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Dyes Derived from Aminothiophenes—Part 3. Application of some Disperse Dyes Derived from 2-Aminothiophenes to Hydrophobic Fibres

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ABSTRACT

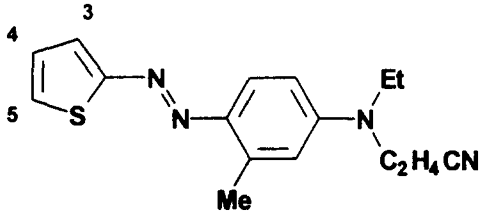
A series of thienyl-2-azo dyes has been milled and the dispersions applied to polyester, nylon and cellulose diacetate by conventional exhaustion dyeing techniques. The colour properties of the dyeings were examined and related to the molecular structure of the colorants. Generally, of the three substrates, polyester was found to be coloured most effectively; the nylon and acetate dyeings had lower colour yields. Although the dyeings were not of standard depth, correlations between dye structure and wash, perspiration and sublimation fastness were identified. Photostability was observed to improve as electron-withdrawing groups were attached to the thiophene ring.

Keywords: Heterocyclic azo dyes, 2-aminothiophenes, dyeing, disperse dyes, photostability, fastness properties.

INTRODUCTION

Monoazo disperse dyes with heterocyclic diazo components have been applied to hydrophobic fibres commercially for many years.[1] However, since the appearance of seminal papers concerning thiazolyl-,[2] thienyl-,[3] benzothiazolyl-[4] and benzisothiazolyl-azo[5] dyes, it is only within the last decade that the majority of the information about the coloration and fastness properties of heterocyclic disperse dyes on synthetic fibres has been divulged outside the patent literature. While extensive amounts of data concerning chloro-[6–8] and nitro-benzothiazolyl-[9,10] as well as nitrobenzisothiazolyl-derived[11–13] dyes have been reported, only scattered accounts that refer to the application and fastness properties of disperse dyes with 2-aminothiophene diazo components have been published, all of which are restricted to polyester.[14–17] Significant discrepancies have been observed by the authors between the colour and fastness properties of some thienyl-2-azo dyes reported by Sabnis and Rangnekar[18–21] and those of some closely related analogues.[22]

The synthesis[23] and spectroscopic properties[24] of a series of thienyl-2-azo dyes **1** have been described. This paper gives an account of their application to three hydrophobic substrates and discusses the colour and fastness properties of the resultant dyeings.



1

3 = CN, CO_2R, $CONH_2$
4 = H, Me
5 = R, Ph, Ac, CN
4,5 = (aryl)alkylene

RESULTS AND DISCUSSION

Dye application

Certain dyes were more resistant to milling than others owing to the nature of their crystals; however, even the most resilient of the solids gave satisfactory dispersions when they were thoroughly ground manually and treated with ultrasound prior to milling.

When the dyes were applied to the three substrates, extents of exhaustion varied greatly, ranging from complete to very poor; this was reflected in the wide variation of colour yields obtained.

Colorimetric properties of the dyeings

Most of the dyes built up well on polyester to give strong, bright colours, although, with a few exceptions, application to nylon and diacetate furnished dyeings of a less satisfactory nature. The hue of each dye on polyester is listed in Table 1, together with the strength of each dyeing expressed as *fk*, a visually weighted function of K/S. While physical factors such as crystal structure, differences in dispersion quality and dye–dispersant interaction may influence depth of shade, the strength of the dyeings can be correlated with molecular structure.

Polyester

Orange to violet hues were obtained on polyester, build-up generally being good, except for dyes which had bulky substituents or low solubility.

For dyes with large substituents, poor uptake can be attributed to an increase in mass, which means that fewer dye molecules will be present in the dyebath at a given application level, as well as to increased size, which reduces rates of diffusion into the polyester. For example, similar colour strengths were shown by **1** (3-CN-4,5-$(CH_2)_4$-) and **1** (3-CN-4,5-$(CH_2)_{10}$-) (*fk* 22.8 and 20.1, respectively) at 0.05% o.m.f., both dyes exhausting fully from the dyebath. At 0.5% o.m.f., the former dye built up well (*fk* 191), while the latter did not exhaust satisfactorily as its larger alkylene ring restricted diffusion into the polyester so that build-up was poor (*fk* 78.9).

One dye (**1**; 3-CN-4-Me-5-CO_2Et) that was bereft of any large substituents did not build up well. This dye had much lower solubility in organic solvents than related derivatives and, presumably, lower solubility in polyester, so that saturation was reached at 0.5–1.0% o.m.f., restricting the depth of shade. Consequently, whereas **1** (3,5-CO_2Et-4-Me), **1** (3-CN-4-Me-5-CO_2Et) and **1** (3,5-CN-4-Me) had similar strengths at 0.05% o.m.f. (*fk* 26.8, 34.9 and 45.5, respectively), which slightly increased in accord with dye intensity,[24] at 1.0% o.m.f., only the first and last dyes exhausted well (*fk* 204, 53.3 and 230, respectively).

Insertion of a methylene group had only a slight effect on build-up. Methyl esters built up slightly more satisfactorily than their ethyl analogues; for example, **1** (3-CO_2Me-4,5-$(CH_2)_4$-) produced a greater depth at 1.0% o.m.f. (*fk* 233) than its ethyl analogue (*fk* 210). Similarly, **1** (3-CO_2Me-5-Me) yielded a marginally higher value of 231 compared with the 5-ethyl derivative (*fk* 225).

Nylon

The nylon dyeings were bluer and of generally lower depth than the corresponding polyester dyeings at 0.5% o.m.f. The effects of molecular size and low solubility appeared to be exaggerated relative to those found with polyester.

Only a few dyes, which tended to be those of smaller molecular size, such as the types **1** (3-CO_2Me-5-R, 3-CO_2R-4,5-Me and 3-CO_2Me-4-R-5-Ac), gave depths approaching those produced on polyester. Bulky substituents and low solubilities restricted depths to pale shades, even more so than on polyester, examples being **1** (3-CN-4,5-$(CH_2)_{10}$-) and **1** (3-CN-4-Me-5-CO_2Et), respectively.

The deepest dyeing was obtained with **1** (3-$CONH_2$-5-Ph); dyes from the corresponding diazo component have been patented specifically for the coloration of nylon.[25]

TABLE 1
Colorimetric and Fastness Properties of the Dyes **1**

Substituents			*Shade on*	*fk*			*WF*[c]			*SF (180°C)*[d]		*SF (210°C)*[d]	
3	*4*	*5*	*polyester*[a]	*P*[b]	*N*[a]	*D*[a]	*D*	*N*	*P*	*C*	*P*	*C*	*P*
CN	-$(CH_2)_3$-		red	27.3/207/235	41.7	23.6	4	3–4	4–5	4	3–4	3	1–2
CO_2Me	-$(CH_2)_3$-		red	23.7/194/259	51.8	31.7	4	4	5	4–5	4	3–4	2
CO_2Et	-$(CH_2)_3$-		red	23.3/177/246	86.2	35.2	4	4	5	4–5	4	3–4	2
CN	-$(CH_2)_4$-		red	22.8/191/229	62.2	19.5	4	4	5	4–5	4	3–4	2
CO_2Me	-$(CH_2)_4$-		dark orange	21.2/167/233	68.3	52.8	4	4	5	4–5	4	3–4	2
CO_2Et	-$(CH_2)_4$-		orange–red	18.6/152/210	89.0	27.7	4	4	5	4–5	4	4	2
COPh	-$(CH_2)_4$-		orange–red	–/113/–	18.7	16.9	4	4	5	5	4–5	4	3–4
COTh	-$(CH_2)_4$-		orange–red	–/123/–	–	–	4	4	5	5	4–5	4	3–4
$CONH_2$	-$(CH_2)_4$-		red	–/174/–	–	–	3–4	3	5	5	4–5	4	3–4
CN	-$(CH_2)_5$-		red	20.5/160/–	37.1	18.6	4–5	4–5	5	4–5	4	3–4	2–3
CO_2Me	-$(CH_2)_5$-		orange	17.4/141/183	61.9	32.7	4–5	4–5	5	4–5	4–5	4	2
CO_2Et	-$(CH_2)_5$-		orange	17.5/132/161	42.6	17.2	4–5	4–5	5	4–5	4	4	2–3
CN	-$(CH_2)_6$-		red	25.5/173/205	48.2	28.5	4–5	4	5	4–5	4	3–4	2–3
CN	-$(CH_2)_{10}$-		pink	20.1/78.9/88.0	13.2	14.7	5	5	5	5	4–5	4–5	4
CN	-PhC_2H_4-		magenta	25.9/133/165	32.5	8.8	4–5	4	5	5	5	4–5	4
CN	-C_2H_4Ph-		red–violet	28.2/135/166	23.5	9.6	5	4–5	5	5	5	4–5	4
CN	Me	Me	red	21.6/153/167	27.0	27.0	4–5	4	5	4	3–4	3	1–2
CO_2Me	Me	Me	orange	19.6/153/208	125	94.6	4	4	5	4	3–4	3–4	1–2
CO_2Et	Me	Me	orange	18.7/151/207	109	77.0	4	4	5	4	3–4	3–4	1–2
CO_2Me	H	Me	orange–red	22.6/169/231	124	118	4	4	5	4	3–4	3–4	1–2
CO_2Me	H	Et	orange–red	20.0/162/225	163	143	4	4	5	4	3–4	3–4	1–2
CO_2Me	H	Bu^n	orange–red	18.9/148/212	129	48.9	4–5	4–5	5	4	4	3–4	2
CO_2Me	H	Ph	crimson	33.1/221/294	138	64.1	4–5	4	4–5	4–5	4–5	4	3

contd.

CO_2Me	H	Ac	maroon	33.7/239/272	142	125	3–4	3–4	5	4	3–4	3–4	2–3
CO_2Me	Me	Ac	crimson	27.6/210/282	107	66.8	3–4	3–4	5	4	3–4	3–4	2–3
CO_2Et	Me	CO_2Et	red	26.8/180/204	33.0	24.5	4	4	5	4–5	4	3–4	2
CO_2Et	Me	CN	magenta	31.1/143/157	22.9	28.3	4	4	5	4–5	4	4	3
CN	Me	CO_2Et	pale rubine	34.8/50.3/53.3	6.6	14.3	5	4–5	5	5	4–5	4–5	4
CN	Me	CN	violet	45.5/209/230	39.0	51.5	4	4	5	4–5	4	4	2–3
CO_2Et	CH_2CO_2Et	CO_2Et	crimson	21.2/139/152	85.9	41.1	3–4	4	4–5	4–5	4–5	4	3–4
CN	CH_2CO_2Et	CO_2Et	red–violet	28.4/189/195	63.5	45.7	3–4	4	4–5	4–5	4–5	4	3–4
$CONH_2$	H	Ph	red–violet	35.5/236/278	195	85.4	4	3	5	5	5	5	4–5

P = polyester; N = nylon; D = diacetate; C = cotton.

[a] 0.5% o.m.f.

[b] 0.05%/0.5%/1.0% o.m.f.

[c] Wash fastness (ISO C06 B2S) of polyester (0.5% o.m.f.); all samples had ratings of 5 for colour change and staining of cotton and acrylic.

[d] Sublimation fastness (ISO P01) of polyester (0.5% o.m.f.).

Diacetate

Generally, the standard of the diacetate dyeings was the poorest of the three substrates. Shades were often pale and uneven. For this reason, the colorimetric data for these dyeings should be treated with caution. The greatest contrasts in dyeing performance were found with this substrate. While some dyes gave deep, level shades of similar depth to those on polyester at 0.5% o.m.f., others only stained the material.

The thienylazo dyes which showed better substantivity were the smaller, compact molecules, for example **1** (3-CO_2Me-5-Me) and **1** (3-CO_2Me-5-Et), which gave depths approaching that on polyester at 0.5% o.m.f. Small structural changes, which made little difference to dyeing properties on polyester, were, in contrast, found to have a significant impact on acetate. For example, methyl esters tended to produce deeper dyeings than their ethyl analogues; one such case was with **1** (3-CO_2Me-4,5-$(CH_2)_4$-) which gave a dyeing of higher strength than the ethyl ester (*fk* 52.8 and 27.7, respectively). A 5-acyl function appeared to confer favourable dyeability towards diacetate; the dyes **1** (3-CO_2Me-5-Ac and 3-CO_2Me-4-Me-5-Ac) gave deep, level shades, presumably aided by the planar, compact nature of the acyl group.

As with the other substrates, the presence of bulky substituents on dyes restricted the depth of dyeing. In the light of the findings above, it is unsurprising that the extent of the curtailment was clearly seen with diacetate; for example, **1** (3-COPh-4,5-$(CH_2)_4$-) and thienyl-2-azo dyes with large 4,5-substituents, such as **1** (3-CN-4,5-$(CH_2)_{10}$-) and **1** (3-CN-4,5-C_2H_4Ph-), all furnished very pale shades at 0.5% o.m.f.

Fastness properties of the dyeings

The performances of the dyeings varied widely; for a given dye, fastness was typically most satisfactory on polyester. After allowing for variations in depth of shade, correlations can be made between fastness and substrate type or dye structure.

Wash fastness

Wash fastness ratings for the polyester dyeings (0.5% o.m.f.) are listed in Table 1. Fastness was generally good: typically, only the diacetate and nylon components of the multifibre were stained.

Members of the 4,5-alkyl(ene)thienyl-2-azo series had similar ratings, typically 5, 4 and 4 for the staining of polyester, nylon and diacetate, respectively. Deviations from this pattern can be explained in terms of dye structure and concentration of dye in the sample. It is likely that the slightly poorer (4–5, 3–4, 4) ratings of **1** (3-CN-4,5-$(CH_2)_3$-) are associated with its relatively small molecular mass which facilitates diffusion out of the sample and also into the multifibre. Additionally, the higher initial concentration of the dye in the sample could have been significant. The slightly better fastness of the pentamethylene derivatives may be for the opposite reasons to those of the trimethylene dye; an extra factor could be the more hydrophobic nature of the pentamethylene dyes caused by the large alkylene ring, making solubilisation in the wash liquor more difficult, lowering the amount of dye in true solution which can diffuse into the multifibre and bring about staining. An extreme example is **1** (3-CN-4,5-$(CH_2)_{10}$-): the pale initial depth of shade of the sample, coupled with the low diffusion rate (out of the sample as well as into the nylon and acetate components of the multifibre), brought about by the presence of the bulky alkylene ring, results in excellent fastness (5 for all ratings). The same reasons could explain the higher than average wash fastness of **1** (3-CN-4,5-PhC_2H_4-) and **1** (3-CN-4,5-C_2H_4Ph-).

The lower than average fastness of **1** (3-$CONH_2$-4,5-$(CH_2)_4$-) seems likely to be associated with the ability of the dye to hydrogen-bond, raising its water solubility and encouraging leaching out of the fibre. The low rating of nylon staining (3) in the case of **1** (3-$CONH_2$-5-Ph) could also be for this reason or simply because of the dye's high substantivity for nylon. The latter reason might also be relevant to the lower than average ratings of the dyes **1** (3-CO_2Me-5-Ac and 3-CO_2Me-4-Me-5-Ac) concerning nylon and diacetate staining.

The introduction of more electron-withdrawing groups appears to make little difference to fastness; for example, **1** (3-CO_2Et-4,5-Me, 3,5-CO_2Et-4-Me and 3-CO_2Et-4-Me-5-CN) all had the same staining ratings (see Table 1). The better than average fastness with **1** (3-CN-4-Me-5-CO_2Et) can be attributed to the low depth of shade of the sample.

Not unexpectedly, the dyed nylon and diacetate samples were less fast than the corresponding polyester dyeings, despite the lower temperature (40 °C) of the wash fastness test used (ISO 105 C06 A2S) compared with that employed with the polyester (50 °C, ISO 105 C06 B2S). This can be ascribed to the more crystalline, hydrophobic nature of the polyester inhibiting diffusion of the dye out of the fibre, so that, on average, better ratings for this fibre were obtained than those for the other two. The poorer fastness of the dyes on nylon and acetate is readily revealed by the few dyes which give dyeings of similar depth on each substrate at 0.5% o.m.f. These include **1** (3-CO_2Me-5-Me) and **1** (3-CO_2Me-5-Ac) (see Table 2).

Similar patterns to that seen with polyester were observed in the cases of the nylon and acetate samples, although, in some instances, these were complicated by variations in depth of shade. For example, **1** (3-CN-4-Me-5-CO_2Et) had improved fastness on nylon at 0.5% o.m.f. when compared with the dyeing on polyester at the same application level, but when one takes into consideration the very pale shade of the nylon dyeing (*fk* 6.6), the improvement is unsurprising.

TABLE 2
Wash Fastness Ratings of Two Dyes of Type **1** (3-CO_2Me) on Three Substrates at 0.5% o.m.f.

Dye	*Fibre*	*Colour change*	*Staining*				
			D	*N*	*P*	*A*	*C*
1 (3-CO_2Me-5-Me)	P	5	4	4	5	5	5
	N	4–5	2–3	3	4	4	4
	D	4–5	3	3	4–5	4–5	4–5
1 (3-CO_2Me-5-Ac)	P	5	3–4	3–4	5	5	5
	N	5	2–3	3	4–5	4	4–5
	D	4–5	2–3	3	4	4	4–5

D = diacetate; N = nylon; P = polyester; A = acrylic; C = cotton.

Many of the diacetate dyeings gave reasonable staining ratings, but with poor ratings for colour change, an extreme example being **1** (3-CN-4,5-$(CH_2)_{10}$-), which had ratings of 5 and 2, respectively, for staining and colour change. The performance can be explained by the low depth of such dyeings, meaning that relatively little dye was available to stain the multifibre and little had to be removed for significant colour loss. Additionally, the diacetate used had a relatively low mass per unit area, which may have exacerbated colour loss, since more wash liquor was present per unit mass of dyed fabric than in the cases of the polyester and nylon samples.

Perspiration fastness

Seven dyes were evaluated for fastness to alkaline perspiration. The fastness of the polyester samples was very good (see Table 3). As expected, dyes of better than average wash fastness had superior perspiration fastness.

TABLE 3
Alkaline Perspiration Fastness Ratings of some of the Dyes **1** on Polyester at 0.5% o.m.f.

Substituents			*Staining*	
3	*4*	*5*	*Diacetate*	*Nylon*
CO_2Et	-$(CH_2)_4$-		4–5	4–5
CN	-$(CH_2)_6$-		4–5	5
CO_2Et	Me	CO_2Et	4–5	5
CO_2Et	CH_2CO_2Et	CO_2Et	5	5
CN	Me	CN	5	5
CO_2Me	H	Me	4–5	4–5
CO_2Me	H	Ac	4–5	4–5

All samples had ratings of 5 for colour change and the staining of polyester, cotton and acrylic.

As was the case for wash fastness, ratings on nylon and diacetate were typically poorer than that for polyester; for example, dyeings of **1** (3-CO_2Me-5-Me) on nylon and diacetate at 0.5% o.m.f., which were of similar depth to that obtained with polyester, had ratings of 4–5, 3–4 and 3–4 for the staining of polyester, nylon and diacetate, respectively.

Light fastness

The dyeings exhibited a wide range of fastness to light, varying from 1 to 6 on polyester and 1 to 4 on nylon and acetate (see Table 4). Ratings were, on average, highest on polyester, with slightly lower values for nylon and diacetate in most cases.

This order is in agreement with that found by Evans and Stapleton,[26] although the work of Peters has revealed some aminoazobenzenes[27–29] and benzothiazolylazo dyes[30] to be more fast on diacetate than polyester.

Fastness was found to be relatively insensitive to the concentration of dye in the polyester. Over the range of a 20-fold increase in application level (0.05–1.0% o.m.f.) to polyester, the maximum difference in fastness between the lightest and heaviest shades for a given dye was 1 point, most of the dyeings having a variation of half a point and some none at all. The one exception was **1** (3-CN-4,5-C_2H_4Ph-) which gave a difference in ratings of 1.5 points. A relative insensitivity over a 0.1%–2.5% o.m.f. application range on polyester (and where reported on diacetate) is apparent in the results of Peters and co-workers with carbocyclic[27–29,31] and heterocyclic[6–8,17,30] monoazo dyes. For this reason, it was considered valid to compare the ratings of the dyeings despite the fact that they were not of a standard depth.

TABLE 4

Light Fastness Ratings of Fabric Coloured with some of the Dyes **1**

Substituents			*Polyester*			*Nylon*	*Acetate*
3	*4*	*5*	*0.05%*	*0.5%*	*1.0%*	*0.5%*	*0.5%*
CN	-PhC_2H_4-		1	1	1	1	1
CN	-C_2H_4Ph-		2	3–4	3–4	3	2–3
CN	Me	Me	1	1–2	1–2	1	1
CO_2Me	Me	Me	1	1	1	1	1
CO_2Et	Me	Me	1	1	1	1	1
CO_2Me	H	Me	2	2	2	2	1–2
CO_2Me	H	Et	2	2	2	2	1–2
CO_2Me	H	Bu^n	1–2	2	2–3	2	1–2
CO_2Me	H	Ph	3	3–4	3–4	3–4	3
CO_2Me	H	Ac	4–5	5	5	4	4
CO_2Me	Me	Ac	4–5	5	5	4	3–4
CO_2Et	Me	CN	5	5	6	4	3–4
CN	Me	CN	5–6	5–6	6	4	4
$CONH_2$	H	Ph	3–4	4	4	4	3

The 4,5-alkylenethienyl-2-azo dyes were very fugitive on each substrate; all of the dyeings from colorants of this kind on polyester, nylon and diacetate had ratings of 1, like the values reported for the analogous 4,5-tetramethylene dyes.[22] An exception was **1** (3-CN-4,5-$(CH_2)_3$-) whose slightly higher ratings (2) on polyester are probably a result of higher concentrations of dye on the fibre relative to the other derivatives, rather than any inherent increase in photostability.

Significant improvements were brought about on all three fibres by the introduction of a phenyl substituent into the 5-position of the thiophene ring. For example, **1** (3-CO_2Me-5-Me) had ratings of 2 on polyester and nylon at 0.5% o.m.f., whereas those of **1** (3-CO_2Me-5-Ph) were 3–4; the value of **1** (3-$CONH_2$-5-Ph) on polyester at 0.5% o.m.f. is an improvement on the rating of 1 found for **1** (3-$CONH_2$-4,5-$(CH_2)_4$-).[22] The importance of the orientation of the substituent can be demonstrated by comparing the isomeric dyes in which a benzene ring is fused to the alkylene ring of **1** (3-CN-4,5-$(CH_2)_4$-). The isomer in which the ring is linked to the 5-position, **1** (3-CN-4,5-C_2H_4Ph-), had improved fastness (3–4, 3, and 2–3 on polyester, nylon and diacetate, respectively, at 0.5% o.m.f.) relative to that of the parent dye (2, 1 and 1)[22] in line with the findings above. However, no improvement was found with the isomer **1** (3-CN-4,5-PhC_2H_4-) in which the phenyl ring is bonded at the 4-position (ratings of 1 on all three substrates at 0.5% o.m.f.). The slight decrease in fastness on polyester compared with the parent dye is probably because of the lower concentration of dye in the sample at 0.5% o.m.f.

Bigger increases in light fastness than that brought about by a 5-phenyl group can be achieved by the introduction of electron-withdrawing groups into the 5-position. For example, replacement of the methyl group in **1** (3-CO_2Me-5-Me) with an acetyl group brings about an increase of 2–3 points on each substrate. The effect parallels that found with aminoazobenzenes in which the increase in electron-withdrawing power of the diazo component serves to reduce electron density on the amino nitrogen atom and photofading occurring by attack at this site by singlet oxygen.[32,33]

The influence of the substituent in the 3-position is less clear. Marginal improvements were shown on polyester on going from **1** (3,5-CO_2Et-4-Me) to **1** (3-CN-4-Me-5-CO_2Et)[22] and from **1** (3-CO_2Et-4-Me-5-CN) to **1** (3,5-CN-4-Me) (see Table 4); there was little effect on nylon or diacetate. Modification of the 4-methyl group to the slightly more electron-accepting 4-methylcarboxyethyl group had a marginal effect on polyester and none on nylon and diacetate.[22]

Sublimation fastness

The dyes possessed a wide range of fastness to dry heat on polyester (see Table 1), varying from excellent, as in the case of **1** (3-$CONH_2$-5-Ph), to poor, for example **1** (3-CN-4,5-$(CH_2)_3$-) and **1** (3-CN-4,5-Me). It is well known that molecular mass and intermolecular interactions affect the dry heat fastness of carbocyclic monoazo dyes;[34] these factors also appear to influence the volatility of the dyes **1**.

The 4,5-alkylene dyes showed similar ratings although fastness tended to improve as the ring size was increased (see Table 1). For example, the staining with **1** (3-CN-4,5-$(CH_2)_{10}$-) was much less than that exhibited by **1** (3-CN-4,5-$(CH_2)_3$-). This finding may stem from the increase in molecular mass reducing the volatility of the dye and thus lowering dye sublimation. Additionally, the bulkier ring system will make diffusion out of the fibre more difficult. However, the initial concentration of the dye in the sample is important. Its influence is emphasised by the above extreme example: the difference in concentration of dye in the case of **1** (3-CN-4,5-$(CH_2)_{10}$-) due to the lower molarity of dye applied to the fibre at 0.5% o.m.f. (and reduced exhaustion in the dyebath because of lower diffusion of dye into the fibre), compared with **1** (3-CN-4,5-$(CH_2)_3$-), is particularly large and so plays an important role in the former having better fastness on polyester at 0.5% o.m.f. The trend of improving fastness with increased ring size probably arises as a result of all of these factors working in concert.

Little difference in fastness was found between 3-alkoxycarbonyl and 3-cyano analogues, for example in the tetramethylene series (see Table 1). However, in this series, the 3-aroyl and 3-carbamyl derivatives had higher fastness, the former, in part, because of the increased bulk of the groups. The amido group confers hydrogen-bonding capabilities on the 3-carbamyl dye: its introduction brings about an improvement in fastness by providing another means of intermolecular interaction between dye and fibre.

A mass effect can be observed with the derivatives in which a benzene ring is fused to the alkylene ring: **1** (3-CN-4,5-PhC_2H_4-) and **1** (3-CN-4,5-C_2H_4Ph-) had improved fastness relative to **1** (3-CN-4,5-$(CH_2)_4$-) with the orientation of the ring not appearing to be a factor (see Table 1). A mass effect is also shown on replacing the 5-methyl group of **1** (3-CO_2Me-5-Me) with a phenyl ring; a further rise in fastness is brought about by swapping the ester function for an amide group which bestows the ability to hydrogen-bond on the dye, further reducing volatility. As a result of the presence of both effects, the dye **1** (3-$CONH_2$-5-Ph) had excellent heat fastness (see Table 1).

EXPERIMENTAL

The synthesis and purification of the dyes **1** have been described previously.[22,23] The dyes were milled and applied to polyester at 130 °C prior to reduction-clearing and stentering as detailed elsewhere.[22] The dye dispersions were also used to dye nylon 6,6 and diacetate (temperature 98 °C and 85 °C, respectively; duration 1 h; liquor ratio 40:1; pH 4.5 ± 0.1; auxiliary Dyapol BD 1 g l^{-1}) and the fabric thoroughly rinsed with cold water and air-dried.

Reflectance spectra of the dyeings were obtained by means of a Colorgen CS-1100 spectrophotometer linked to a personal computer with Colorgen QC version 6.70 software.

Standard fastness testing procedures were employed.[35] Wash fastness tests that simulated one domestic or commercial laundering for each of the three fibre types at 0.50% o.m.f. were chosen: ISO 105 C06, colour fastness to domestic and commercial laundering. For polyester samples, the B2S test was used; Multifibre DW, steel balls and ECE reference detergent were employed. The samples were air-dried without a souring procedure. For nylon and acetate samples, the A2S test was used and, as above, multifibre, steel balls, ECE detergent and drying without souring were employed. Alkaline perspiration fastness was tested for by the ISO 105 E04 method on polyester, nylon and secondary acetate at 0.50% o.m.f. using Multifibre DW as adjacent fabric. The ISO 105 B02 test was used to assess the light fastness of every dyeing. The sublimation fastness of each dyeing on polyester (0.5% o.m.f.) was evaluated using the ISO 105 P01 test with cotton and polyester as adjacent fabrics.

CONCLUSIONS

Application of the dyes to synthetic polymers was accompanied by varying degrees of success to give dyeings with a range of performance. The coloration of nylon and acetate was not as fruitful as that of polyester in terms of colour yield and fastness.

Despite the dyeings not being of standard depths, correlations with dye structure could be found. Overall, as expected, the dyes were most fast to washing on polyester, with variations in fastness dependent on dye structure, either directly, by affecting diffusion out of the dyed fabric and into the multifibre, or indirectly, by affecting the initial depth of the dyed fabric. Wash fastness on nylon and acetate tended to be poor, a common failing of disperse dyes on these substrates. Perspiration fastness followed a similar pattern. Light fastness was observed to improve when the dispersal of electron density from the thiophene ring π-system was promoted through the attachment of a phenyl ring or an electron-acceptor to a conjugative position. Thienyl-2-azo dyes having bulky molecular structures or the ability to hydrogen-bond had superior fastness to dry heat.

From the results, it is not difficult to see why red thienyl-2-azo dyes have not been marketed commercially for polyester. Despite the relative ease of manufacture of the diazo components with quite inexpensive materials, dye synthesis presents problems in terms of diazotisation and product purity,[23] although the most obvious obstacle to commercial acceptance is the extremely poor light fastness of these dyes on polyester and other substrates. However, the violet dyes did have improved properties with respect to synthesis and fastness.

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