

## THE PHOTOCHEMISTRY OF SULPHAMIC-ACID-TREATED WOOL

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### Summary

The photoyellowing and phototendering of sulphamic-acid-treated wool has been investigated. Sulphamic acid introduces sulphonate and sulphamate groups into wool's structure. Studies of photoyellowing indicate that initially there is a "photobleaching" effect followed by photoyellowing. Studies of the phosphorescence due to tryptophan indicate that the tryptophan is masked in some way and that this could lead to the lower relative increase in photoyellowing observed.

Measurements of phototendering indicate that the treatment of wool with sulphamic acid has no significant effect on the strength loss observed in the wool when it is exposed to simulated sunlight.

Sulphamic-acid-treated wool has an increased uptake of basic dyes compared with untreated wool. Measurements of the light fastness have indicated that the light fastness of basic dyes on sulphamic-acid-treated wool is increased to values comparable with those achieved on acrylics. The increase in light fastness has been investigated using model PVA films.

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### 1. Introduction

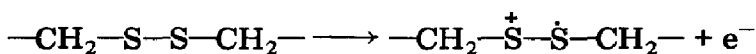
Photoyellowing, the light-induced discolouration of wool, occurs on exposure to sunlight for relatively short periods of time, while phototendering, the loss in strength and abrasion resistance, occurs over prolonged exposure to sunlight. Analysis has shown that these undesirable changes in wool are brought about by the degradation of certain amino acids, these being principally tryptophan, histidine, cystine, tyrosine, phenylalanine and methionine [1].

Photoyellowing of wool is caused when it is exposed to UV radiation in the wavelength range 300 - 380 nm [2]. Photoyellowing appears to occur mainly because of photo-oxidative processes involving tryptophan. Nakagawa *et al.* [3] have proposed a reaction scheme for the degradation of tryptophan via photo-oxidative processes. There is evidence to suggest that

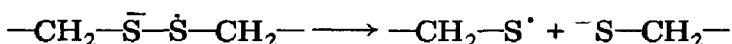
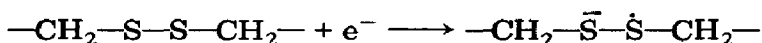
these pathways may exist as kynurenine, a yellow-coloured oxidation product of tryptophan, has been isolated and identified in irradiated wool [4].

Phototendering is thought to involve the breakdown of disulphide bonds along with main chain breakdown at the peptide bonds. Meybeck and Meybeck [5] have postulated that main chain breakdown occurs via photochemical cleavage of the peptide bonds at glycine and alanine residues. The mechanism was proposed, in part, to explain the photoyellowing of wool by the  $\alpha$ -ketoacyl groups formed (glyoxylic and pyruvic acids), but since it involves the breakdown of the main chains, subsequent losses in strength would also be expected. Main chain breakdown has also been shown to occur at other amino acids, *viz.* glutamic acid, threonine, serine and tyrosine [6].

The disulphide bond may be degraded via two pathways [7]: (1) photoejection of electrons leading to bond fission



or (2) the rearrangement of a cystinyl radical anion formed by the trapping of an electron



It was thus the aim of this present work to investigate the effects of treatment with sulphamic acid on the photoyellowing and phototendering of the wool. It is known that wool treated with sulphamic acid is slightly yellowed and that the strength loss is minimal [8].

It is well known [9] that the introduction of sulphonate groups into the structure of acrylics increases the light fastness of basic dyeings. It was thus a further aim of this work to investigate the properties of basic dyed sulphamic-acid-treated wool, especially with respect to the light fastness ratings achieved.

## 2. Experimental details

### 2.1. Treatment of wool with sulphamic acid

Wool fabric (2/2 twill, 266 g m<sup>-2</sup>) supplied by John Vicars Fabrics, Sydney, was treated in a solution comprising 20% (w/v) sulphamic acid, 20% (w/v) urea and 0.1% Lissapol TN450 on a laboratory jig for 30 min at 40 °C. The wool was passed through a pad mangle to achieve 70% pick-up, dried at 80 °C for 15 min and cured at 150-160 °C for 4-5 min. This treatment resulted in an uptake of 8.5% of bound sulphamic acid in the form of sulphonates and sulphamates [8, 10].

## 2.2. Analysis of tryptophan in wool

The method employed was that of Cegarra and Gacén [11]. This method gave reproducible results for both untreated and sulphamic-acid-treated wool. A set of calibration solutions was included in each analysis and all analyses were run in triplicate.

## 2.3. Simulated sunlight exposures

The wool samples were exposed to an artificial light source (mercury vapour, tungsten filament, internally phosphor-coated lamp, 500 W, as per Australian Standard 2001.4.21) for the desired time. The yellowness of the samples was measured using a Spectrogard Computer Colour Control System [12]. The following yellowness index, from ASTM D1925, was calculated for illuminant C [13]:

$$YID = \frac{100(1.28X_{CIE} - 1.06Z_{CIE})}{Y_{CIE}}$$

The yellowness index measurements were reproducible to  $\pm 1\%$ .

## 2.4. Tensile tests

The tensile strength of the wool samples was determined according to Australian Standard 2001.2.3 [14], using a ravelled strip test. The experimental error in the determination of the tensile strength was  $\pm 2\%$ .

## 2.5. Measurement of total luminescence from wool

The measurement of luminescence from wool keratin was achieved using a spectrofluorophosphorometer constructed in the School and described elsewhere [15]. This instrument is able to detect the phosphorescent emission from tryptophan in wool keratin at room temperature.

## 2.6. Dyeing of wool and acrylic fabric

3 g samples of wool were dyed according to the ITW method [16] with dye concentrations of 0.5%, 2.0% and 4.0% o.w.f. (on weight of fibre), at a liquor ratio of 50:1 in a Horsfall Engineering Co. dyeing machine. C.I. Basic Blue 3, C.I. Basic Red 51 and C.I. Basic Yellow 11 were the dyes employed. 3 g samples of an acrylic substrate (Acrilan 16, plain weave,  $300 \text{ g m}^{-2}$ , supplied by Bradmill Australia) were also dyed by the same method.

## 2.7. Poly(vinyl alcohol) substrates

The method employed was essentially that of Mason *et al.* [17], except that 8.0 ml of a 4% solution of poly(vinyl alcohol) (PVA) was cast onto a 75 mm  $\times$  50 mm slide. A stock solution (300 ml) of PVA was prepared, to which 0.03 g of basic dye was added. The effects of sulphonate and carboxylate anions were determined by adding to 100 ml of the stock solution equimolar quantities of either sulphamic acid (0.1 g) or trichloroacetic acid (0.17 g).

The method of adding the sulphamic acid to the PVA film involves raising the temperature to 80 °C. At this temperature rapid hydrolysis of the sulphamic acid occurs [18 - 20] to yield sulphonate-like groups in the film.

### 2.8. Light fastness of basic dyeings

The light fastnesses of the basic dyeings were determined according to Australian Standard 2001.4.21 [21].

## 3. Results and discussion

The photoyellowing and phototendering of both the untreated and the sulphamic-acid-treated wools were investigated by exposing wool samples to the light source for 2 weeks. The results of photoyellowing (given in Table 1) indicate that over this period of time there is actually a decrease in the yellowness of the sulphamic-acid-treated wool (and thus a "photobleaching" effect) while the untreated wool is slightly yellowed. Thus it would seem that in some way the introduction of sulphonate and sulphamate groups via sulphamic acid [1, 2] initially inhibits the photoyellowing of the wool.

Data for the photoyellowing of wool over a longer period of time is also given in Table 1. The observed increases indicate that after the initial photobleaching effect the sulphamic-acid-treated wool begins to photoyellow. The per cent increases in yellowness index observed over the 8 week period are also given in Table 1. The results indicate that the relative increase in yellowing of the sulphamic-acid-treated wool is not as severe as that of untreated wool (although the treated wool is initially more yellow).

It is well known that the process of photoyellowing of wool is mainly due to the photo-oxidation of tryptophan. The tryptophan contents of the wool substrates are given in Table 2. These results, as expected, indicate that the tryptophan content of both wool substrates decreased as the time of exposure increased. The initial value of sulphamic-acid-treated wool is lower

TABLE 1

Photoyellowing of sulphamic acid and untreated wool substrates

<i>Exposure time</i> (weeks)	<i>Untreated wool</i>		<i>Sulphamic-acid-treated wool</i>	
	YID	<i>Percentage change</i>	YID	<i>Percentage change</i>
0	25.77	0.0	36.92	0.0
2	31.91	23.8	34.47	-6.6
4	38.83	50.7	45.06	22.0
6	44.00	70.7	53.08	43.8
8	47.41	84.0	57.24	55.0

TABLE 2

Tryptophan contents of wool substrates before and after exposure

Exposure time (weeks)	Content ( $\mu\text{g g}^{-1}$ )	
	Untreated wool	Sulphamic-acid-treated wool
0	435	320
4	200	170
8	190	160

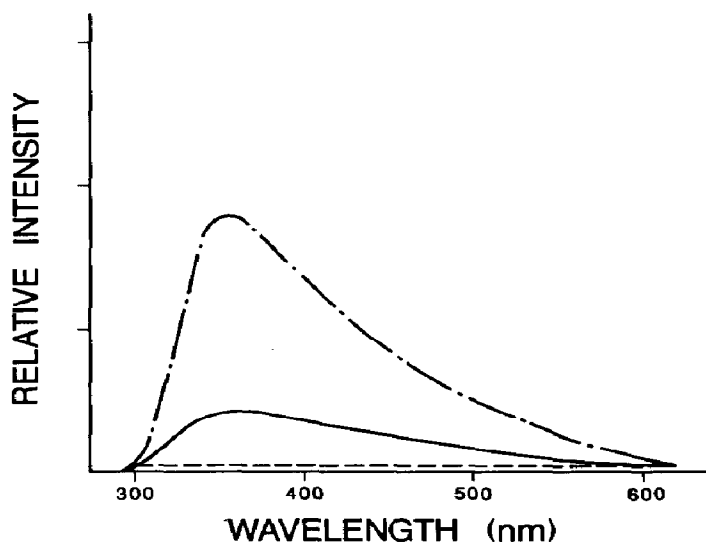


Fig. 1. Fluorescence emissions from wool substrates at 20 °C under an atmosphere of dry nitrogen (280 nm excitation): - · -, untreated wool; —, sulphamic-acid-treated wool; — · —, untreated and sulphamic-acid-treated wool exposed to the light source for 4 (weeks)

than that for untreated wool, probably owing to destruction of some of the tryptophan during the curing process involved in the treatment of wool with sulphamic acid.

Figure 1 shows the total luminescence emission of sulphamic-acid-treated and untreated wool together with the total luminescence of both wool substrates after exposure to the light source for 4 weeks. The results clearly illustrate the total fluorescence of wool which includes that of tryptophan at 340 nm. However, the fluorescence of sulphamic-acid-treated wool is much less than that of untreated wool. As shown in Table 2, sulphamic-acid-treated wool has a lower tryptophan content than untreated wool. While being significant, the decrease in tryptophan content could not account for the decrease in total luminescence observed. Hence there is some form of masking, filtering or quenching of total luminescence resulting from treatment of wool with sulphamic acid.

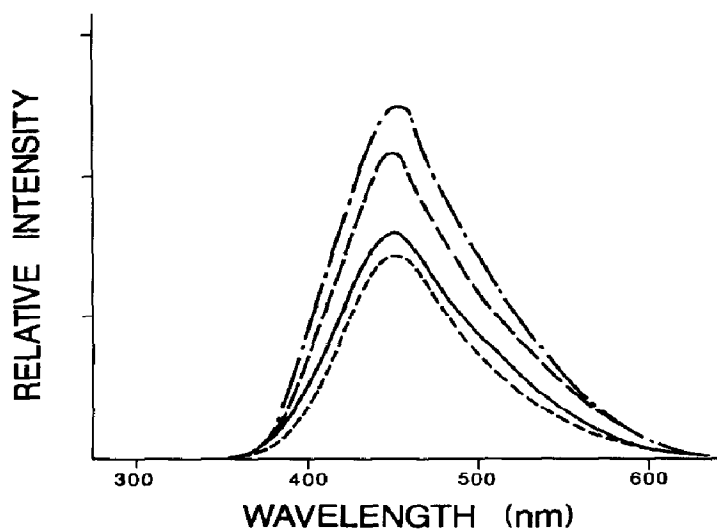


Fig. 2. Phosphorescence emissions from wool substances at 20 °C under an atmosphere of dry nitrogen (280 nm excitation): - · -, untreated wool; —, sulphamic-acid-treated wool; ---, untreated wool exposed to the light source for 4 weeks; · · · ·, sulphamic-acid-treated wool exposed to the light source for 4 weeks.

The total luminescence from both sulphamic-acid-treated and untreated wool after exposure to the light source is virtually zero. The probable reason for this observation is that the total luminescence emitted is reabsorbed by the yellow pigmentation of the exposed wools.

Evidence for the observed masking or quenching effect can be obtained from the phosphorescence of tryptophan at 450 nm as shown in Fig. 2. The phosphorescence emission from tryptophan is observed for both sulphamic-acid-treated and untreated wool. As expected, the phosphorescence of sulphamic-acid-treated wool is less than that of untreated wool owing to its lower tryptophan content. Thus the reason for the observed lack of total luminescence is that the yellow pigmentation of the wool can absorb both the excitation energy and the total luminescence emission energy. This effect has been observed by others [22, 23] in work with fluorescent whiteners for wool, where the expected fluorescence is not observed because of absorption of incident radiation by the coloured pigments of the wool. This leads to distortion of the fluorescence excitation and emission spectra.

While no fluorescence is observed for either the untreated wool or the sulphamic-acid-treated wool after 4 weeks exposure, the phosphorescence due to tryptophan is still observed in each case. Measurements of the tryptophan contents have indicated that tryptophan is still present in substantial quantities. The reason for the phosphorescence still being observed after 4 weeks exposure is that it is red shifted and thus the yellow pigments of the wool substrates do not significantly absorb the excitation phosphorescence emission energy.

The phototendering of sulphamic-acid-treated wool was examined by exposing samples for periods of 2 and 6 weeks. The results given in Table 3

TABLE 3

Breaking force measurements before and after exposure

Exposure time (weeks)	Breaking force (N)			
	Untreated wool		Sulphamic-acid-treated wool	
	Warp	Weft	Warp	Weft
0	472	453	465	482
2	389	360	400	413
6	243	240	254	253

TABLE 4

Lightfastness of basic dyes on wool and acrylic substrates

Dye	Untreated wool	Sulphamic-acid-treated wool	Acrylic <sup>a</sup>	Colour index (acrylic) [28]
<i>Basic Blue 3</i>				
4.0%	1	4	4 - 5	—
2.0%	1	4	4 - 5	4 - 5
0.5%	1	4	4 - 5	4 - 5
<i>Basic Red 51</i>				
4.0%	3	6	6	6 - 7
2.0%	3 - 4	6	6	6
0.5%	3	6	6	5
<i>Basic Yellow 11</i>				
4.0%	4 - 5	6	6	7
2.0%	4	6	6	7
0.5%	4	6	5	5 - 6

<sup>a</sup> Acrylic substrate, Acrilan 16.

indicate that both wool substrates lose strength when exposed to the light source. As with the photoyellowing of sulphamic-acid-treated wool, it appears that phototendering is initially reduced. After prolonged exposure the "protective" effect is reduced, until after 6 weeks exposure the sulphamic-acid-treated wool behaves in a similar fashion to untreated wool with approximately the same loss in strength.

Sulphamic-acid-treated wool has an increased uptake of basic dyes compared with untreated wool. The light fastness ratings of the basic dyeings are given in Table 4. The results indicate that at dyeing depths of 0.5%, 2.0% and 4.0% (o.w.f.) the treatment of wool with sulphamic acid has had a marked effect on the light fastnesses achieved. The increases observed bring the treated wools' light fastness ratings up to values similar to those achieved on acrylic substrates. The increase in light fastness is attributed to the introduction of sulphonate groups ( $\text{SO}_3^-$ ) via reaction with sulphamic acid.

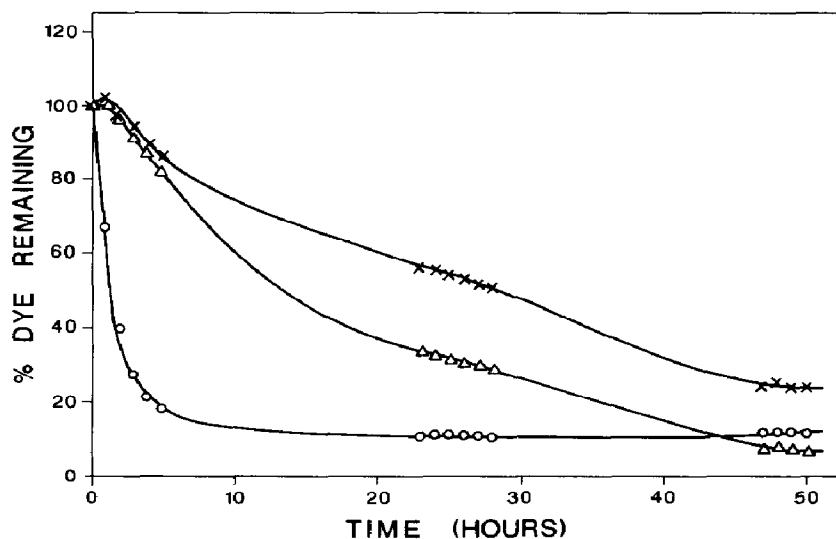


Fig. 3. Fading curves for C. I. Basic Blue 3 in PVA films containing various additives: x, sulphamic acid;  $\Delta$ , trichloroacetic acid; o, dye only (no additives).

In studies with other polymers some workers [10, 24] have observed that the nature of the dyesite within the polymer affects the rate of fading of basic dyes. This is particularly true for the sulphonate group which gives rise to lower rates of fading when compared with other typical dyesites (*viz.* carboxylate groups) employed in basic dyeable substrates. Matthews [24] has shown that providing the  $pK_a$  of the dyesites are the same there is no difference in the rate of fading, but sites of different  $pK_a$  give markedly different results in terms of basic dye fading in PVA films. Matthews suggested that this was due to the acidic nature of the particular dyesite.

The effects of sulphamic acid on the fading rates of basic dyes were investigated using model PVA films containing the dye and sulphamic acid. Films were also prepared which contained trichloroacetic acid as a source of carboxylate groups in order to compare the effects of sulphonate and carboxylate groups. Figure 3 illustrates an example of fading for C.I. Basic Blue 3, a dye which has poor light fastness on untreated wool. The initial apparent increase in percentage dye remaining is believed to be due to disaggregation of the dye [25]. The curves clearly show that the introduction of either sulphamic acid or trichloroacetic acid, even though only in a physical sense, has a marked effect on decreasing the initial fading rate of C.I. Basic Blue 3. Sulphamic acid in PVA films also significantly reduced the rate of fading of both C.I. Basic Red 51 and C.I. Basic Yellow 11.

Matthews [24] studied the effects of a range of acids and bases (including sulphuric acid, benzenesulphonic acid, trichloroacetic acid, sodium benzene sulphonate and sodium hydroxide) on the fading rate of basic dyes in PVA films and demonstrated that the rate of fading was related to the acid strength of the dyesite, the stronger acids giving the greatest reduction in the fading rates of the dyes. Since the  $pK_a$  of trichloroacetic acid is



0.64 [26] and the  $pK_a$  of sulphamic acid is 0.988 [27], trichloroacetic acid, being the stronger acid, should have a greater effect in reducing the fading rate of basic dyes. Matthews [24] thus concluded that the degree of fading was dependent upon three major factors, these being (1) the dye structure, (2) the acidity of the dyesite and (3) the chemical nature of the dyesite.

From Fig. 3 it is clear from this work that the presence of sulphamic acid decreases the rate of fading to a greater extent than does trichloroacetic acid. Hence it is the sulphonate groups introduced into wools' structure via the sulphamic acid which leads to the increased light fastness of basic dyes on the treated wool. If it was only a pH effect, then trichloroacetic acid should have had a greater effect than sulphamic acid. Therefore, there must also be some effect related to the nature of the dyesite, possibly as postulated by Zollinger [10], where the sulphonate group, unlike the carboxylate group, has little tendency to decompose and thus reduces dye fading.

#### 4. Conclusions

The treatment of wool with sulphamic acid has no detrimental effects on the photoyellowing and phototendering of the treated wool. It would appear that initially the effects of photoyellowing and phototendering are reduced but, after prolonged exposure, the sulphamic-acid-treated wool behaves in a similar fashion to the untreated wool.

When dyed with basic dyes, the light fastness of the dyes on sulphamic-acid-treated wool is greatly increased so much so that the values obtained are comparable with those obtained on acrylic substrates. The improvement in the light fastness is attributed to the introduction of sulphonate groups into the wools' structure.

#### Acknowledgment

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