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Influence of Dyeing Parameters and Fibre Setting on the Lightfastness Properties of Acid Dyed Nylon 6,6 Fibres

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ABSTRACT

The influence of various dyeing and manufacturing processes have been examined with respect to the lightfastness properties of three acid dyes, namely Tectilon Red 2B, Tectilon Yellow 3R and Tectilon Blue4RS (Ciba-Geigy Ltd), and their interrelationship with the formation of photoactive luminescent carbonylic species and hydroperoxide groups in Nylon 6,6 fibres. Thus, neutral dyeing conditions, and the use of an anionic levelling agent, in conjunction with fibres which had been heat-set under dry conditions, were found to exhibit the higher lightfastness. At low and high pH conditions the dyes were found to be more prone to photofading. These conditions were found to have a marked effect on the excited state properties of the polymer fibre in terms of the formation of photoactive carbonylic species and hydroperoxides. The quenching and interaction of these species with the dyes was found to play an intricate role in the photostability of the dyed fibre system. The addition of a reducing agent to the dyebath operation, and prior extraction of the fibre with methanol to minimise the formation of these species, were found to markedly enhance the dye lightfastness. © 1997 Elsevier Science Ltd

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INTRODUCTION

The stability of dyes to light in polymeric media encompasses a number of problems of technological interest and importance. Thus, the relationship between dye and polymer stability and their associated interactions is important from an industrial point of view, especially in long-term applications involving fibres.[1,2] In an earlier study we examined the photostability of a number of acid dyes in Nylon 6,6 film and found that dye and polymer stability correlate closely.[3] Within the context of this work, it was found that the stability of acid dyes, which do not contain a central metal atom (direct dyes), is determined by the absorption (colour) of the dye, and that this, in turn, is related to the stability of the polymer. For acid dyes containing a central metal atom, the stabilities of the dye and polymer were found to be enhanced by the deactivating effect of the metal atom on the excited state of the dye. In addition to these effects, the relative stabilities of the dye and polymer were found to correlate closely with the ability of the dyes to quench the excited states of the phosphorescent species in the polymer, with metal complex dyes being the most efficient. Moving on from this work a study was then undertaken on the effect of dye concentration, since this parameter is known to be important in triplet energy transfer.[4] Here there was a linear correlation between the quenching of the phosphorescent species in the polymer and dye lightfastness and the influence of the dye on the polymer stability.

The luminescent species in Nylon 6,6 polymer, and related analogues, are known to be important in the photooxidation of the polymers, with α-ketoimides being responsible for the fluorescence and cycloaliphatic α,β-unsaturated carbonyl compounds based on cyclopentanone being responsible for the phosphorescence.[5] The relative concentration of these chromophores in the polymer is known to be influenced by its manufacturing and processing history.[6] In a more recent study on complex dye mixtures it was found that, whilst the quenching of luminescent carbonyl species is important in controlling the photostability of the polymer, the effects of thermal history and nature of the delustrant play an overriding role.[6] Furthermore, the dye bath operation was found to have a detrimental effect on the physical characteristics of the fibre.

In this study we have extended our earlier studies to examine the influence of various dyeing and manufacturing processes on the lightfastness properties of three acid dyes, namely Tectilon Red 2B, Tectilon Yellow 3R and Tectilon Blue 4RS (Ciba-Geigy Ltd), in Nylon 6,6 fibres. From FTIR and FT nmr analysis, the first two dyes were found to be sulphonated monoazo structures, while the latter is a sulphonated aminoanthraquinone. The interrelationship of dye lightfastness is ascertained with the formation of photoactive luminescent carbonylic species and hydroperoxide groups in the polymer. This includes the influence of pH during dyeing, and the use of different levelling agents, together with the effect of fibres which had been heat-set under dry conditions (Suessen set) and steam-set (Superba set), on dye lightfastness. These conditions were found to have a marked effect on the excited state properties of the polymer fibre in terms of the formation of photoactive carbonylic species and hydroperoxides and these, in turn, markedly influenced the dye stabilities.

EXPERIMENTAL

Materials

Nylon 6,6 fibres were provided by DuPont (Deutschland) Ltd. and are coded in terms of amine end group concentration, titanium dioxide content, dyeability and aftertreatment by dry heat (Suessen set) or steam heat (Superba set) setting in Table 1. The first method uses a dry heat setting system (with a little steam) for 60–90 s at 195–205°C and results in an enhancement in the fibre crystallinity, and hence reduced dye affinity, while the second involves a saturated steam treatment for 90 s at 136°C causing the fibres to swell, thus decreasing the crystallinity and increasing the dye uptake.

The acid azo dyes, Tectilon Yellow 3R and Tectilon Red 2B and acid anthraquinone dye, Tectilon Blue 4RS were supplied by Ciba-Geigy (UK) Ltd, Manchester, as were the levelling agents, Univadine NT (anionic), Albegal W (non-ionic), Albegal SW (slightly cationic) and Tinegal W (strongly cationic). the sodium phenyl phosphinate was supplied by DuPont (UK) Ltd, and 2,2,2-trifluoroethanol was obtained from Aldrich Chem. Co. Ltd, UK.

Dyeing operation

The red and yellow dyes (0.01 g) and blue dye (0.025 g) were dissolved in 250 cm^3 of distilled water followed by boiling for 5 minutes to ensure complete

TABLE 1
Properties of Nylon 6,6 Fibres Unset (un), Suessen Set (SS) and Superba Set (SB)

Fibre sample	Titanium dioxide content (%)	Amine end groups (g equ./10^6 g)	Dyeing property
1 (UN)	0.3	80–85	Deep
2 (SB)	0.3	80–85	Deep
3 (UN)	0.3	45–50	Regular
4 (SB)	0.3	45–50	Regular
5 (UN)	1.0	80–85	Deep
6 (SB)	1.0	80–85	Deep
7 (UN)	0.3	80–85	Deep
8 (SS)	0.3	80–85	Deep
9 (SB)	0.3	80–85	Deep

solution. Nylon 6,6 fibre (4 g) was placed in the dyebath at 50°C, followed by the addition of dye solution (0.02% on weight of fibre), 1% w/w of levelling agent, sodium acetate (1 g/litre) and sodium dihydrogen phosphate (1 g/litre). Acetic acid and ammonium acetate were used to vary the pH as required through the range 2–10. The dyebath was brought to the boil over a period of 30 min, held for 60 min, and was then left to cool before the fibres were rinsed in cold distilled water.

Samples of Nylon 6,6 fibre were also soxhlet extracted for 10 h over methanol to remove extractable active species.

Irradiation

Lightfastness assessments were obtained using a Microscal Unit, Microscal Ltd, London utilising a 500 watt high pressure Hg/W fluorescent lamp (ambient temperature and humidity, $\lambda > 300$ nm). Lightfastness determinations were measured with respect to the Blue Wool standards[7] by comparing the extent of fading of the dyed fibre samples with those of the Blue Wool series to achieve the equivalent of fade to that of a Grey Scale change of 3. From these data, graphs were plotted of time to achieve each Blue Wool standard. The time to achieve the differential in fade for Blue Wool 5 was taken as the most appropriate point of measurement in days.

Spectroscopic and hydroperoxide analysis data

Hydroperoxide measurements were obtained as described for the iodometric method.[8] Fluorescence and phosphorescence analysis were obtained for the fibre samples using 1% w/w solutions of the polymer in 2,2,2-trifluoroethanol. Fluorescence maximum was taken at 420 nm with an excitation wavelength at 360 nm, while the phosphorescence maximum was taken at 390 nm with an excitation wavelength at 290 nm.[3–6]

RESULTS AND DISCUSSION

pH Effects

All the dyeing operations used in this study, except where quoted, used the anionic levelling agent Univadine NT. This condition imparted maximum lightfastness to the dye. The effect of pH on the dyeing operation is crucial, since it not only controls the rate of dye uptake into the fibre, but also the subsequent properties of the dyed polymer system. Light stability is one such factor and here this is related to variation in pH of the dye bath in Fig. 1 for

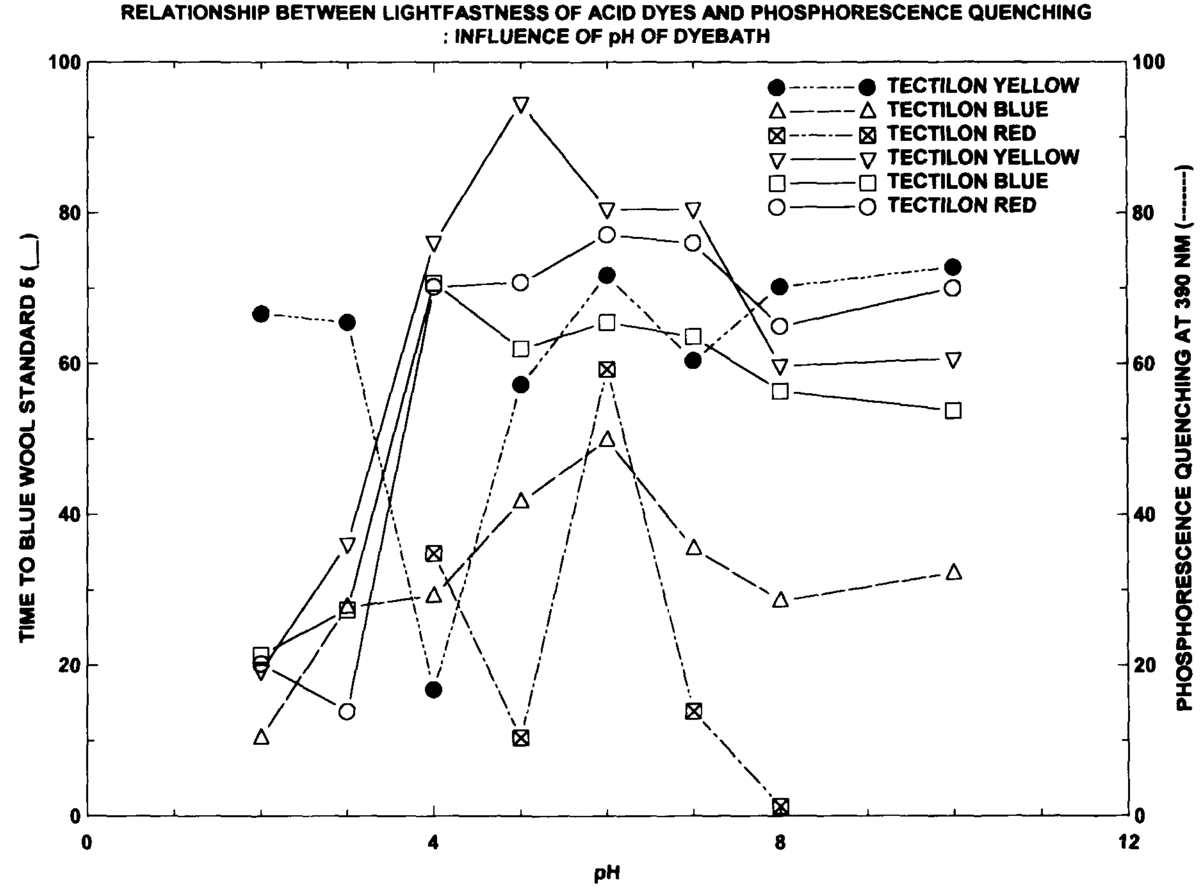

Fig. 1. Time to achieve Blue Wool standard 5 for Tectilon Yellow 3R (▽), Red 2B (○) and Blue 4RS (□) (days) in relation to phosphorescence quenching at 390 nm for Tectilon Yellow 3R (●), Red 2R (□) and Blue 4RS (△) versus pH of dyebath for Nylon 6,6 fibre sample (1).

all three dyes. These results are significant and illustrate similar trends for all three dyes in the polymer fibre. Over the pH range 2–5 there was a marked increase in light stability of the three dyes by almost a factor of 5. Thereafter variations in dye lightfastness are less significant and appear to plateau, apart from the yellow dye which decreases from pH 5 to 10. Maximum dye light stability is observed for the red and blue dyes at pH 6. The levels of photoactive luminescent species in the polymer were also found to exhibit a similar trend. For example, the presence of the phosphorescent species were found to be reduced over the pH range 2–6 and thereafter increased up to a pH of 10. Again, there was a plateau effect for the yellow dye from pH 6 to 10.

Maximum dye lightfastness, therefore, appears to be consistent with a higher degree of phosphorescence reduction (called quenching here). The quenching is relative to the values of the original dyebath control samples. Under low and high pH, dye fading can be accentuated via photoreduction processes. This would involve hydrogen atom abstraction at low acidic pH, and electron abstraction at high basic pH.[1] High concentrations of cations and anions also appear to have significant influence on the rate of formation of the luminescent species and this, in turn, has a marked effect on dye light stability.

Effect of levelling agent

The influence of the levelling agent on the lightfastness of the dyes is illustrated by the data in Table 2 for the blue dye. The order in dye light stability follows the trend

anionic > strongly cationic > slightly cationic > non = ionic.

The nature of the levelling agent was also found to influence the concentration of luminescent species in the fibre. Thus, phosphorescence and fluorescence quenching data show that high light stability correlates with maximum quenching or reduction. In this case the ionic strength of the levelling agent

TABLE 2
Influence of Levelling Agent on Lightfastness of Tectilon Blue Dye in Nylon 6,6 Fibre Versus Luminescence Quenching

Levelling agent (1% w/w)	Time to Blue Wool 5 (days)	% Phosphorescence quenching	% Fluorescence quenching
Univadine NT	34	50.0	51.0
Albegal W	24	26.5	31.4
Albegal SW	28	21.0	38.4
Tinegal W	30	35.0	35.6

TABLE 3

Light Fastness Versus Phosphorescence Quenching for Tectilon Red 2B in Nylon 6,6 Fibre Unset and Superba Set

Fibre sample (red dye)	Time to Blue Wool 5 (days)	Phosphorescence quenching (%)
1 (UN)	40	43.6
2 (SB)	34	13.3
3 (UN)	42	40.5
4 (SB)	40	36.0
5 (UN)	37	6.5
6 (SB)	36	4.3

may be important in terms of quenching the singlet and triplet states of the active carbonyl species in the polymer. The levelling agents may also be forming some type of complex with the dyeing which the excited state of the dye can be effectively quenched by the levelling agent. The stronger the ionicity of the complex the greater the degree of quenching. The ionic levelling agent may also function by decomposing active hydroperoxides in the polymer. This will be examined further.

Effect of fibre setting

The relationship of the lightfastness of the dye to the concentration of phosphorescent species in the polymer is further illustrated by the data in Tables 3 and 4 for the red and blue dyes as examples for both unset and Superba set fibres. Here the range of fibre types 1–6 were examined and related to degree of phosphorescence reduction (quenching) in the polymer. Thus, fibres 1, 3 and 4 all exhibited higher degrees of light stability for the red dye and these correlated with high degrees of quenching. Similar results were obtained for fibres 1 and 5 for the blue dye (Table 4), although not always consistent such as in the case of fibre 2. Comparisons of Suessen and

TABLE 4

Light Fastness Versus Phosphorescence Quenching for Tectilon Blue 4RS in Nylon 6,6 Fibre Unset and Superba Set

Fibre sample (blue dye)	Time to Blue Wool 5 (days)	Phosphorescence quenching (%)
1 (UN)	34.1	50.0
2 (SB)	27.7	3.3
3 (UN)	25.0	21.0
4 (SB)	24.0	7.1
5 (UN)	30.3	19.5
6 (SB)	29.5	17.0

TABLE 5
Light Fastness Versus Luminescence Quenching for Tectilon Blue 4RS and Red 2B in Nylon 6,6 Fibre Suessen Set and Superba Set

Nylon fibre sample	Time to Blue Wool 5	Phosphorescence quenching (%)	Fluorescence quenching (%)
Tectilon Blue 4RS			
8 (SS)	52.4	44.9	56.3
9 (SB)	31.3	25.9	32.1
Tectilon Red 2B			
8 (SS)	73.5	65.1	32.4
9 (SB)	35.6	53.7	29.9

Superba setting were also made and related to fluorescence and phosphorescence quenching effects (Table 5). The Suessen setting process imparted the higher degree of light stability to the dyes compared to that of the Superba set process. In the former case the dry heating processes enhances the degree of polymer crystallinity, reducing the rate of oxygen diffusion and the levels of luminescent species. The dry heating process probably removes a substantial amount of the luminescent species through volatilisation compared with that of the steam process. The manufacturing history of the fibre is, therefore, also important in controlling the concentration of photoactive luminescent species, and this, in turn, influences the light stability of the dye.

Effect of reducing agent

Sodium phenyl phosphinate is a known stabiliser for Nylon 6,6 polymer.[6] It was, therefore, of interest to determine its effect on the light fastness of the dyes and how this correlates to the concentrations of photoactive hydroperoxides and luminescent chromophores. Data for the luminescence is shown in Table 6 in relation to lightfastness for fibres 7–9. It is seen that for both

TABLE 6
Effect of Sodium Phenyl Phosphinate on the Lightfastness Versus Luminescence Quenching for Tectilon Blue 4RS and Red 2B in Nylon 6,6 Fibre Suessen Set and Superba Set

Nylon fibre sample	Time to Blue Wool 5	Time to Blue Wool 5 (reducing agent)	Phosphorescence quenching (%)	Fluorescence quenching (%)
Tectilon Blue 4RS				
7 (UN)	36.3	69.0	54.8	31.1
8 (SS)	52.4	79.4	73.5	34.9
9 (SB)	31.3	65.3	62.4	23.6
Tectilon Red 2B				
7 (UN)	48.6	64.8	59.3	7.4
8 (SS)	73.5	78.2	67.7	33.3
9 (SB)	35.6	66.4	64.1	23.9

TABLE 7
Effect of Sodium Phenyl Phosphinate on the Hydroperoxide Concentrations in Nylon 6,6 Fibres Sussen Set and Superba Set

Nylon fibre sample	Initial [POOH] μg/g control undyed	Dyebath controls undyed	[POOH] after dyeing with SPP μg/g	% Decrease in [POOH] after SPP treatment (Undyed)
7 (UN)	180	223	138	38
8 (SS)	463	450	164	64
9 (SB)	206	367	77	79

the blue and red dyes, prior treatment of the fibre in the dyebath with 1% w/w of the phosphinate markedly enhances the dye stabilities. Furthermore, the results are consistent with high degrees of quenching of both the fluorescent and phosphorescent species in the fibre, relative to the control samples, with the highest lightfastness and degree of quenching being observed for the Suessen set fibre.

Phosphinates are known to decompose and react with hydroperoxides [6,7] and this is further illustrated here in Nylon 6,6 fibre by the data in Table 7. Both Suessen and Superba set fibres exhibit higher initial levels of hydroperoxides both before and after undergoing a dye bath operation (without dye). In this regard the heat set (Suessen set) fibre exhibits the highest concentration in both controls compared with the unset and Superba set fibres. Temperature and oxidation during the Suessen setting operation are certainly responsible for this enhancement. In this case, the enhanced lightfastness of the dyes is associated with increased crystallinity of the fibre and reduced oxygen diffusion through the polymer matrix. After dyeing the fibres with the phosphinate, significant reductions in hydroperoxide levels are observed for all three types of fibres. The highest reductions are observed for the set fibres at over 60%. This effect in reducing the hydroperoxide levels in the fibre would also be consistent with increased lightfastness of the dyes. Photochemical reactions of the hydroperoxides would be expected to be detrimental toward the dyes.

Methanol extraction

In previous work we showed that prior alcohol extraction of Nylon 6,6 polymer markedly improved its light stability in terms of loss in viscosity.[7,9] Analysis of the products extracted showed the presence of nylon cyclic oligomer, cycloaliphatic unsaturated ketones, cyclopentanone, organic acids, low molecular weight aldehydes, ketones and peroxidic chromophores.[5] It was therefore of interest to examine the effect of this treatment on dye light

TABLE 8
Effect of 10 h Methanol Soxhlet Extraction on the Lightfastness Versus Fluorescence Quenching for Tectilon Red 2B in Nylon 6,6 Fibre Suessen Set And Superba Set

Nylon fibre sample	Time to Blue Wool 5	Time to Blue Wool 5 extracted	Fluorescence		
			Control undyed	Extracted dyed	% Quenching
7 (UN)	48.6	86.1	125	83	33
8 (SS)	73.5	94.2	145	64	56
9 (SB)	35.6	85.8	141	97	31

stability in fibre. The results on the red dye are shown in Tables 8 and 9, together with the effect on respective fluorescence and phosphorescence emissions. Significant enhancements in lightfastness are observed for unset and set fibres, with Superba set fibres exhibiting the greatest increase. In all cases there is a marked reduction in phosphorescence intensity of the polymer and to a lesser extent for the fluorescence. Since the latter species are mostly bound to the polymer, this change would be expected.[3,5]

Accompanying the reductions in luminescent species are decreases in hydroperoxide concentrations (Table 10), although not as significant as the phosphinate treatment. Again, the set fibres showed the greater change in hydroperoxide concentration, possibly due to a higher incidence of low molecular weight fragments from the thermal setting operations. These observations, coupled with the luminescence, will contribute significantly toward the enhanced light stabilities of the dyes. Actual numerical changes in the phosphorescence and fluorescence intensities are shown in Table 11 for the undyed, unextracted and extracted fibres. The high levels of extractable phosphorescent species, with respect to the fluorescent chromophores, is strongly evident.

TABLE 9
Effect of 10 h Methanol Soxhlet Extraction on the Lightfastness Versus Phosphorescence Quenching for Tectilon Red 2B in Nylon 6,6 Fibre Suessen Set and Superba Set

Nylon fibre sample	Time to Blue Wool 5	Time to Blue Wool 5 extracted	Fluorescence		
			Control undyed	Extracted dyed	% Quenching
7 (UN)	48.6	86.1	254	69	73.1
8 (SS)	73.5	94.2	320	81	74.7
9 (SB)	35.6	85.8	251	84	66.6

TABLE 10
Effect of 10 h Methanol Soxhlet Extraction on the Hydroperoxide Concentrations in Nylon 6,6 Fibre Suessen Set and Superba Set

Nylon fibre sample	Initial [POOH] μg/g control undyed	Extracted fibre	% Decrease in [POOH] after extraction (undyed)
7 (UN)	180	152	16
8 (SS)	463	263	43
9 (SB)	206	163	21

TABLE 11
Effect of 10 h Methanol Soxhlet Extraction on the Luminescence Levels in Nylon 6,6 Fibre Suessen Set and Superba Set (Undyed)

Nylon fibre sample	Phosphorescence			Fluorescence		
	Control undyed	Dyebath control	Extracted fibre	Control undyed	Dyebath control	Extracted fibre
7 (UN)	254	318	78.5	125	138	112
8 (SS)	320	323	44.0	145	124	93
9 (SB)	251	273	54.5	141	115	106

CONCLUSIONS

The ability of acid dyes to quench the photoactive luminescent species in Nylon 6,6 polymer has been found to be closely related to their lightfastness. Since the dyes are also ionically bonded to the fibre, they are able to protect the polymer and the dye chromophore through excitation energy transfer via the bond. The optimum dyeing conditions were found to be at a pH of 6, together with the use of an anionic levelling agent. These conditions also produced the greatest degree of phosphorescence quenching. The thermal history of the fibre is important, with a dry heat (Suessen set) process giving enhanced photostability to the dye, which is associated with increased crystallinity of the polymer reducing oxygen diffusion coupled with a higher degree of quenching of the luminescent species.

The addition of a reducing agent (sodium phenyl phosphinate) to the dyebath was found to decrease the hydroperoxide concentration in the polymer fibres, and subsequently enhance the lightfastness of the dyes. The luminescent species were also reduced in concentration by this process resulting in a marked enhancement in dye lightfastness. Thus, the initial hydroperoxide levels in the fibres also play an integral role in dye photostability. Soxhlet extraction of the fibres with hot methanol prior to dyeing removed a substantial amount of these photoactive luminescent species and, to a lesser extent, hydroperoxides, giving rise to a marked enhancement in dye light stability. The latter was more effective with the heat set fibre (Suessen set) possibly due to an increased concentration of low molecular weight oxidation products and ease of extraction by the methanol.

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