5	7	4	1–2
IIa	CH_3	H	2	5	6	2	1
IIb	CH_3	CH_3	3	5	5	3	1–2
IIc	$CH_3(CH_2)_{15}$	H	2	4	4	2	1
IId	$CH_3(CH_2)_{15}$	CH_3	2	4	4	2	1
III	(2-hydroxyphenylbenzotriazole)[a]		3	7	11	9	3

[a] Taken from Ref. 13.

THEORETICAL PROTECTIVE SCREENING EFFECT

The theoretical screening effect of a UV absorber in a polymer has been defined[19] as the inverse of the residual absorption (r), where r is the fraction of the incident radiation that is absorbed by the substrate in the presence of an absorber. The residual absorption is thus a measure of the susceptibility of the material to photooxidation. The smaller the numerical value of r, the better is the protective effect of the absorber. The screening effect of a UV absorber in wool fabric can be calculated in a similar fashion by using the following expression for the residual absorption:[12]

$$r = \frac{[1/R_s - 1]}{[1/R - 1]} \tag{3}$$

where R, R_s are the reflectances of the absorber-treated and untreated fabrics, respectively, at a given wavelength.

Table I shows the theoretical improvement in light stability (r^{-1}) that can be achieved by treating wool fabric with each of the benzophenone absorbers at the 1% level. The values obtained previously[13] for the benzotriazole absorber, sodium 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole sulfonate (III), are included for comparison. The calculated improvement factors clearly show that all six benzophenones are capable of giving good protection in the UV region between 320 and 340 nm. The influence of the strong protein absorption around 300 nm is evidenced by a significant decrease in screening power at this wavelength. The screening efficiency of the benzophenones in the long wavelength region of the UV spectrum is generally rather poor, although a moderate level of protection (up to 360 nm) could possibly be achieved by using the 2-hydroxybenzophenone-5-sulfonates, which have somewhat stronger absorption in this region than the 2-hydroxybenzophenone-2'-sulfonates. None of the benzophenones absorbs as strongly, or over as wide a spectral region, as does the 2-hydroxyphenylbenzotriazole sulfonate (III), the useful absorbing range of which extends up to 380 nm.

ABSORBER DISTRIBUTION IN THE FIBER

The rationale behind the synthesis of 2-hydroxybenzophenone absorbers with long alkyl side chains was to try and achieve a "ring-dyeing" effect

during the application of these compounds to wool.[8] In this way it was hoped that any damage to the wool caused by exposure to light might be confined to the surface of each fiber, thereby protecting the bulk of the material from photodegradation. A microscopic examination of cross-sections of treated fibers indicated[8] that absorbers of this type were located preferentially near the fiber surface.

It is well known[20-22] that the reflectance, and hence the color, of a dyed fabric is related to the distribution of dye in the fibers of which the fabric is composed. The reflectivity of a fabric comprised of ring-dyed fibers is generally greater than that of an evenly dyed sample, for the same amount of dye present in the fiber.

Spectral evidence for ring dyeing in absorber-treated wool fabrics was sought by determining the relative absorption coefficients of fabrics, containing the three hexadecyloxy-substituted benzophenones, before and after treatment with formic acid. Wool swells extremely rapidly when immersed in anhydrous formic acid at room temperature, and a brief treatment with formic acid has been used[8] to achieve a uniform distribution of sulfonated long-chain-substituted 2-hydroxybenzophenones which fail to penetrate the fiber during conventional application. The results are summarized in Table II.

In no case did the formic acid treatment of wool lead to an increase in fabric absorptivity, as might be expected if a significant redistribution of the absorber had occurred. In the case of the 2-hydroxybenzophenone-5-sulfonate (compound Ib), the removal of absorber from the fabric during the formic acid treatment resulted in a small decrease in absorption. The fluorescence yields of the absorber-treated fabrics, likewise, were not significantly affected by the formic acid treatment (see Table II). The optical quenching of the fluorescence of wool was analyzed theoretically[14] using a simplified form of an equation, derived by Allen[23] and Morton,[24] which relates the luminescence yield of a scattering material to its diffuse reflectance properties. The experimental fluorescence ratios were in accord with the calculated values (see Table II), assuming a uniform distribution of absorber.

From the data in Table II it can be concluded that the UV screening efficacy of the long-chain-substituted 2-hydroxybenzophenones is not affected by the absorber distribution within the fiber. Although a microscopic examination of cross-sections of fibers treated with Ib has previously revealed[8]

TABLE II
Effect of Formic Acid Treatment on the Absorption and Fluorescence Properties
of Fabrics Containing 4-Hexadecyloxy-Substituted 2-Hydroxybenzophenones

UV Absorber	After treatment	k_{uv}/S (340 nm)	Fluorescence intensity[a]	
			Exptl.	Calc.
Ib	—	10.7	0.16	0.18
Ib	Formic acid	8.7	0.17	
IIc	—	5.8	0.40	0.42
IIc	Formic acid	5.4	0.43	
IId	—	4.9	0.47	0.52
IId	Formic acid	4.8	0.51	

[a]Measured relative to the fluorescence intensity of untreated wool fabric. The excitation wavelength was 340 nm, and the emission was monitored at 450 nm.

evidence for ring dyeing, the effect of incomplete penetration on the amount of UV radiation that is actually absorbed by the wool appears to be negligible. It is possible that the influence of a moderate ring-dyeing effect might be obscured by the nonuniform distribution of the absorber in the fabric (see Fig. 3). If this were so, then the protective screening effect of the absorber would depend, not only on the annular distribution of the absorber within each fiber, but also on the concentration profile of the absorber across the fabric.

LUMINESCENCE PROPERTIES

The exceptionally high photostability of 2-hydroxybenzophenones is attributed[25] to the occurrence, in the excited state, of a rapid intramolecular proton transfer reaction which provides an efficient pathway for dissipating the absorbed energy. Radiative deactivation processes, such as fluorescence and phosphorescence, seldom occur at room temperature. The emission of radiation from such molecules is an indication that the internal hydrogen bond has been disrupted, probably by hydrogen bonding interactions between the absorber and the substrate. The low photoprotective efficiency of the 2-hydroxyphenylbenzotriazole sulfonate (III) in wool has been explained[13–15] on this basis.

None of the 2-hydroxybenzophenones studied in this work exhibited fluorescence emission at room temperature. The only detectable fluorescence was that originating from the wool itself. The quenching of this emission was satisfactorily accounted for by the UV screening action of the absorber. All of the benzophenones did, on the other hand, phosphoresce at room temperature. The relative phosphorescence intensities and lifetimes of treated fabrics, measured in the presence of air and after flushing the sample with oxygen-free nitrogen, are given in Table III.

All six 2-hydroxybenzophenones showed phosphorescence when the absorbers were applied to the wool from solutions acidified with acetic acid (pH = 4). In most cases the emission was strongly quenched in air, and

TABLE III
Room Temperature Phosphorescence Behavior of Wool Fabrics Containing Sulfonated
2-Hydroxybenzophenones (Absorber Concentration = 1%). Application pH = 4

UV Absorber	Excitation max. (±2 nm)	Relative phosphorescence intensity at 450 nm		Lifetime (ms)
		Air	Nitrogen	
Ia	390	0.09	0.42	> 3[a]
Ib	390	0.04	0.24	> 4
IIa	380	0.05	0.37	> 8
IIb	420	0.43	1.00 (0.68)[b]	2.4
IIc	380	< 0.01	0.22	> 8
IId	420	0.02	0.16 (0.31)[b]	> 3
Control wool	(420)	< 0.01	0.11	> 5

[a] The > symbol signifies that the decay of the phosphorescence emission was nonexponential; the value given is the approximate lifetime of the shortest component of the decay.

[b] Application pH = 2. Only the 3-methyl-substituted 2-hydroxybenzophenone sulfonates showed phosphorescence when the absorbers were applied to the wool at pH2.

vigorous outgassing of the sample with oxygen-free nitrogen was thus a prequisite for the detection of phosphorescence. The 3-methyl-substituted compound (absorber IIb) showed the strongest emission; it was the only compound to emit appreciable phosphorescence when the fabric sample was equilibrated in air. The persistence of the phosphorescence of this absorber in air is probably due to the short lifetime (2.4 ms) of the triplet state, which does not allow appreciable quenching of the emitting species by oxygen molecules as the latter diffuse through the fiber. In all other cases the phosphorescence decayed in a nonexponential fashion. The emission comprised a distribution of lifetimes ranging from 3 to about 40 ms, indicating the occurrence of a variety of hydrogen bonding interactions between the absorber molecules and the fiber substrate.

The pH at which the 2-hydroxybenzophenones were applied to wool also had a marked effect on their phosphorescence behavior. Only those benzophenones (compounds IIb and d) with a 3-methyl substituent phosphoresced when the absorbers were applied to wool from solutions acidified with sulfuric acid (pH = 2). Compound IId phosphoresced more strongly at pH 2 than at pH 4. The relative phosphorescence intensities of the fabrics treated at pH 2 are given in parentheses in Table III.

The maxima in the phosphorescence excitation spectra of the treated fabrics (see Table III) lie well outside the envelope of the absorption spectra of the 2-hydroxybenzophenones (see Fig. 2). In order to identify the phosphorescent species, the phosphorescence excitation spectrum of each absorber was measured in a film of poly(vinyl alcohol) and then compared to the absorption spectra of the undissociated and dissociated forms of the 2-hydroxybenzophenone in neutral and in alkaline solution, respectively (see Fig. 4). Apart from minor variations in intensities and absorption bandwidths, the phosphorescence excitation spectra were similar to the absorption spectra of the respective compounds in alkaline solution, showing that the phenolate
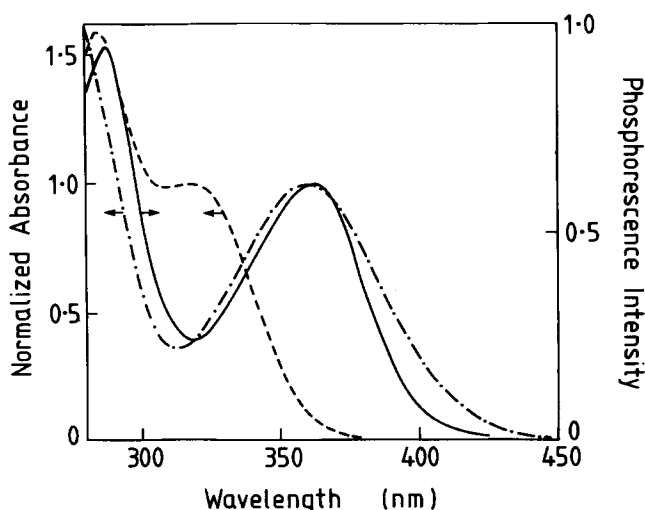

Fig. 4.   Corrected phosphorescence excitation spectrum of Ia in a film of poly(vinyl alcohol) (—) and the absorption spectrum of the phenolate anion of Ia in 10^{-5}M NaOH (– · –). The absorption spectrum of the undissociated absorber in water is shown by the dashed curve (- - -). The spectra have been normalized at the peak of the long wavelength absorption maximum.

anion, generated by the dissociation of the phenolic group, is the species that is responsible for the phosphorescence.

The pH dependence of the phosphorescence of the 2-hydroxybenzophenones in wool can thus be explained in terms of the acid/base behavior of the molecules in the adsorbed state. The anomalous ionization behavior of the 3-methyl-substituted benzophenones (compounds IIb and d) must derive from the influence of the methyl group on the stability of the intramolecular hydrogen bond. This effect may stem from a decrease in the acidity of the hydroxyl group, which would lessen its ability to form a stable intramolecular hydrogen bond[19] with the carbonyl group. The ground state pKa values for the methyl-substituted compounds (IIb and IId) are about one unit higher than those for the unsubstituted compounds (L. A. Holt, personal communication), showing that the methyl group does have an influence on the acidity of the hydroxyl group.

The influence of the long alkyl side chain on the phosphorescence behavior of the 2-hydroxybenzophenones is noteworthy. The replacement of the 4-methoxy group (in compounds Ia, IIa and IIb) with a 4-hexadecyloxy group resulted in a significant decrease in the intensity of the phosphorescence emission (Ib verssus Ia, IIc versus IIa, and IId versus IIb). A probable explanation for this result is that the long alkyl side chain sterically inhibits the interaction between the hydroxyl group of the benzophenone and the surrounding medium, thereby reducing the effects of hydrogen bonding interactions between the adsorbed molecules and the substrate.

PHOTOPROTECTION OF WOOL

Fabric samples were exposed to the unfiltered output of fluorescent erythemal sunlamps (maximum energy at 310 nm) in order to assess the UV screening effectiveness of each absorber under conditions where the substrate exhibits strong absorption. The protective effect of the absorber was measured in terms of the ratio of the yellowness index increments $\delta(YI)$ and $\delta(YI)_0$ for treated and untreated fabrics, respectively. The results are given in Figure 5.

All six 2-hydroxybenzophenones protected wool from photoyellowing. 2-Hydroxybenzophenones with a 4-methoxy group (solid symbols) were slightly more effective than those with a 4-hexadecyloxy group (open symbols), but allowing for differences in absorptivity (see Fig. 1), changes in molecular structure generally had very little influence on photoprotection. The levels of photoprotection given by the absorbers are in quite good agreement with the predicted improvement factors (see Table I), based on UV screening at 300 nm. An accurate comparison of the theoretical and experimental values is not possible because of the rather broad envelope of the lamp output (50% of peak emission at 293 nm and 330 nm), but the protection given to the wool under these conditions of irradiation would seem to be close to the maximum value that can be achieved by UV screening.

The results in Figure 5 clearly show that the sulfonated 2-hydroxybenzophenones have adequate absorbing power to protect wool fabric against photodegradation, even when the incident radiation is strongly absorbed by the wool. Even higher levels of photoprotection are predicted (see Table I) when fabrics are exposed to wavelengths between 320 and 360 nm; these
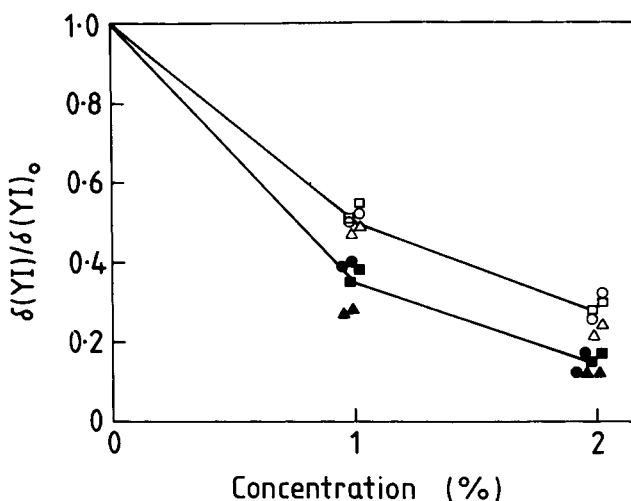
Fig. 5. Effect of absorber concentration on the photoyellowing of wool fabric caused by exposure to fluorescent sunlamps (maximum energy at 310 nm). Solid symbols: R = CH$_3$, (●) Ia, (■) IIa (R′ = H), (▲) IIb (R′ = CH$_3$). Open symbols: R = CH$_3$(CH$_2$)$_{15}$, (○) Ib, (□) IIc (R′ = H), (△) IId (R′ = CH$_3$). The left-hand and right-hand symbols in each pair of data refer to exposure periods of 20 h and 40 h, respectively.

wavelengths are mainly responsible for the damage that occurs in wool when fabrics are exposed to sunlight behind window glass. Exposure tests have shown,[8,9] however, that compounds Ia and IIa give very little photoprotection to wool when fabrics are exposed for long periods to simulated sunlight. Wool treated with Ia actually yellows more than untreated wool after exposure to sunlight behind glass.[9] An improvement in performance is achieved[8] by the introduction of a 3-methyl group or (in the case of the 2-hydroxybenzophenone-5-sulfonates) by increasing the chain length of the 4-alkoxy substituent, but the level of photoprotection is still much smaller than that predicted on the basis of UV screening (see Table I).

Four reasons for the moderate improvement in photoprotection brought about by the introduction of a long alkyl substituent into the phenolic ring have been advanced.[8] Of these, increased absorption by the 4-hexadecyloxy-substituted absorbers can be ruled out, since the absorption coefficients of compounds Ib, IIc, and IId in wool are smaller (on a weight basis) than those of the 4-methoxy analogues. The preferential location of the 4-hexadecyloxy substituted absorbers at the fiber surface is also unlikely to have an effect on photoprotection, for reasons that were discussed previously. It is probable that the long alkyl side chain in the molecule functions by shielding the hydroxyl group from the hydrogen bonding influence of the fiber, thereby reducing the tendency of the substrate to disrupt the intramolecular hydrogen bond, which is essential for photostability. The alternative explanation, that absorbers with long side chains are preferentially adsorbed in nonpolar regions of the fiber which offer a more favorable environment for the preservation of the intramolecular hydrogen bond, would also be consistent with the observed luminescence behavior of the molecules.

Changes in photoprotective effectiveness stemming from the introduction of an alkyl substituent ortho to the hydroxyl group may be due to a combination of factors. On the one hand, any increase in the degree of ionization of the 2-hydroxybenzophenone in wool would be likely to have a deleterious effect on photostability. The phenolate anion of the 2-hydroxyphenylbenzotriazole (III) is known[15] to act as a photosensitizer and promote the photodegradation of wool[14,15] even in visible light. It is interesting to note[9] that compounds Ia and Ib both accelerate photoyellowing when wool fabrics are exposed to sunlight behind glass. The hypsochromic shift in absorption (see Fig. 1) caused by the introduction of a 3-alkyl group would tend to reduce further the protective effectiveness. On the other hand, a bulky substituent in the 3-position might be expected to improve the performance of the absorber by shielding the internal hydrogen bond from the polar groups in the fiber.[19] The most effective 2-hydroxyphenylbenzotriazolesulfonates[4,5] are those which have a t-butyl group adjacent to the hydroxyl group. However, results obtained in another study[9] show that sulfonated 2-hydroxybenzophenones possessing a t-butyl group in the 3-position are not particularly effective photoprotective agents for wool.[9] Thus, steric effects appear to be less important in 2-hydroxybenzophenones than in the analagously substituted 2-hydroxyphenylbenzotriazoles.[4,5]

CONCLUSIONS

The mechanism of the photoprotection of wool by a range of 2-hydroxybenzophenones has been examined. At the 1% level of application, the 2-hydroxybenzophenones have adequate absorption to protect fabrics from photodegradation by those wavelengths (300–360 nm), present in sunlight, which are most damaging to wool. 2-Hydroxybenzophenone-5-sulfonates show slightly stronger absorption than 2-hydroxybenzophenone-2'-sulfonates at wavelengths beyond 360 nm.

All of the benzophenones studied in this work retard photoyellowing when treated wool fabrics are exposed to fluorescent sunlamps (maximum energy at 310 nm). The levels of protection achieved under these exposure conditions are in accord with the predicted values based on UV absorption. In practice, however, the sulfonated 2-hydroxybenzophenones give little, if any, protection to wool against photoyellowing. The poor long-term performance of these absorbers may stem from the formation of luminescent species, such as the phenolate anion, which can initiate unwanted photochemical reactions that lead to a deterioration in fiber properties, and thus counteract the beneficial screening effect of the absorber.

Fabrics treated with sulfonated 2-hydroxybenzophenones at pH 4 all show phosphorescence at room temperature. The decay of the phosphorescence (emitted by the phenolate anion) is generally nonexponential, suggesting that the wool fiber presents a variety of hydrogen bonding environments to the absorber molecules. The nature of substituents in the 3-position and 4-position of the phenolic ring is important in controlling the degree of ionization of the 2-hydroxybenzophenones in wool.

References

1. L. A. Holt, I. H. Leaver, B. Milligan, P. J. Waters, and J. F. K. Wilshire, *Proc. 7th Int. Wool Text. Res. Conf., Tokyo*, **IV**, 31 (1985).

2. Nicholls, C. H., in *Developments in Polymer Photochemistry - 1*, N. S. Allen, Ed., Applied Science, London, 1980, p. 125.

3. J. A. Maclaren and B. Milligan, in *Wool Science. The Chemical Reactivity of the Wool Fibre*, Science Press, Marrickville, NSW, 1981, Ch. 13.

4. N. A. Evans, I. H. Leaver, J. Rosevear, P. J. Waters, and J. F. K. Wilshire, Intern. Pat. Appl. PCT/AU83/00179 (1983).

5. N. A. Evans, J. Rosevear, P. J. Waters, and J. F. K. Wilshire, *Polym. Degrad. Stab.*, **14**, 263 (1986).

6. J. Cegarra, J. Ribe, and P. Miro, *J. Soc. Dyers Colour*, **88**, 293 (1972).

7. W. G. Rose, M. K. Walden, and J. E. Moore, *Textile Res. J.*, **31**, 495 (1961).

8. B. Milligan and L. A. Holt, *Polym. Degrad. Stab.*, **5**, 339 (1983).

9. B. Milligan and L. A. Holt, *Polym. Degrad. Stab.*, **10**, 335 (1985).

10. P. J. Waters, N. A. Evans, and B. Milligan, *Proc. 7th Int. Wool Text. Res. Conf., Tokyo* **IV**, 60 (1985).

11. N. A. Evans, B. Milligan, and P. J. Waters, Australian Pat. Appl. PG8461/84 (1984).

12. I. H. Leaver, *J. Polym. Sci.: Polym. Chem. Ed.*, **20**, 2417 (1982).

13. C. M. Carr, I. H. Leaver, and J. F. K. Wilshire, *Proc. 7th Int. Wool Text. Res. Conf., Tokyo* **IV**, 50 (1985).

14. I. H. Leaver, *J. Polym. Sci.: Polym. Chem. Ed.*, **20**, 2429 (1982).

15. I. H. Leaver, P. J. Waters, and N. A. Evans, *J. Polym. Sci.: Polym. Chem. Ed.*, **17**, 1531 (1979).

16. I. H. Leaver, *Aust. J. Chem.*, **32**, 1961 (1979).

17. I. H. Leaver, *Text. Res. J.*, **48**, 610 (1978).

18. P. Kubelka and F. Munk, *Z. Tech. Phys.*, **12**, 593 (1931).

19. H. J. Heller, *Eur. Polym. J. Suppl.*, 105 (1969).

20. D. A. Garrett and R. H. Peters, *J. Text. Inst.*, **47**, T166 (1956).

21. T. H. Morton, *J. Soc. Dyers Colour*, **92**, 149 (1976).

22. Y. H. Lee and D. Patterson, *J. Soc. Dyers Colour*, **101**, 314 (1985).

23. E. Allen, *J. Opt. Soc. Am.*, **54**, 506 (1964).

24. T. H. Morton, *J. Soc. Dyers Colour*, **79**, 238 (1963).

25. N. S. Allen, *Polym. Photochem.*, **3**, 167 (1983).