

Photoprotective Agents for Wool. Synergism Between UV Absorbers and Antioxidants

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Synopsis

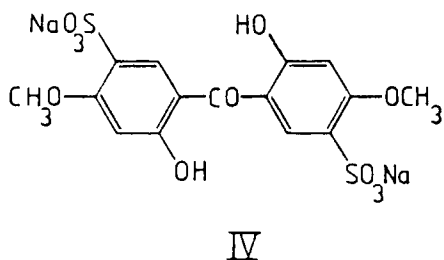
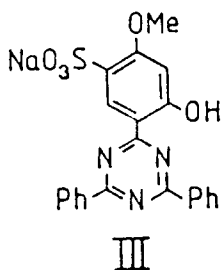
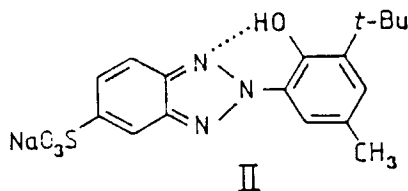
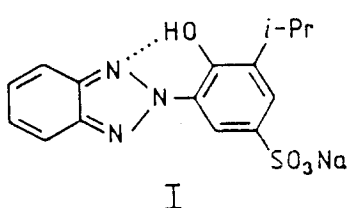
Several antioxidants alone, and in combination with sulfonated UV absorbers, have been evaluated as photoprotective agents for wool. Mixtures of phenolic antioxidants and sulfonated UV absorbers of the 2-hydroxyphenylbenzotriazole class were found to exhibit synergistic behavior; the most effective UV absorber also gave the strongest synergistic effect with the antioxidants. Of the systems studied, the hindered phenol, calcium bis ((ethyl-(3,5-di-*t*-butyl-4-hydroxybenzyl)-phosphonate)) (Irganox 1425), when used in conjunction with a sterically hindered benzotriazole-sulphonate, afforded wool the best protection against photoyellowing and phototendering in sunlight, behind window glass. Sulfonated derivatives of hindered phenols acted synergistically with UV absorbers when treated fabrics were exposed to an artificial light source, but not when fabrics were exposed to sunlight through glass.

INTRODUCTION

Prolonged exposure to sunlight affects the color, strength, and abrasion resistance of wool, and numerous photoprotective treatments have been examined in an effort to minimize the damage. One of the most effective methods of photoprotection involves the application of a sulfonated UV absorber.¹ Many sulfonated absorbers of the 2-hydroxybenzophenone,² 2-hydroxyphenylbenzotriazole,^{3,4} and 2-hydroxyphenyl-*s*-triazine^{5,6} types have recently been synthesized and evaluated as photoprotective agents for wool. Some of these absorbers give very good protection against phototendering; however they are usually less effective against photoyellowing, particularly when treated fabrics are exposed to sunlight through window glass.¹⁻⁶

Mixtures of UV absorbers and antioxidants sometimes give better photoprotection than do the individual components,^{7,8} and the photostability of polymers can often be markedly improved by the careful selection of stabilizer compositions which function synergistically. Particularly effective antioxidants in this regard are peroxide decomposers and free radical scavengers which can diffuse to the sites in the polymer where the photoreactions occur. Recently it was reported⁹ that antioxidants which carry a hindered phenol moiety enhance the protective effect of a sulfonated 2-hydroxyphenylbenzotriazole UV absorber in wool. In this paper we examine the ability of antioxidants to enhance further the protection already afforded to wool by a selection of sulfonated UV absorbers. Absorbers studied included the *i*-propyl and the *t*-butyl 2-hydroxyphenylbenzotriazoles (I and II), a 2-hydroxyphenyl-*s*-triazine (III) and a commercial 2,2'-dihydroxybenzophenone (Uvinul DS49,

BASF) (IV):



Scheme 1.

EXPERIMENTAL

Materials

The wool was a plain weave fabric woven from 20 μm Merino wool. The syntheses of the sulfonated benzotriazole absorbers^{3,4} and the sulfonated triazine absorber⁶ are described elsewhere. Uvinul DS 49 was a gift from BASF, Australia. Calcium bis((ethyl-(3,5-di-*t*-butyl-4-hydroxybenzyl)phosphonate)) (Irganox 1425) was supplied by Ciba Geigy Australia Ltd. Two sulfonated hindered phenols were kindly provided by Dr. B. Milligan, and a sulfonated hindered amine was kindly provided by Mr. P. J. Waters.

Treatments

Sulfonated absorbers were applied to wool fabric using an Ahiba dyeing machine. Fabric samples were treated with an aqueous solution (liquor: wool ratio = 60:1) containing the absorber, sodium sulfate (5% owf), and sulfuric acid (4% owf). The temperature of the dyebath was raised from 50 to 80°C over 45 min, and kept at 80°C for 15 min. Sulfonated antioxidants (5% owf) and UV absorber were applied concurrently.

Irganox 1425 was applied as an aqueous dispersion by adding a mixture containing equal amounts of antioxidant and dispersing agent, Teric 16A22 (ICI Australia Operations Pty. Ltd.), to the dyebath at 45°C. The bath temperature was raised to 95°C over 45 min and then maintained at the boil for 30 min. Bleaching with 6% (owf) sodium formaldehydesulfoxylate (Blankit D, BASF) was carried out concurrently with the application of UV absorber.

Tensile Tests and Yellowness Index Measurements

An Instron tensile testing machine was used to measure the tear strengths of the irradiated and unirradiated fabrics. Tear strengths were assessed by the method described in ASTM-D2261. Lifetime improvement factors were determined as previously described.¹⁰ Yellowness indexes (ASTM-D1925-70) were measured with a Gardner Spectrogard Color System. The yellowness index of each fabric was taken as the mean of four readings, obtained with a single layer of fabric placed against a black background.

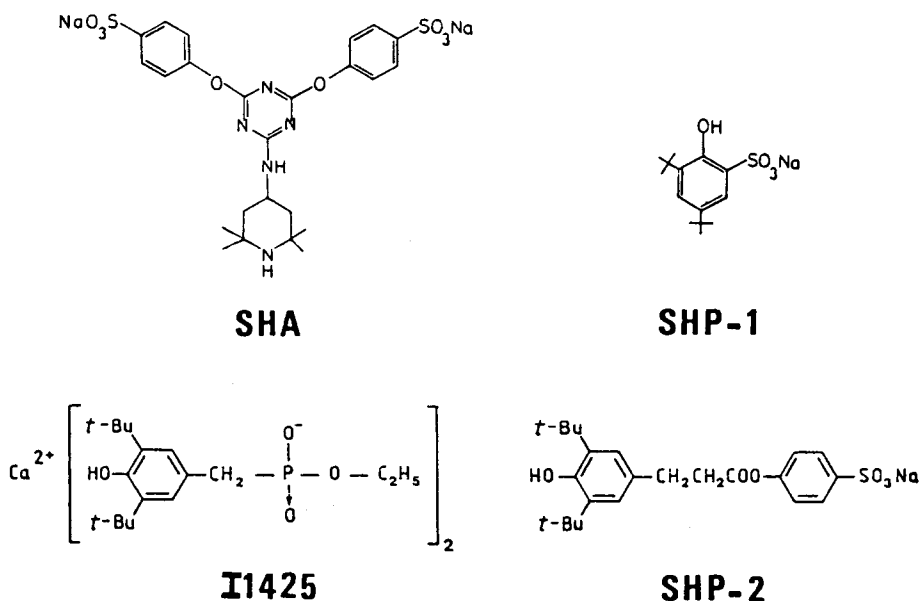
Exposures

Simulated sunlight tests were conducted using a Philips ML 500W mercury vapor/tungsten filament lamp. Details of the lamp irradiators are described elsewhere.¹⁰ Sunlight exposures (behind window glass) were carried out in Melbourne from December 1984 to May 1985, with fabric samples inclined at 20° to the horizontal and facing north.

RESULTS AND DISCUSSION

Artificial Exposure Tests

The initial study involved the evaluation in wool of a large range of commercially available antioxidants, comprising nickel chelates, hindered phenols, hindered amines, phosphites, organometallic compounds, and sulfur-containing compounds. More than 30 compounds were tested, alone and in combination with the *i*-propyl and the *t*-butyl benzotriazole absorbers (I and II). Three water-soluble antioxidants, namely two hindered phenols (SHP-1 and SHP-2) and a hindered amine (SHA), were also examined. The tests were



Scheme 2.

TABLE I
Effect of UV Absorber I and Antioxidants on the Photoyellowing
and Phototendering on Wool Fabric, Caused by Exposure to
Simulated Sunlight^a for 336 h at 75°C

Absorber (5% owf)	Antioxidant (5% owf)	Yellowness index			Tear strength improvement factor ^b
		Unexposed	Exposed	Difference	
—	—	14	50 (40) ^c	36	1.0
I	—	13	36 (33)	23	1.7
I	I1425	15	30 (28)	15	2.2
—	I1425	16	47 (37)	31	1.1
I	SHP-1	13	33	20	1.4
—	SHP-1	13	55	42	0.9
I	SHP-2	13	29 (28)	16	1.9
—	SHP-2	14	49 (42)	35	1.2
I	SHA	13	36	23	1.5
—	SHA	13	52	39	1.1

^a Philips 500-W mercury vapor/tungsten filament lamp.

^b Lifetime improvement factor based on tear strength data.

^c Figures in parentheses refer to samples which were exposed for 2000 h at 45°C.

carried out using an artificial light source to simulate the effects of sunlight exposure.

Of all the antioxidants studied, only those which contained a hindered phenol moiety showed any useful synergistic effect with the UV absorbers. When applied alone, the antioxidants afforded little or no protection. Irganox 1425 (I1425) was the most effective antioxidant when used in combination with I (Table I); it gave a significant improvement in strength retention as well as giving added protection against photoyellowing. Most of the solvent-soluble antioxidants tested gave no enhancement in photostability, and a few displayed a weak antagonistic effect. Of the water-soluble compounds, only the hindered phenol SHP-2 gave a significant synergistic effect. SHP-1 gave slight protection against yellowing, but it accelerated the phototendering behavior.

Absorber-treated fabrics containing either I1425 or SHP-2, together with the appropriate controls, were exposed for a longer period at a lower temperature, to assess whether thermal oxidation processes play a role in the synergism. The tear strength improvement factors obtained at temperatures of 45 and 75°C were the same, within experimental error, but the effectiveness of the absorber/antioxidant treatments in protecting the fabric against photoyellowing was reduced at the lower temperature. The results of these tests are given in parentheses in Table I. Fabrics containing antioxidant and absorber yellowed to about the same degree under both conditions of exposure, whereas fabrics which contained no stabilizer showed a much greater propensity to yellow at 75°C than at 45°C. Although the mode of action of the antioxidants is unclear at present, the relative improvement in photoprotection at the higher temperature suggests that antioxidant diffusion is probably involved in the synergistic process.

TABLE II
Effect of UV Absorbers (II, III, and IV) and Antioxidants on the
Photoyellowing and Phototendering of Wool Fabric, Caused by
Exposure to Simulated Sunlight^a for 336h at 75°C

Absorber (5% owf)	Antioxidant (5% owf)	Yellowness index			Tear strength improvement factor ^b
		Unexposed	Exposed	Difference	
—	—	14	48	34	1.0
II	—	25	34	9	2.7
II	SHP-2	25	27	2	2.5
II	I1425	24	28	4	3.1
—	—	14	52	38	1.0
III	—	16	31	15	2.0
III	SHP-2	16	24	8	2.5
III	I1425	17	25	8	2.8
III	— ^c	17	32	15	1.7
IV ^d	—	16	43	27	N.D. ^f
IV	SHP-2	16	40	24	N.D.
IV	I1425 ^e	19	41	22	N.D.

^a Philips 500-W mercury vapor/tungsten filament lamp.

^b Lifetime improvement factor based on tear strength data.

^c Disperse dyeing treatment without antioxidant.

^d 4% owf.

^e 7% owf.

^f Not determined.

The two most promising antioxidants, I1425, and SHP-2, were then tested in combination with the *t*-butyl benzotriazole (II), the triazine (III), and the benzophenone (IV). The first two absorbers give good protection against photoyellowing and phototendering, and are two of the most effective photoprotective agents for wool.¹ The third absorber gives some protection against phototendering, but it is not very effective in reducing photoyellowing.² Treatment of wool with a combination of either I1425 or SHP-2 and II gave almost complete protection against photoyellowing when fabrics were exposed to simulated sunlight (Table II); there was a small improvement also in strength retention in the case of I1425. It should be noted that the *t*-butyl benzotriazole absorber causes a significant increase in the initial yellowness of the fabric. This yellow color of the absorber is a disadvantage, and methods of reducing the color it imparts to the wool are discussed in more detail below. Both antioxidants enhanced, to a smaller extent, the protective effect of the triazine absorber (III). Photoyellowing was halved by the application of each antioxidant, and strength retention was significantly improved. The benzophenone absorber (IV) showed only a slight improvement in protective effectiveness when it was used in combination with the antioxidants.

The *t*-butyl benzotriazole absorber (II) affords the best protection against photoyellowing, and it gives the strongest synergistic effect with antioxidants. The benzophenone absorber (IV, Uvinul DS49) gives the poorest protection against photoyellowing, and exhibits only weak synergism with the antioxidants. Thus, it appears that the magnitude of the synergistic effect of an absorber/antioxidant mixture is related to the protective effectiveness of the absorber.

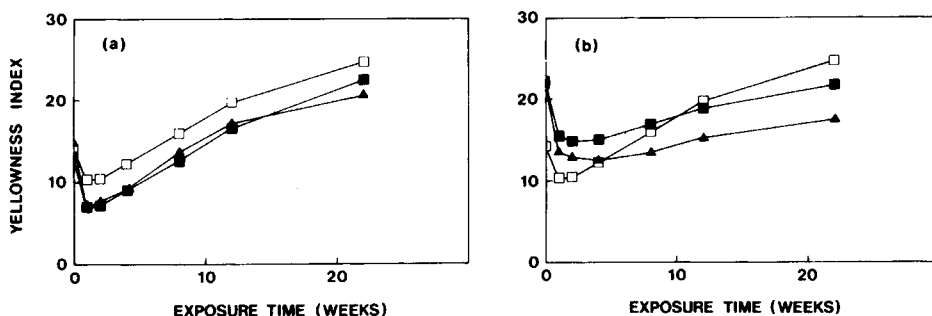


Fig. 1. Effect of UV absorber/antioxidant combinations on the photoyellowing of wool fabric in sunlight, behind glass: (a) (□) no additives; (■) absorber I (5% owf); (▲) absorber I (5% owf) + I1425 (5% owf); (b) (□) no additives; (■) absorber II (3.7% owf); (▲) absorber II (3.7% owf) + I1425 (5% owf).

Sunlight Exposures

Artificial exposure tests are useful for rapidly assessing the performance of a large number of absorber/antioxidant treatments, but the changes in fabric properties induced by artificial exposures are not exactly the same as those resulting from exposure to sunlight.¹¹ It is important, therefore, to establish that any useful synergistic effects can be duplicated when fabrics are exposed to natural sunlight. The most effective antioxidant studied, I1425, was selected for a more detailed investigation of its synergistic interaction with each of the absorbers (I–IV) studied above. Fabrics were exposed to sunlight, behind glass, for a period of 22 weeks during the summer months. Under these conditions, fabrics undergo rapid photobleaching (within a few days), followed by photoyellowing. The results are shown in Figures 1 and 2.

The behavior of the various antioxidants in sunlight correlates well with their behavior under artificial exposure conditions, although the synergistic effect of the absorber/antioxidant mixtures is generally less pronounced in sunlight. Irganox 1425 strongly enhanced the photoprotective effectiveness of the *t*-butyl benzotriazole in retarding yellowing [Fig. 1(b)], but it had little effect on the effectiveness of the *i*-propyl benzotriazole [Fig. 1(a)]. The combination {II + I1425} gave the best protection against photoyellowing; the presence of the antioxidant also gave some improvement in strength retention (Table III), even when the absorber concentration was reduced to 2% owf.

The triazine absorber (III), when used in combination with I1425, appeared to give slightly better protection against photoyellowing than when used alone [Fig. 2(a)]. However, the small improvement in performance was due mainly to the antioxidant blank dyebath treatment, rather than to any synergistic interaction between the absorber and antioxidant.

The benzophenone absorber/antioxidant combination gave no reduction in photoyellowing [Fig. 2(b)]; in fact the presence of the antioxidant was detrimental because it increased slightly the initial yellowness of the fabric. Sunlight exposure tests were also carried out using combinations of the various UV absorbers with the sulfonated hindered phenol derivative SHP-2. Although this antioxidant combined synergistically with UV absorbers to give

TABLE III
Effect on Absorber II and I1425 Combinations on the
Phototendering of Wool Fabric in Sunlight^a

Absorber concentration (%)	Antioxidant ^b	Tear Strength ^c
—	—	3 ± 1
3.7	—	34 ± 4
3.7	I1425	44 ± 6
2	—	27 ± 4
2	I1425	35 ± 4
—	I1425	6 + 1

^a Exposed behind glass to summer sunlight for 22 weeks.

^b Antioxidant concentrations were 5% owf.

^c Expressed as a percentage of the value for unexposed fabric. 95% confidence limits included.

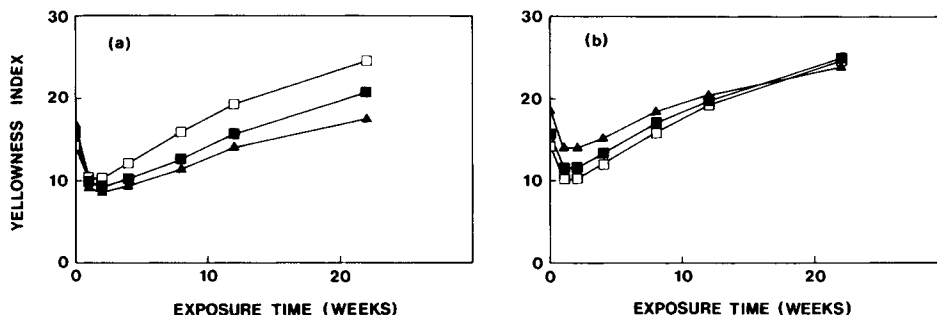


Fig. 2. Effect of UV absorber/antioxidant combinations on the photoyellowing of wool in sunlight, behind glass: (a) (□) no additives; (■) absorber III (5% owf); (▲) absorber III (5% owf) + I1425 (5% owf); (b) (□) no additives; (■) absorber IV (4% owf); (▲) absorber IV (4% owf) + I1425 (7% owf).

enhanced photoprotection under artificial exposure conditions, it was found to give no added protection when fabrics were exposed to sunlight. The reason for this behavior is not clear at present, but it presumably stems from differences in the wavelength distribution and light intensity under natural and artificial exposure conditions.

Mode of Action of Antioxidants in Wool. Although the results obtained in this work clearly demonstrate that a cooperative interaction occurs between certain types of UV absorbers and antioxidants in wool, there is insufficient evidence to draw any firm conclusions concerning the mechanism of synergism. The fact that a strong synergistic effect is observed only when an antioxidant is combined with a UV absorber that is itself an effective photostabilizer suggests that the antioxidant may only inhibit certain types of photoreactions in wool, and that a high level of protection by UV screening is necessary before the protective effect of the antioxidant becomes apparent.

It is interesting to note that antioxidants of the hindered phenol type are the only compounds which function synergistically with UV absorbers in wool. Free radical scavenging is the main process⁸ by which hindered phenols protect polymers against photodegradation. It seems likely therefore that free radical reactions (possibly involving alkyl and hydroperoxy radicals) are

TABLE IV
Effect of Reductive Bleaching on the Photoyellowing of Wool
Fabrics Caused by Exposure to Simulated Sunlight^a for 336 h at 75°C

Absorber (2% owf)	Antioxidant (5% owf)	Bleach ^b (6% owf)	Yellowness index		
			Unexposed	Exposed	Difference
—	—	—	14	48	34
—	—	+	8	49	41
II	—	—	19	32	13
II	I1425	—	19	27	8
II	—	+	16	34	18
II	I1425	+	16	29	13

^a Philips 500-W mercury vapor/tungsten filament lamp.

^b Blankit D reductive bleach.

involved in the long-term photoyellowing and phototendering reactions in wool. An alternative explanation for the synergism is that the antioxidant functions by inhibiting the photodegradation reactions of the UV absorber itself, thereby causing an enhancement of the protective function of the latter. Elucidation of the operative mechanism would entail a detailed examination of the light stability characteristics of wool as a function of the composition of the UV absorber/antioxidant mixture.

Reductive Bleaching

Although the *t*-butyl benzotriazole absorber, in combination with I1425, confers excellent protection against photoyellowing and phototendering in sunlight, the initial color imparted to the wool might preclude its use in some applications. Further tests with this absorber were therefore carried out using lower levels of application, coupled with a reductive bleaching treatment, in an effort to reduce the initial yellowing to a more acceptable level. The results of simulated sunlight exposure tests on fabrics containing 2% of II, alone and in the presence of I1425 (5% owf), are summarized in Table IV.

At the 2% level, absorber II still gives quite good protection against photoyellowing; the protective effect is considerably enhanced by the application of I1425. Lowering the absorber concentration from 5 to 2% reduces the initial fabric yellowness by six units (cf. Tables II and IV). A further reduction in yellowness can be achieved by reductive bleaching with Blankit D (sodium formaldehydesulfoxylate), but only with partial loss of photoprotection. The propensity of chemical bleaching treatments to accelerate the photoyellowing of wool is well known,¹² and the added protection given by the antioxidant (I1425) offsets the accelerated yellowing due to the bleaching treatment.

CONCLUSION

The photoprotection afforded to wool by UV absorbers can be considerably enhanced by the application of antioxidants of the hindered phenol type. In the case of photoyellowing, the magnitude of the synergistic effect is related to the protective effectiveness of the UV absorber. Absorbers which give good photoprotection when used alone give strong synergistic effects with antioxi-

dants, while absorbers which give poor photoprotection show little synergistic activity. Sulfonated and unsulfonated hindered phenols are shown to interact synergistically with several types of UV absorber under artificial exposure conditions, but only the unsulfonated compounds give any protection in sunlight. The commercially available hindered phenol derivative, Irganox 1425, showed the strongest synergistic effect when it was combined with a sterically hindered 2-hydroxyphenylbenzotriazole UV absorber. This combination gave the best protection to wool against photoyellowing and phototendering in sunlight. The initial yellow color imparted to the wool by this absorber can be reduced by a reductive bleaching treatment, but only with partial loss of photoprotection.

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