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〈研究論文(學術)〉

에틸렌이민 유도체를 갖는 아조계 분산염료의 염색성에 관한 연구(Ⅲ)

- 폴리에스테르 및 나일론 6.6 극세사 섬유에의 응용 -

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A Study on the Properties of Azo Disperse Dyes Containing Ethyleneimine Derivatives(Ⅲ)

-Application to Microfibre Polyester and Nylon 6.6 Fabrics -

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요 약

이 연구의 목적은 에틸렌이민 유도체를 갖는 아조계 분산 염료의 나일론 6.6 섬유에의 응용과 최적화된 폴리에스테르 및 나이론 극세사 섬유 염색 조건의 확립이다.

세가지 아지리디닐 모노 아조 염료와 이들 염료의 가수분해 된 형태 그리고 디메틸아닐린계 아조 염료의 폴리에스테르 및 나일론 6.6 극세사 섬유에 대한 염색 및 견뢰도 성질이 조사되었다.

염색 조건 중 pH의 변화에 따른 섬유상의 염착량 변화 조사에서 뚜렷한 경향을 얻을 수 없었으며, 이는 극세사 섬유의 물리적 성질이 두드러지게 착용한 이유라 여겨진다.

염색된 폴리에스테르 극세사 섬유상에서, 아지리디닐 염료는 이들의 가수 분해된 형태 그리고 디메틸아닐린계 아조 염료와 비교하여 개선된 견뢰도 성질을 나타내었다.

아지리디닐 아조 염료의 나일론 극세사 섬유 염색 시 pH 증가에 따라 세탁 및 광견뢰도가 개선되었고, pH8의 염색 조건에서 최적 견뢰도 개선을 나타내었다.

아지리디닐 아조 염료가 이들 염료의 가수분해 된 형태 그리고 디메틸아닐린계 아조 염료와 비교하여 폴리에스테르 및 나일론 섬유상에서 보다 개선된 견뢰도 성질을 나타내었고 이는 섬유와 염료간의 공유결합으로 기인한 것으로 여겨진다.

1. Introduction

The trend towards finer polyester fibres stems from the desire to produce silk-like polyester fibre and, historically, this development occurred over several decades[1,2]. The lower linear density of microfibre results in disperse dyes exhibiting a faster rate and greater extent of uptake on polyester microfibres than on conventional decitex fibre[3~6]. The rate of dye uptake increases with increasing fibre fineness so that the higher surface area of the microfibre fabrics means that such fibres require more dye than conventional polyester to give the same visual colour strength.

The lightfastness of microfibre polyester fabric decreases with decreasing decitex due to a corresponding increase in the surface exposed to incident light. Wet fastness properties, which are not critical for conventional decitex polyester fibre dyeings, do become important. Dye selection must be considered when the dyeings are exposed to high temperature[3].

In high temperature dyeing, shorter times are required to achieve good dye penetration[5,6] and, as a consequence of the faster rate of dyeing of polyester microfibres, the levelling behaviour of disperse dyes on microfibre is often poorer than on conventional decitex fibres. Thus, in order to improve levelling, microfibre dyeing is usually commenced at a lower temperature than that employed for conventional fibres[1,3,7].

As with polyester microfibres, polyamide microfibres have been produced since the 1970's and have become popular in sports/leisure wear, underwear and 'cotton-look' outerwear[8~10].

When compared to conventional decitex fibres, dyed polyamide microfibre has a paler appearance, resulting from the greater extent of surface reflection from the greater surface area[10~12] and microfibre nylon needs more dye than conventional fibre to give the same depth of shade.

When the dye distribution across dyed nylon filaments was examined during the course of dyeing, the extent of 'ring dyeing' was found to be greater for microfibre than conventional decitex nylon fibre[11]. Such a propensity of the microfibre to ring dye was considered[12] to be due to the rate and extent of dye diffusion within the microfibre being lower than that within its conventional counterpart owing to the lower internal volume of the former type of fibre.

During dyeing, dye molecules will be adsorbed on to the nylon fibre surface and then diffuse within the interior of the fibre. The rate of dye diffusion within the fibre is governed by the concentration of dye at the fibre surface and the available volume within the interior of the substrate in which the dye molecules diffuse. In the case of nylon microfibres, dye adsorption at the fibre surface was found to be high because of the large surface area, whilst the available internal volume within fibre is low[10]. Thus, there must be a limit to the amount of dye that can be accommodated within the fibre, which, in turn, limites the rate of dye uptake and the extent of dyebath exhaustion[10]. At higher concentrations of applied dye, more dye, which cannot diffuse into the small available internal volume, will be present at the fibre surface. Thus, the wet fastness of a given dye on polyamide microfibre is lower than that on a conventional decitex fibre[4,11].

Also, when the same concentration of dye was present within micro and conventional nylon 6.6 fabrics, it was found that dyed microfabric displayed lower wash fastness, due to the larger surface area of the microfibre from which dye desorption occurred[12].

When aminoazobenezene disperse dyes containg ethyleneimine ring applied to conventional decitex polyester and nylon 6.6 fabrics, the fastness properties to washing and light were higher then that of 2-β-hydroxyethylaniline azo dyes and conventional disperse dye, *N,N'*-dimethylaniline azo dye 13), which may be due to the covalent bond or self polymerisation ; this was confirmed using solvent extraction of the dyeings13).

In this paper, aminoazobenezene disperse dyes containg ethyleneimine ring applied to microfibre polyester and nylon 6.6 fabrics. The 2-β-hydroxyethylaniline azo dyes, as a hydrolysed form, and conventional disperse dye, *N,N'*-dimethylaniline azo dye were also applied to microfibre fabrics in reference.

2. Experimental

2.1. Dye application

2.1.1. Experimental materials

2.1.1.1. Fabrics

2.1.1.1.1. Polyester fabrics

Commercially available, woven microfibre (warp : polyester filament 75f36, 2.08 dtexpf ; weft : drawn textured yarn 150f144, 1.04 dtexpf ; density : 137×84) fabrics were used throughout the study.

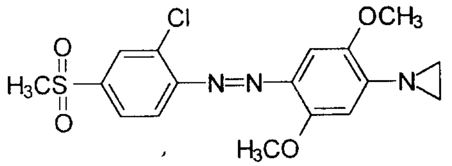
2.1.1.1.2. Nylon 6.6 fabrics

Commercially available, woven microfibre (warp : nylon 66 filament 70f24, 2.9 dtexpf ; weft : drawn textured yarn 150f144, 1.04 dtexpf ; density : 138 89) fabrics were used.

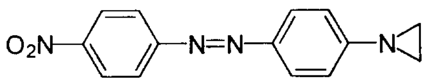
2.1.1.2. Dyes

The ethyleneimine dyes(A-1, C-1 and D-1), the 2-hydroxyethylaniline azo dyes(A-2, C-2 and D-2) and the *N,N'*-dimethylaniline azo dye B-4, which were prepared in previous work as described in Sunwoo's paper14), were used throughout the study.

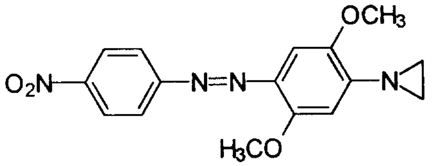
- 2-chloro-4-methanesulphonylaniline→1-(2,5-dimethoxyphenyl)aziridine (Dye A-1)



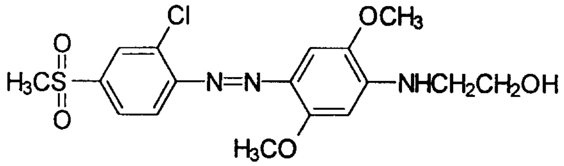
- 4-nitroaniline→1-phenylaziridine(Dye C-1)



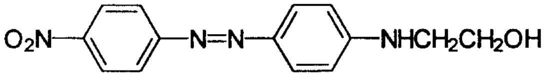
- 4-nitroaniline→1-(2,5-dimethoxyphenyl)aziridine (Dye D-1)



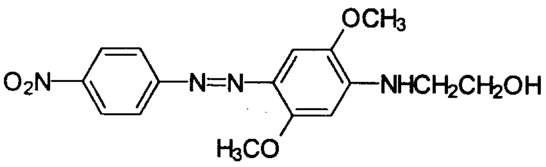
- 2-chloro-4-methanesulphonylaniline→2,5-dimethoxy-*N*-β-hydroxyethylaniline (Dye A-2)



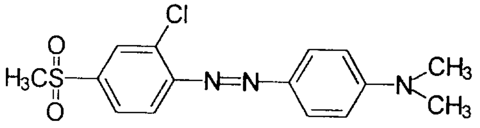
- 4-nitroaniline→*N*-β-hydroxyethylaniline (Dye C-2)



- 4-nitroaniline→2,5-dimethoxy-N-β-hydroxyethylaniline (Dye D-2)



- 2-chloro-4-methanesulphonylaniline→*N,N'*-dimethylaniline (Dye B-4)



2.1.1.3. Chemicals and auxiliaries

Commercial samples of Ufoxane 2 (YCL), which was employed as dispersing agent in dyeing and Sandozin NIE (Sandoz) which was used in the reduction clearing of dyed polyester, were supplied by the respective makers. HPLC grade acetonitrile was obtained from Aldrich.

All chemicals used in the work were laboratory grade reagents obtained either from Aldrich or BDH ; sodium acetate, acetic acid (99% w/w) and sulphuric acid (98% w/w8 were used to control dyebath pH and sodium hydroxide and sodium dithionite were used for the reduction clearing of dyed polyester.

2.1.2. Preparation of dye samples

1.0g of dye, 2.0g of dispersing agent (Ufoxane 2) and 100㎤ of distilled water were placed in a 250㎤ capacity glass jar. The jar was then filled to two thirds capacity with 1㎝ diameter ceramic balls and the sealed jar rotated on a laboratory-scale ball mill for 24 hours at room temperature.

2.1.3. Dyeing

Dyeing was carried out in sealed, stainless steel dyepots of 200㎤ capacity housed in a Zeltex laboratory scale dyeing machine using a liquor ratio of 30 : 1. The appropriate mass of stock dye solution was placed in the dyepot and sufficient appropriate buffer solution (described below) and additional dispersing agent (Ufoxane 2 ; 1gℓ$^{-1}$) were added to make the volume up to 60㎤.

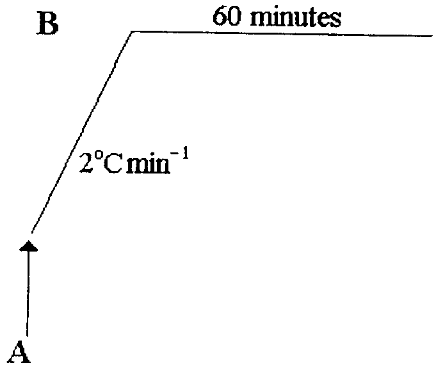


Fig. 1 Dyeing method

A Fabric(1g) added
60℃ for microfibre polyester
40℃ for microfibre nylon 6.6
B 130℃ for microfibre polyester
98℃ for microfibre nylon 6.6.

2.1.3.1 Dye build-up at various pH

Various of dyeings (Table 1) using ethyleneimine azo dyes (A-1, C-1 and D-1 in section 2.1.1.2.), hydrolysed dyes (A-2, C-2 and D-2 in section 2.1.1.2.) and the *N,N'*-dimethylaniline azo dye (B-4 in section 2.1.1.2.) were carried out at 130℃ for polyester and at 98℃ for nylon fabrics in the presence of 1gℓ$^{-1}$ Ufoxane 2 as described in section 2.1.3.

Buffer solution of pH 5 was prepared by the dissolution of acetic acid (0.0042M) and sodium acetate (0.026M) in 1 litre of distilled water. A buffer solution of pH 6 was obtained by the dissolution of acetic acid (0.02M) and sodium acetate (0.17M) in 1 litre of distilled water ; the final pH was secured by the addition of either 0.1M of acetic acid solution or 0.1M of sodium acetate solution.

Buffer solutions of pH 8 and 10 were obtained by the dissolution of disodium hydrogenphosphate (5g) and potassium dihydrogenphosphate (1g) in

Table 1. % omf dye applied to microfibre fabric

Dye	pH	Polyester Fabric	Nylon Fabric
A-1	6.0	0.5, 1.0, 1.5, 2.0	0.5, 1.0, 1.5, 2.0
	8.0	0.5, 1.0, 1.5, 2.0	0.5, 1.0, 1.5, 2.0
	10.0	0.5, 1.0, 1.5, 2.0	0.5, 1.0, 1.5, 2.0
A-2	6.0	0.5, 1.0, 1.5, 2.0	0.5, 1.0, 1.5, 2.0
C-1	6.0	0.5, 0.7, 1.0, 1.5, 2.0	0.5, 1.0, 1.5, 2.0
	8.0	0.5, 0.7, 1.0, 1.5, 2.0	0.5, 1.0, 1.5, 2.0
	10.0	0.5, 0.7, 1.0, 1.5, 2.0	0.5, 1.0, 1.5, 2.0
C-2	6.0	0.3, 0.5, 0.7, 1.0, 1.5, 2.0	0.5, 1.0, 1.5, 2.0
D-1	6.0	0.5, 1.0, 1.5, 2.0	0.5, 1.0, 1.5, 2.0
	8.0	0.5, 1.0, 1.5, 2.0	0.5, 1.0, 1.5, 2.0
	10.0	0.5, 1.0, 1.5, 2.0	0.5, 1.0, 1.5, 2.0
D-2	6.0	0.5, 1.0, 1.5, 2.0	0.5, 1.0, 1.5, 2.0

1 litre of distilled water ; the appropriate pH value was secured by the addition of either 0.1M aqueous hydrochloric acid or 0.1 M aqueous sodium hydroxide solution to the mixed phosphate buffer solution.

2.1.3.2. Reduction clearing

Dyed microfibre polyester fabrics was reduction cleared by stirring in an aqueous solution containing $2g\ell^{-1}$ sodium hydroxide (pellet), $2g\ell^{-1}$ sodium dithionite and $1g\ell^{-1}$ Sandozin NIE at 70℃ using a liquor ratio of 30 : 1 for 30 minutes. The reduction cleared sample was then rinsed thoroughly in water and allowed to dry in the open air.

2.1.4. Standard depth dyeings

Commercially available, scoured, woven microfibre polyester fabric and commercially available, scoured, and microfibre nylon 6.6 fabric were used to obtain standard depth dyeings. A series of dyeings of each of the dyes A-1, A-2, B-4, C-1, C-2, D-1 and D-2 were carried out at 130℃ for microfibre polyester fabrics and at 98℃ in the case of microfibre nylon fabrics, in the presence of $1g\ell^{-1}$ Ufoxane 2 at pH 6, 8 and 10 for polyester fabrics and at pH 5, 8 and 10 for nylon 6.6 fabrics, as described in section 2.1.3. At the end of dyeing, the dyed polyester fabric was rinsed thoroughly in cold tap water, reduction cleared as described in section 2.1.3.2. and dried in the open air ; the dyed nylon 6.6 fabric was rinsed thoroughly in cold tap water and dried in the open air.

The depth of shade of each of the dyed microfibre polyester and nylon 6.6 fabrics was visually compared with the appropriately coloured Society of Dyers and Colourists' matt standard depth shades[15] in an *ICS/Texicon* (ICS, UK) viewing cabinet under illuminant D_{65}. Dyeings were repeated to achieve a 1/1 standard depth of shade for each of the dye samples on both types of polyester and nylon 6.6 fabrics. Some of dyeings which could not be obtained at 1/1 standard depth of shade were examined at either 1/3 or 1/6 standard depth.

2.1.5. Dyeing nylon 6.6 fabrics using ammonia

The dyeing of conventional and microfibre nylon 6.6 fabric was carried out as follows :

- dyeing at 98℃ for 1 hour
- pH 10 adjusted using NH_4OH
- 0.5, 1.0, 1.5, 2.0% omf of dye A-1 (dyeing was repeated to achieve the 1/1 standard depth)
- $1g\ell^{-1}$ dispersing agent (Ufoxane 2)
- liquor ratio 30 : 1
- dyeing procedure was as described in section 2.1.3.

2.1.6 Colour measurement

The reflectance values of the dry, reduction cleared, dyed microfibre polyester fabrics and the dry, dyed microfibre nylon 6.6 fabrics were measured using an *ICS Micromatch 2000* colour measurement system under the following viewing conditions : illuminant D_{65} ;

10° standard observer ;

UV component included ;

specular component excluded.

The CIELab coordinates and Kubelka-Munk (K/S) values[16] were calculated from the reflectance values. Each sample was folded twice to provide a total of four thickness of fabric and each sample was presented so that the measurement was carried out on the same side of the fabric using identical orientation. An average of four measurements per sample was taken.

2.1.7. Fastness properties of the dyed samples

2.1.7.1. Wash fastness assessment

Rinsed and reduction cleared, dyed polyester fabrics and rinsed dyed nylon 6.6 fabrics were subjected to the ISO CO6/C2 and ISO CO6/C4 wash test and the changes in shade and staining of S.D.C. multifibre test fabric were assessed using the appropriate grey scale (S.D.C. grey scale)[17]

2.1.7.2. Light fastness assessment

Lightfastness assessment was carried out in accordance with the ISO B02 test method housed in a Xenotest 150S (Heraeus). The conditions used for the test are given as follows :

- Black panel temperature : 45~50℃
- Relative humidity : 60%
- Exposure time : 24 hours

3. Results and Discussion

3.1. Application to microfibre polyester fabrics

In this study, dye build-up on microfibre polyester fabric at pH 6, 8 and 10 as well as the fastness to washing and light of standard depth dyeings was examined.

3.3.1. The λ_{max} of dyed microfibre polyester

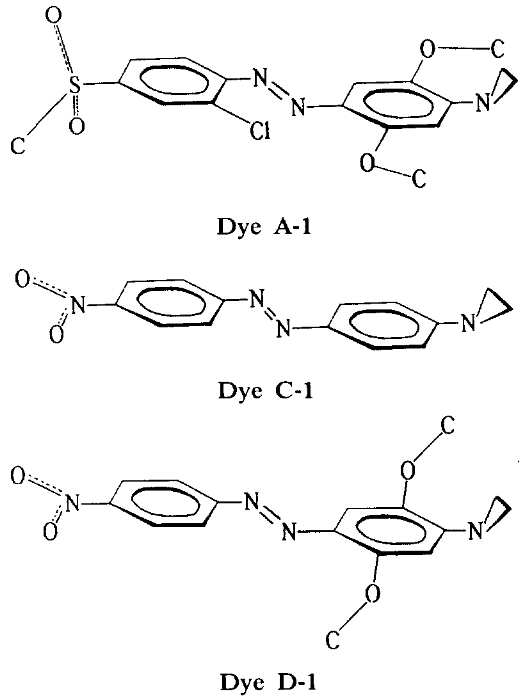
The colour strength (*K/S*) of microfibre polyester fabric, which had been dyed with both azo disperse dyes containing ethyleneimine group (dye A-1, C-1 and D-1) and 2-hydroxyethylaniline azo disperse dyes (dye A-2, C-2 and D-2) as a hydrolysed form, was measured at the λ_{max} of the dyeing (Table 2) as described in section 2.1.6. and a comparison of λ_{max} was made between the ethyleneimine dyes and their hydrolysed counterparts (Table 2). As the polymer used in the microfibre was the same as that employed in conventional decitex fabric, the λ_{max} of each dye on microfibre polyester fabric was the same as that on the conventional decitex polyester fabric[13]. The pairs of dyes A-1/A-2 and D-1/D-2 displayed no λ_{max} difference on the fibre, although the λ_{max} of the dyes in acetone in each pair differed (Table 2). For dyes C-1 and C-2, a difference of 68.4nm in λ_{max} in acetone was observed although only a difference of 20nm was obtained on dyed microfibre polyester.

Table 2. Comparison of the λ_{max} of dyed microfibre polyester fabrics and of the dye in acetone

Dye	pH	λ_{max} of dyed microfibre polyester fabrics		λ_{max} in acetone	
		λ_{max}	$\Delta\lambda$	λ_{max}	$\Delta\lambda$
A-1	6.0	500	0	448.4	45.6
	8.0	500			
	10.0	500			
A-2	6.0	500		494.0	
B-4	6.0	480		462.4	
C-1	6.0	460	20	388.4	68.4
	8.0	460			
	10.0	460			
C-2	6.0	480		456.8	
D-1	6.0	520	0	455.2	43.2
	8.0	520			
	10.0	520			
D-2	6.0	520		498.4	

3.1.2. The structural characteristics of the ethyleneimine dyes

It was considered helpful to discuss the structural characteristics of the ethyleneimine dyes A-1, C-1 and D-1 before presenting a discussion of the build-up properties of the dyes on microfibre polyester since differences in molecular structure may affect the build-up properties on the physically compact microfibre. When the hydrophilic/hydrophobic characteristics of the ethyleneimine azo dyes are considered, dye A-1 (IOR value : 0.691[13)]) containing two methoxy groups in the coupling component as well as a methanesulphonylester group and chlorine in the diazo component, is the most hydrophilic of the three dyes. D-1 (IOR value : 0.615[13)]) which contains two methoxy groups in the coupling component and a nitro group in the diazo component is less hydrophilic than dye A-1 but more hydrophilic than dye C-1 (IOR value : 0.571[13)]) which contains only one nitro group in the diazo component. When the molecular mass and size of the three dyes is compared, A-1 has the greatest M_r (395.86) and also the bulkiest structure with two methoxy groups in the coupling component and the methanesulphonylester and chlorine group in the diazo component (Fig. 2).



Dye A-1

Dye C-1

Dye D-1

Fig. 2 The three-dimensional molecular structures of the three ethyleneimine azo dyes

Dye C-1 has the smallest M_r (268.27) and the most planar structure with the ethyleneimine ring being perpendicular to the benzene ring. The M_r of dye D-1 is 328.32 and its molecular structure is bulkier than that of C-1 because of the two methoxy groups in the coupling component (Fig. 2). It is well known that the build-up of dyes of planar structures is higher than dyes of more bulky structure in that the saturation level of planar is higher than that of the non-planar dyes[18].

3.1.3. Dye build-up

In order to observe the build-up of three ethyleneimine dyes (A-1, C-1 and D-1), three hydrolysed dyes (A-2, C-2 and D-2) and one conventional disperse dye (B-4) under consideration, a series of dyeings on microfibre polyester fabrics was carried out using 0.5, 1.0, 1.5 and 2.0% omf dye, with the hydrolysed dyes and the *N,N'*-dimethylaniline azo dye applied at pH 6 and the ethyleneimine dyes at pH 6, 8 and 10.

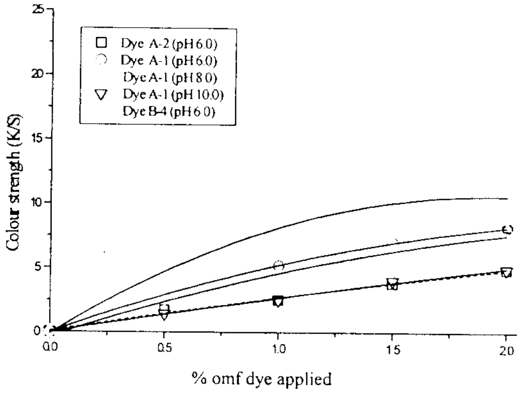


Fig. 3 Build-up of dye A-1, A-2 and B-4 on microfibre polyester fabric

Fig. 3 shows the build-up profiles of dyes A-1, A-2 and B-4 on microfibre polyester ; it is clear that the build-up of the such dyes was markedly lower than that on conventional decitex polyester fabrics[13].

Also, the build-up profiles of dye A-1 at pH 6, 8 and 10 were lower than those of B-4. This finding may be because the M_r of B-4 is lower than that of A-1 and the melting point of B-4 is lower than that of A-1, with the result that the microfibre polyester may be capable of adsorbing B-4 more easily than dye A-1. Dye A-2 showed a similar build-up profile to dye A-1 at pH 10 which also was the lowest of the five build-up profiles in Fig. 3 ; this could be due to the low substantivity of A-2 towards the polyester fibre together with the greater M_r of A-2 and poor dispersion properties of dye A-1 at pH 10. The build-up of dye A-1 on the microfibre decreased with increasing pH of application (Fig. 3).

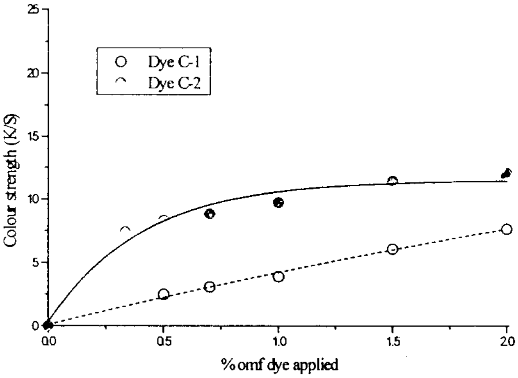


Fig. 4 Build-up of dye C-1 and C-2 on microfibre polyester at pH 6.0

Fig. 4 shows that the build-up of dye C-1 was lower than dye C-2, it may be accounted for by the low tinctorial strength (ε_{max}) of dye C-1 as well as the low substantivity of dye C-1, which can be considered to aggregate readily in alkaline conditions. Furthermore, the substantivity of dye C-2 towards the fibre may be high because of its linear and planar structure as well as the fact that its melting point was much lower than that of dye C-1 (Fig. 2).

The build-up of dye C-1 increased with increasing pH of application, in contrast to the results secured with dye A-1 ; this may be attributable to the fact that, although C-1 dye molecules aggregated under alkaline conditions, the aggregation of C-1 was less than that of either the more bulky A-1 or D-1, the molecular structure of C-1 is nearly planar and linear. (Fig. 2).

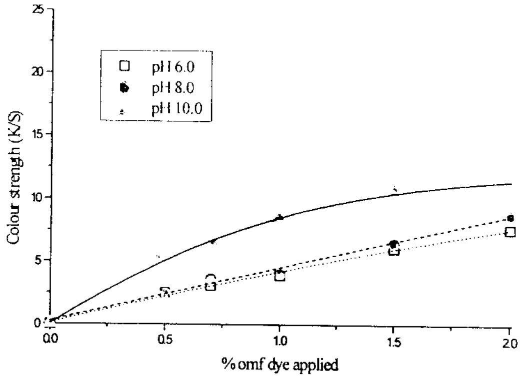


Fig. 5 Build-up of dye C-1 on microfibre polyester

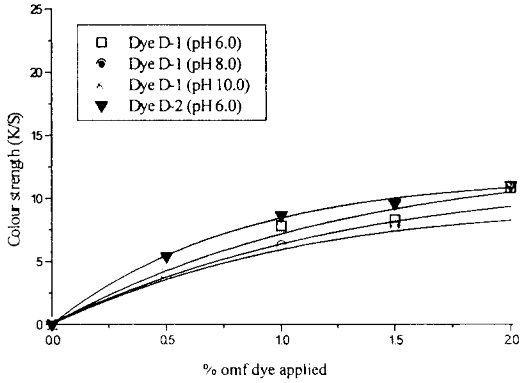


Fig. 6 Build-up of dye D-1 and D-2 on microfibre polyester

Fig. 6 shows that the build-up of dye D-1 on microfibre polyester decreased slightly with increasing pH of application was also found with dye A-1. This finding can be explained in terms of the bulkiness of dye D-1, in that when dye D-1 aggregates, the size of the aggregates will be greater than that of dye C-1. However, when a comparison of dye build-up on the microfibre was made between D-1 and D-2, that of D-1 was slightly lower than that of D-2, although the substantivity of D-1 towards the conventional decitex polyester fabric had been found to be higher than D-2 (Fig. 6). This finding may also be attributable to the steric differences between the dyes.

3.1.4. Standard depth dyeing

Owing to the poor build-up of the three ethyleneimine dyes (A-1, C-1 and D-1) and the hydrolysed dyes A-2 and D-2 on microfibre polyester, it was possible to achieve only a 1/3 standard depth dyeing of microfibre polyester rather than a 1/1 standard depth, whilst with dyes B-4 and C-2, a 1/1 standard depth was achievable. This can be attributed to the greater surface area of the microfibre.

Table 3. Dye concentration (% omf) required to give standard depth dyeings on microfibre polyester

Dye	pH	Concentration (% omf)
A-1	6.0	0.8 (1/3)
	8.0	0.8 (1/3)
	10.0	1.7 (1/3)
A-2	6.0	2.0 (1/3)
B-4	6.0	1.2 (1/1)
C-1	6.0	0.8 (1/3)
	8.0	0.8 (1/3)
	10.0	0.6 (1/3)
C-2	6.0	0.4 (1/1)
D-1	6.0	0.7 (1/3)
	8.0	0.8 (1/3)
	10.0	0.8 (1/3)
D-2	6.0	0.7 (1/3)

3.1.5. Wash-fastness assessment

As a result of the larger surface area of microfibre and the consequent propensity for dye to desorb from dyed microfibre, as described in section 2, generally dyed microfibre polyester displayed low wash fastness(Table 4, Table 5).The wash fastness of microfibre dyeings was assessed using the ISOC06/C2 (60℃, 30 minutes) and ISOC06/C4 (95℃, 30 minutes) test methods as described in section 2.1.7.1.

Table 4 shows the colour fastness to the ISOC06/C2 test of standard depth dyeings from which it is apparent that the wash fastness of the ethyleneimine dyes A-1, C-1 and D-1 increased slightly with increasing pH of application, in terms of staining of adjacent acetate and/or nylon fabrics. A comparison of the wash fastness of dye A-1 which had been applied at pH 6, 8 and 10 and the wash fastness of dye A-2 which had been applied at pH 6 reveals that the wash fastness of dye A-2 was lower in the case of staining of acetate, nylon and wool fabrics. When dye A-1 and B-4 were compared, the wash fastness of dye A-1 which had been applied at pH 10 was identical to that of dye B-4. When the wash fastness of dye C-1 which had been applied at pH 10 was compared with that of C-2, no clear difference was found and, furthermore, dye C-1, when applied at pH 10, exhibited slightly greater staining of nylon adjacent fabric. The wash fastness of dye C-1 which had been applied at pH 6 and 8 was marginally lower than that of C-2. No difference was found between the fastness of dye D-1 when applied at pH 10.0 and D-2 when applied at pH 6, whilst the level of staining of nylon adjacent fabric of dye D-1 which had been applied at pH 6.0 and 8.0 demonstrated the slightly poorer fastness than dye D-2 in staining on nylon adjacent fabric (Table 4).

The more severe ISOC06/C4 (95℃, 30 minutes) wash test was carried out to obtain a clearer picture of the fastness of the dyes (Table 5). As was expected, higher wash fastness was shown by the ethyleneimine dyes when applied at pH 10 than that of the 2-hydroxyethylaniline dyes and the *N*, *N*'-dimethylaniline dye. Also, the wash fastness of the ethyleneimine dyes increased with increasing pH of application.

Table 4. Colour fastness to washing (ISOC06/C2) of standard depth dyeings on microfibre polyester

Dye	pH	Colour depth	Ch	Adj	Ac	Co	Ny	PET	Acr	Wo
A-1	6.0	1/3	4/5	4/5	4	5	4	4/5	4	5
	8.0	1/3	4/5	4/5	4	5	4	4/5	4	5
	10.0	1/3	5	5	4/5	5	4/5	5	5	5
A-2	6.0	1/3	4/5	5	3/4	5	3/4	5	5	4/5
B-4	6.0	1/1	5	5	4/5	5	4/5	5	5	5
C-1	6.0	1/3	5	5	4/5	5	4/5	5	5	5
	8.0	1/3	5	5	4/5	5	4/5	5	5	5
	10.0	1/3	5	5	5	5	4/5	5	5	5
C-2	6.0	1/1	5	5	5	5	5	5	5	5
D-1	6.0	1/3	5	5	4/5	5	4	5	5	5
	8.0	1/3	5	5	4/5	5	4	5	5	5
	10.0	1/3	5	5	4/5	5	4/5	5	5	5
D-2	6.0	1/3	5	5	4/5	5	4/5	5	5	5

Table 5. Colour fastness to washing (ISOC06/C4) of standard depth dyeings on microfibre polyester

Dye	pH	Colour depth	Ch	Adj	Ac	Co	Ny	PET	Acr	Wo
A-1	6.0	1/3	3/4	4/5	3/4	5	3/4	4/5	4/5	4/5
	8.0	1/3	3/4	4/5	4	5	3/4	4/5	4/5	4/5
	10.0	1/3	4/5	5	4	5	4	5	5	5
A-2	6.0	1/3	4/5	5	2/3	5	2/3	5	5	4
B-4	6.0	1/1	4/5	4/5	3/4	5	3/4	4/5	4/5	4/5
C-1	6.0	1/3	4/5	4/5	4	5	3/4	4/5	5	4/5
	8.0	1/3	4/5	4/5	4/5	5	3/4	4/5	5	5
	10.0	1/3	5	5	4/5	5	4	5	5	5
C-2	6.0	1/1	5	5	4	5	3	5	5	5
D-1	6.0	1/3	5	4/5	3/4	5	3	4/5	5	5
	8.0	1/3	5	4/5	4	5	3/4	4/5	5	5
	10.0	1/3	5	5	4	5	4	5	5	5
D-2	6.0	1/3	4/5	5	3/4	5	3	5	5	4/5

3.1.6. Light fastness assessment

Assessment of the light fastness of microfibre fabric which had been dyed with the ethyleneimine azo dyes (A-1, C-1 and D-1), the hydrolysed azo dyes (A-2, C-2 and D-2) and the *N,N'*-dimethylaniline azo dye was carried out as described in section 2.1.7.2.

Table. 6 Light fastness of the dyed microfibre polyester

Dye	%	pH	Colour Depth	Light Fastnes
A-1	0.8	6.0	1/3	3
	0.8	8.0	1/3	3
	1.7	10.0	1/3	4-5
A-2	2.0	6.0	1/3	2
B-4	1.2	6.0	1/1	4-5
C-1	0.8	6.0	1/3	3-4
	0.8	8.0	1/3	4
	0.6	10.0	1/3	4
C-2	0.4	6.0	1/1	3
D-1	0.7	6.0	1/3	3
	0.8	8.0	1/3	4
	0.8	10.0	1/3	4
D-2	0.7	6.0	1/3	2

Generally, the lightfastness of a given dye on microfibre polyester fabric is lower than on conventional decitex fibre due to the large surface area that is exposed to the incident light[19].

The lighfastness of the three ethyleneimine dyes (A-1, C-1 and D-1) generally increased with increasing pH of dyeing although lightfastness was not high (Table 6). The lightfastness of the hydrolysed dyes A-2, C-2 and D-2 was lower than that of the corresponding ethyleneimine dyes.

3.2. Application to microfibre nylon 6.6 fabrics

3.2.1. The λ_{max} of dyed microfibre nylon 6.6 fabric

The colour strength (*K/S*) of microfibre nylon 6.6 fabric which had been dyed with the ethyleneimine dyes A-1, C-1 and D-1 and their hydrolysed forms (A-2, C-2 and D-2) was measured at the λ_{max} of the dyeing as described in section 2.1.3. (Table 7).

A comparison was made between the ethyleneimine dyes and their hydrolysed counterparts in terms of the λ_{max} of the dyeings (Table 7). As was found with conventional decitex nylon 6.6 fabric, the two pairs of dyes A-1/A-2 and D-1/D-2 showed no difference in λ_{max} on the fabric although they displayed 45.6 nm and 43.2 nm of lmax difference in acetone respectively. In the case of the pair of dye C-1/C-2, 20 nm difference in λ_{max} was observed although λ_{max} in acetone displayed 68.4 nm difference.(Table 7).

3.2.2. Dye build-up at various pH

In order to observe the build-up of the three ethyleneimine dyes (A-1, C-1 and D-1), three hydrolysed dyes (A-2, C-2 and D-2) and one conventional disperse dye (B-4) under consideration, a series of dyeings on microfibre nylon 6.6 fabrics was carried out using 0.5, 1.0, 1.5 and 2.0% omf dye, with the hydrolysed dyes at pH 5 and the *N,N'*-dimethylaniline azo dye applied at pH 6 and the ethyleneimine dyes at pH 5, 8 and 10 as described in section 2.1.3.1. The dyed microfibre nylon 6.6 fabric was rinsed in cold tap water and allowed to dry in the open air.

Fig. 7 shows the build-up profiles of dyes A-1, A-2 and B-4 on microfibre nylon 6.6 fabrics ; it is clear that the build-up of the dyes on microfibre nylon 6.6 fabric was markedly low. The build-up of dye A-1 was lower than that of B-4 on microfibre fabric, a finding that agrees with that found using microfibre polyester fabric (Fig. 7).

This finding may be due to the difference in the molecular structure of A-1 and B-4, in that dye A-1 has two methoxy groups in the coupling component and a methanesulphonyl and chlorine group in the diazo component which makes the dye bulkier than dye B-4 which has only a methanesulphonyl and chlorine group in the diazo component : Also, the melting point of dye B-4 is lower than that of dye A-1. These factors may affect the substantivity of A-1 towards microfibre nylon 6.6 and leads to low build up of the dye on microfibre nylon 6.6 fabric as was previously found in the case of microfibre polyester fabric (Fig. 7).

When the effect of pH on build-up of the ethyleneimine dye A-1 on microfibre nylon 6.6 fabric was considered, It was found that pH did not markedly affect build-up (Fig. 7). The build up of A-2 was lower than that of dye A-1 presumably due to the low substantivity of A-2 towards the microfibre nylon 6.6.

Table 7. The lmax of dyed microfibre nylon 6.6 fabrics

Dye	pH	λ_{max} of dyed microfibre nylon fabrics		λ_{max} in acetone	
		λ_{max}	$\Delta\lambda$	λ_{max}	$\Delta\lambda$
A-1	6.0	500	0	448.4	45.6
	8.0	500			
	10.0	500			
A-2	5.0	500		494.0	
B-4	5.0	480		462.4	
C-1	5.0	460	20	388.4	68.4
	8.0	460			
	10.0	460			
C-2	5.0	480		456.8	
D-1	5.0	520	0	455.2	43.2
	8.0	520			
	10.0	520			
D-2	5.0	520		498.4	

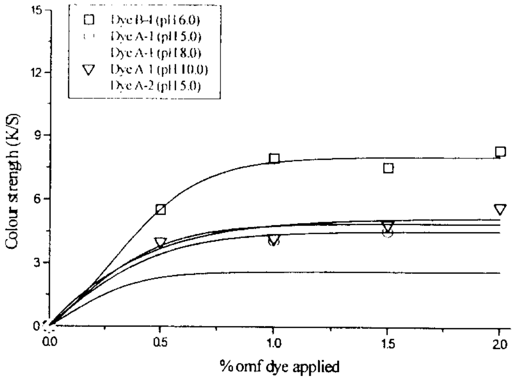


Fig. 7 Build-up of dyes A-1, A-2 and B-4 on microfibre nylon 6.6 fabric

Fig. 8 shows that the build up of dye C-1 on microfibre nylon increased with increasing application pH, although the extent of this increase in dye build-up was not major. The build up of dye C-1 was lower than that of dye C-2 on microfibre nylon 6.6, which may be due to the lower tinctorial strength (ε_{max}) of dye C-1 as well as the excellent substantivity of the dye C-2 towards the microfibre nylon 6.6 resulting from its planar structure.

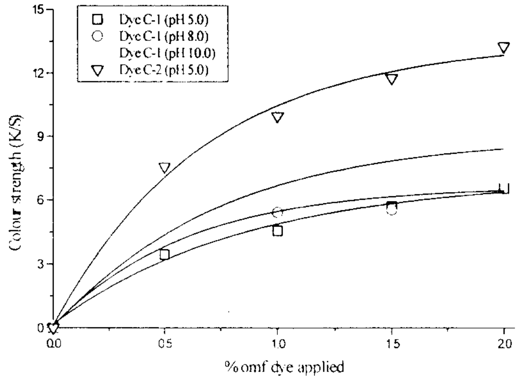


Fig. 8 Build-up of dyes C-1 and C-2 on microfibre nylon 6.6 fabric

Fig. 9 reveals that the shape of the build-up curve was similar for two pairs of dyes namely, dyes D-1(pH 5)/D-1(pH 8) and dyes D-1(pH 10)/D-2(pH 5). Furthermore, each of the dyes D-1 and D-2 exhibited very poor build-up on microfibre nylon 6.6, although Fig. 9 clearly shows that the build-up of D-2 did not reach a maximum value ; indeed, the gradients of the curves obtained imply that the build-up of D-2 would continue to increase with further increase in concentration of the applied to the microfibre.

The build-up of D-1 decreased slightly with increasing pH ; however, this trend was not marked.

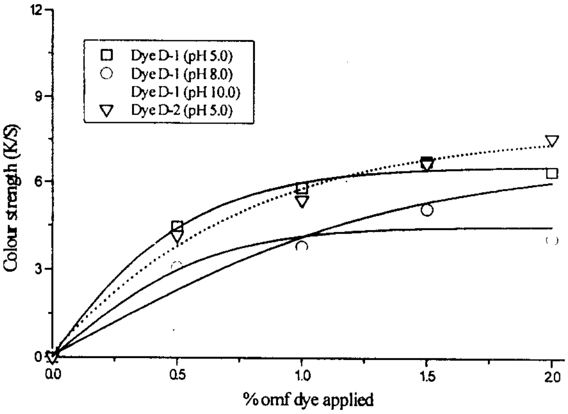


Fig. 9 Build-up of dyes D-1 and D-2 on microfibre nylon 6.6 fabric

3.2.3. Effect of pH

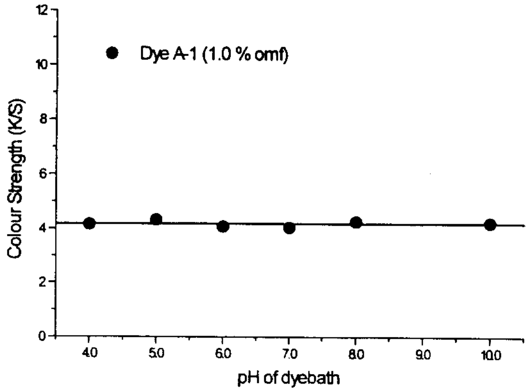


Fig. 10 Effect of pH on colour strength of microfibre nylon 6.6 which had been dyed with dye A-1 (1.0% omf)

A investigation of the effect of pH on the exhaustion of the ethyleneimine dye A-1, the 2-hydroxyethylaniline dye A-2 and the *N,N'*-dimethylaniline dye B-4 was carried out as described in section. The dyed microfibre nylon 6.6 fabric was rinsed in cold tap water and allowed to dry in the open air.

It is evident that the colour strength of microfibre nylon 6.6 which had been dyed with A-1, A-2 increased slightly with increasing of pH (Fig. 10, Fig. 11). In case of dye B-4, the colour strength increased slightly.

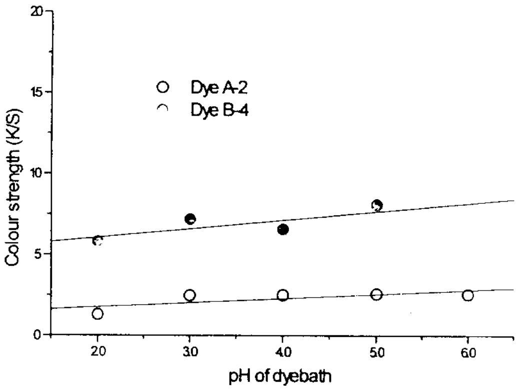


Fig. 11 Effect of pH on colour strength of conventional decitex and microfibre nylon 6.6 fabric which had been dyed with dye A-2 and B-4 (1.0% omf)

The colour strength of microfibre nylon 6.6 which had been dyed with A-1 was independent of pH whereas that of the dye C-1 slightly increased (Fig. 8), whilst that of the dye D-1 marginally decreased, with increasing pH of application (Fig. 9).When the effect of pH on colour strength of dyed microfibre polyester and nylon 6.6 fabrics which had been dyed with dyes C-1 and D-1 is considered, the findings from the variation of colour strength of C-1 and dye D-1 on microfibre nylon 6.6 fabrics agree with the results from the colour strength on microfibre polyester fabric (Table 8).

Table 8. The variation of colour strength with increasing pH of application

Dye	Microfibre fabric	
	Polyester	Nylon 6.6*
A-1	Decreasing	Nearly constant
C-1	Slightly increasing	Slightly increasing
D-1	Slightly decreasing	Slightly decreasing

*At pH values of 5 to 10

Therefore the colour strength of both polyester and nylon 6.6 microfibre which had been dyed with C-1 and D-1 at various pH values may be affected not by the characteristics of the polymer used in the fibre but by the physical characteristics of the microfibre, such as the fineness, compact structure and large surface area. When dyeing was carried out using microfibre nylon and polyester, therefore, the physical characteristics of the microfibre must be the dominant factors. Work is in hand to investigate further this particular aspect.

3.2.4. Standard depth dyeing

The dye concentrations required to achieve standard depths on microfibre nylon 6.6 fabric are given in Table 9. The dyeing of microfibre nylon 6.6 fabric was carried out until standard depth dyeings were obtained as described in section. As build-up of the dye A-1 did not change, that of dye C-1 slightly increased, and that of dye D-1 slightly decreased with increasing pH as mentioned before, it follows that the amount of the dyes required to obtain the standard depth on microfibre nylon 6.6 fabric changed.

Owing to the poor build-up of dye A-1 and A-2 (Fig. 7), it was possible to achieve only a 1/3 or 1/12 standard depth dyeing of microfibre nylon 6.6 fabric with dye A-1 and A-2 rather than the 1/1 standard depth which was achieved using dye C-1 and D-1.

Table 9. Dye concentration (% omf) required to give standard depth dyeings on conventional decitex and microfibre nylon 6.6 fabrics

Dye	pH	Concentration required (%)
A-1	5.0	1.1 (1/3)
	8.05	1.1 (1/3)
	10.0	1.2 (1/3)
A-2	5.0	2.0 (1/12)
B-4	5.0	0.8 (1/1)
C-1	5.0	0.4 (1/1)
	8.0	0.4 (1/1)
	10.0	0.35 (1/1)
C-2	5.0	0.4 (1/1)
D-1	5.0	1.0 (1/1)
	8.0	1.4 (1/1)
	10.0	1.6 (1/1)
D-2	5.0	0.8 (1/1)

3.2.5. Wash fastness assessment

Wash fastness assessment according to the ISOC 06/C2 (60℃, 30 minutes) test method[17], was carried out as described in section 2.1.7.1. The wash fastness of dyeings of dye A-1 at pH 8 and 10 was higher than that of dyeings at pH 5. In case of dye C-1, pH 10 was the best condition for excellent wash fastness property. The wash fastness of dyeings which had been dyed with D-1 at pH 8 and 10 was higher than that of the dyeing at pH 5 (Table 10).

The dyeing of microfibre nylon 6.6 fabric with ammonia did not give any improvement in wash fastness. The wash fastness of dyeings with dye A-1 using ammonia (Table 10) was marginally lower that that of dyeings carried out using dye A-1 in the absence of ammonia in the case of staining of adjacent wool fabric (Table 10). When the wash fastness of ethyleneimine dyes which had been applied at pH 10 is compared to that of their hydrolysed counterparts, the wash fastness of the

Table 10. Colour fastness to washing (ISOC06/C2) of standard depth dyeings on microfibre nylon 6.6

Dye	pH	Standard Depth	Ch	Adj	Acetate	Cotton	Nylon	PET	Acryl	wool
A-1	5.0	1/3	4	3	2/3	4	2	4/5	4/5	3/4
	8.0	1/3	4/5	3/4	3/4	4/5	3	5	5	4
	10.0	1/3	4/5	3/4	3	5	3	5	5	4/5
A-1*	10.0	1/3	4/5	3/4	3	5	3	5	5	4
A-2	5.0	1/12	3	3	2/3	4/5	2/3	5	5	3/4
B-4	5.0	1/1	4/5	3/4	2	4/5	2/3	4	4/5	3/4
C-1	5.0	1/1	3/4	4/5	3/4	5	3/4	5	5	4/5
	8.0	1/1	4/5	5	4	5	4	5	5	5
	10.0	1/1	5	5	4	5	4	5	5	5
C-2	5.0	1/1	3/4	3/4	2/3	4/5	2	5	5	4
D-1	5.0	1/1	4	3	2/3	4	2	4/5	5	3/4
	8.0	1/1	5	4	3/4	5	3/4	5	5	4/5
	10.0	1/1	4/5	4	3/4	5	3/4	5	5	4/5
D-2	5.0	1/1	4	2/3	1/2	3/4	1/2	4/5	5	3

*Dyeing with ammonia solution

Table 11. Colour fastness to washing (ISOC06/C4) of standard depth dyeings on microfibre nylon 6.6

Dye	pH	Standard Depth	Ch	Adj	Acetate	Cotton	Nylon	PET	Acryl	wool
A-1	5.0	1/3	2/3	3	1/2	4/5	1/2	4/5	4/5	3/4
	8.0	1/3	3	3/4	2/3	4/5	2/3	4/5	5	4
	10.0	1/3	3/4	3/4	2/3	4/5	2/3	4/5	4/5	3/4
A-1*	10.0	1/3	3/4	3/4	2/3	4/5	2/3	4/5	4/5	3/4
A-2	5.0	1/12	1/2	3	1/2	4/5	1/2	5	4/5	3/4
B-4	5.0	1/1	1/2	1/2	1	4/5	1/2	3/4	4	3
C-1	5.0	1/1	1/2	3/4	3/4	5	2/3	4	4/5	4/5
	8.0	1/1	3	4	4	5	3	4	4/5	4/5
	10.0	1/1	4	4/5	4	5	3	4	4/5	4/5
C-2	5.0	1/1	1	2	1/2	4/5	1	3/4	4	4
5.0	1/1	2	2/3	2	4/5	2	4	4	3	
D-1	8.0	1/1	3	3/4	2/3	4/5	2/3	4/5	4/5	3/4
	10.0	1/1	2/3	3/4	2/3	4/5	2/3	4	4	3
D-2	5.0	1/1	2	1/2	1	4	1	3/4	4	2

*Dyeing with ammonia solution

hydrolysed dyes was clearly lower than that of ethyleneimine dyes. Comparison of dyes A-1 and B-4 revealed that the fastness of A-1 was slightly higher than dye B-4 in the case of staining of adjacent acetate, nylon, polyester, acrylic and wool fabrics.

However, as the differences in wash fastness between dyeing at pH 8 and 10 were not clear, the more severe wash fastness test method (ISOC 06/C4) was used as described in section.

Wash fastness at 90°C for 30 minutes gave much clearer results (Table 11). The three ethyleneimine dyes (A-1, C-1 and D-1) were applied at pH 8 and 10 exhibited higher wash fastness compared to application at pH 5 ; the wash fastness of the dyes at pH 8 and 10 were the same. As observed using the ISOC06/C2 test method, the wash fastness of the dyeings of the ethyleneimine dyes at pH 10 was much higher than that of their hydrolysed counterparts. It is evident that the wash fastness of dyeings of A-1 were higher than that of dyeings with dye B-4.

3.2.6. Light fastness assessment

Assessment of the light fastness of microfibre nylon 6.6 fabric which had been dyed with the ethyleneimine azo dyes (A-1, C-1 and D-1), the hydrolysed azo dyes (A-2, C-2 and D-2) and the *N,N'*-dimethylaniline azo dye was carried out as described in section 2.1.7.2.

It was found that the light fastness of the ethyleneimine dyes increased slightly with increasing pH of application(Table 12).

Generally, as discussed earlier, the light fastness of a given dye on microfibre nylon 6.6 fabric is lower than on conventional decitex fibre owing to the large surface area that is exposed to the incident light as mentioned before.

Table 12. Colour fastness to light of standard depth dyeings on microfibre nylon 6.6

Dye	%	pH	Colour Depth	Light Fastness
A-1	1.1	5.0	1/3	3-4
	1.2	8.0	1/3	4
	1.3	10.0	1/3	4-5
A-1*	1.1	10.0	1/3	3
A-2	2.0	5.0	1/12	2-3
B-4	0.8	5.0	1/1	3-4
C-1	0.4	5.0	1/1	3-4
	0.4	8.0	1/1	4
	0.35	10.0	1/1	4
C-2	0.4	5.0	1/1	3-4
D-1	1.0	5.0	1/1	3
	1.4	8.0	1/1	3-4
	1.6	10.0	1/1	4
D-2	0.8	5.0	1/1	2

4. Conclusions

The wash fastness of ethyleneimine dyes on microfibre polyester fabrics was higher than that of the hydrolysed forms of the dyes and the *N,N'*-dimethylaniline dye (B-4). The superiority of the ethyleneimine dyes in terms of their wash fastness properties was emphasised when fastness testing was carried out at 95℃ rather than 60℃. These findings imply that the ethyleneimine dyes may be covalently bound to the fibre or that dimers may have been formed during dyeing.

The wash fastness of ethyleneimine dyes on micro fibre nylon 6.6 was also higher than that of the hydrolysed forms of the dyes and the *N, N'*-dimethylaniline dye (B-4).

In the case of the ethyleneimine disperse dyes A-1, C-1 and D-1, the light fastness on nylon 6.6 fabric was similar to that on polyester fabric. Generally, the light fastness of ethyleneimine dyes was either higher than or similar to that of their hydrolysed counterparts and the *N,N'*-dimethylaniline azo dye (B-4). The results obtained imply that ethyleneimine disperse dyes may offer advantages over conventional disperse dyes in that the level of wash fastness achievable is generally higher, on both polyester and nylon 6.6 fabrics, than conventional disperse dyes. This can be attributed either to covalent attachment of the ethyleneimine dyes to the substrate or to dimerisation of the dyes within the fibre. The observed superior wash fastness of ethyleneimine disperse dyes is especially interesting in view of the trend towards the use of microfibre polyester and nylon 6.6. Perhaps ethyleneimine disperse dyes may offer some potential with regards wash fastness on such substrates.

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