

〈研究論文(學術)〉

에틸렌이민 유도체를 갖는 아조계 분산염료의 염색성에 관한 연구(I)

— 폴리에스테르 섬유에의 응용 —

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A Study on Dyeing Property of Azo Disperse Dyes Containing Ethyleneimine Derivatives(I)

— Application to Polyester Fabrics —

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요 약

이 연구의 목적은 에틸렌이민 유도체를 갖는 아조계 분산 염료의 폴리에스테르 섬유에의 응용과 최적화된 폴리에스테르 염색 조건의 확립이다.

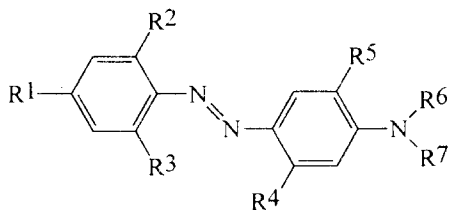
이들 아지리디닐 염료는 구조가 유사하며 말단에 하이드록시기를 갖는 염료(아지리디닐 염료의 가수분해 형태)와 비교하여 최대 흡수 파장의 천색적으로 천이 됨을 알 수 있었다. 세가지 아지리디닐 모노 아조 염료와 이들 염료의 가수분해 된 형태 그리고 디메틸아닐린계 아조 염료의 폴리에스테르 섬유에 대한 염색 및 견뢰도 성질이 조사되었다. 아지리디닐 아조 염료는 산성 조건에서보다 염기성 조건하에서 보다 안정하였고, 뛰어난 build-up이 높은 pH조건에서 얻어졌으며, 폴리에스테르 염색 시 130°C, pH 10의 조건에서 최적화된 색상 강도를 얻었다.

아지리디닐 염료는 이 염료의 가수분해 형태와 디메틸아닐린 염료와 비교하여 개선된 세탁 견뢰도를 나타내었고 이는 용매 추출을 이용하여 확인 하였다. 아지리디닐 아조 염료는 역시 광 견뢰도에서도 또한 상용화된 분산 염료에 비교하여 높은 결과를 나타내었다.

1. Introduction

Many researchers have studied the relationship between dyeing properties, such as colour and fas-

tness property, and constitution of aminoazobenzene dyes. The most important representatives are aminoazobenzene dyes of general formula(Structure 1)^{1,2)} :

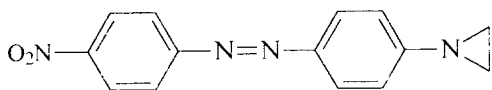


R1 = an electron-attracting group ;
 R2 and R3 = H or electron-attracting groups ;
 R4 and R5 = H or electron-repelling groups ;
 R6 and R7 = H or Alkyl which are often further substituent.

Structure 1 The general formula of aminoazobenzene dyes

Aminoazobenzene dyes containing terminal cyclic ring has been investigated by several workers^{3,4}. The introduction of an ethyleneimine group into dyes based on 4-aminoazobenzene and related heterocyclic compounds has been the subject of intense research activity for many years^{3,4,5}.

The ring-opening reaction of the terminal ethyleneimine ring (i.e. aziridiny ring), involved in the dyeing mechanism, leads to substantial bathochromic effects⁶. For example, the nitro derivative (Structure 2) undergoes rapid solvolysis⁷, resulting in the ring-opened azonium ion which shows a bathochromic shift.



Structure 2 Aziridinyl aminoazobenzene dye

2. Experimental

2.1 Synthesis of azo disperse dyes

2.1.1 Synthesis of aziridinyl azo disperse dyes

The procedure of synthesis to produce aziridinyl azobenzene disperse dyes and yields of product

were described in detail in previous work⁸. Overall scheme of aziridinyl azo dye synthesis is as follows (Fig. 1).

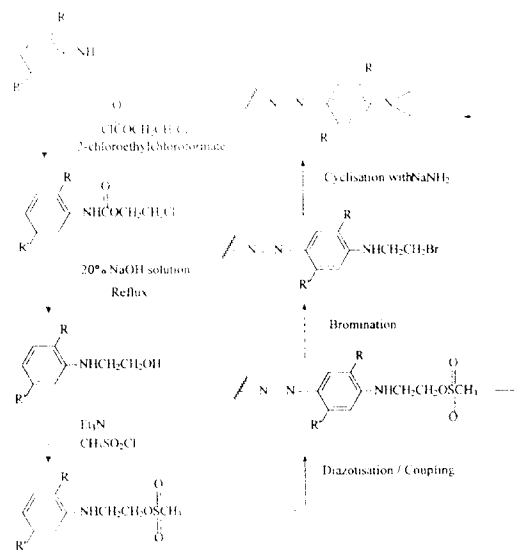
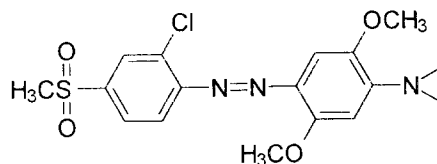


Fig. 1 Synthesis of aziridinyl azobenzene dye

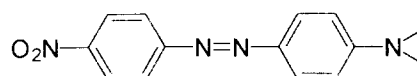
Provided that methanesulphonyl compounds are stable during reaction, direct cyclisation from methanesulphonates derivatives is more efficient than using lithium bromide in acetone.

Three aziridinyl azo dyes were obtained using the procedure as described in previous work⁸.

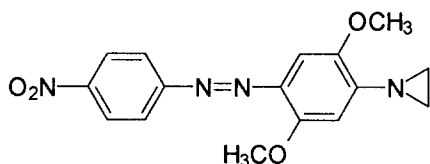
- 2-chloro-4-methanesulphonylaniline → 1-(2,5-dimethoxyphenyl)aziridine (Dye A-1)



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



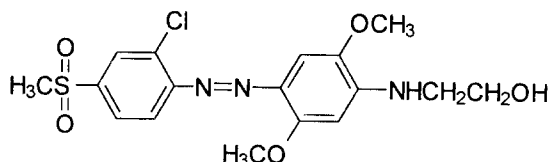
- 4-nitroaniline → 1-(2,5-dimethoxyphenyl)aziridine(Dye D-1)



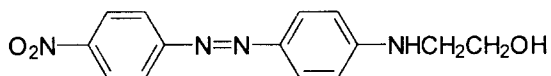
2.1.2 Synthesis of 2-hydroxyethyl azo disperse dyes

Three 2-hydroxyethyl azo disperse dyes were prepared using the procedure described in previous work⁸⁾ that were the hydrolysed form of the aziridinyl azo dyes.

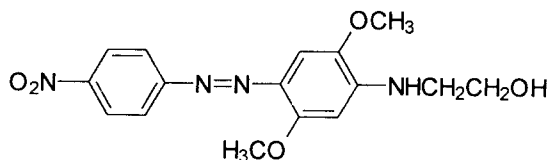
- 2-chloro-4-methanesulphonylaniline → 2,5-dimethoxy-N,β-hydroxyethylylaniline(Dye A-2)



- 4-nitroaniline → N-β-hydroxyethylylaniline (Dye C-2)



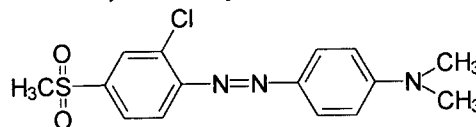
- 4-nitroaniline → 2,5-dimethoxy-N-β-hydroxyethylylaniline(Dye D-2)



2.1.3 Synthesis of N,N'-dimethylaniline azo dye

N,N'-dimethylaniline azo disperse dye, as a commercialised dye, was prepared using the procedure described in previous work⁸⁾ that was compared dyeing properties on polyester fabrics with aziridinyl azo disperse dyes.

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



2.1.4 Determination of zmax values

The ϵ_{\max} values of dyes was determined using a Perkin-Elmer Lambda 15 UV/VIS Spectrophotometer. 1mole of dye was dissolved in 100ml of acetone with stirring to prepare stock dye solution and an aliquot(20ml) of stock dye solution was pipetted into another 100ml of acetone.

The dilution of dye was repeated until absorbance of dye-acetone solution was obtained at close to unit value of optical density. ϵ_{\max} value was calculated⁹⁾ as follows.

$$A = \epsilon cl$$

where A = absorbance

ϵ = molar extinction coefficient

c = the concentration of solute(mol/litre)

l = path length through the sample(cm)

2.2 Dye application

2.2.1 Experimental materials

2.2.1.1 Polyester fabrics

Commercially available, scoured, knitted conventional(167f32, 5.2 dtexpf) fabrics were used throughout the study.

2.2.1.2 Dyes

The aziridinyl dyes(A-1, C-1 and D-1), the 2-hydroxyethylylaniline azo dyes(A-2, C-2 and D-2) and the N,N'-dimethylaniline azo dye B-4 that were used throughout the study were described in section 2.1.

2.2.1.3 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/w) were used to control dyebath pH and sodium hydroxide and sodium dithionite were used for the reduction clearing of dyed polyester.

2.2.2 Preparation of dye samples

1.0g of dye, 2.0g of dispersing agent(Ufoxane 2) and 100cm³ of distilled water were placed in a 250cm³ capacity glass jar. The jar was then filled to two thirds capacity with 1cm diameter ceramic balls and the sealed jar rotated on a laboratory-scale ball mill for 24 hours at room temperature. The stock dye solution obtained as above was applied to conventional decitex polyester fabrics as described in sections 2.2.3. and 2.2.7.

Dyeing was carried out in sealed, stainless steel dyepots of 200cm³ capacity housed in a Zeltex laboratory scale dyeing machine(UK) 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 : 1g l⁻¹) were added to make the volume up to 60cm³.

2.2.3 Dyeing

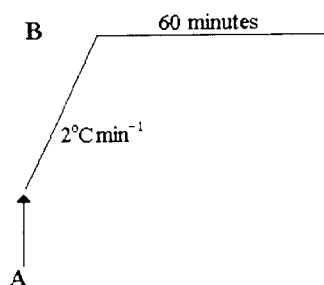


Fig. 2 Polyester dyeing method

A Polyester fabric(2g) added(60°C) ; B
130°C

2.2.3.1 Effect of dyeing temperature

Dyeings were carried out in using the equipment as described in section 2.2.3. A dye pot was removed from the dyeing machine after 10 minutes(80°C), 20 minutes(100°C), 30 minutes(120°C), 35 minutes (130°C), 50 minutes(130°C), 65 minutes(130°C), 80 minutes(130°C) and 95 minutes(130°C) from the beginning of the dyeing procedure.

The dyed fabrics were rinsed in cold tap water and dried in the open air and reduction cleared as described in section 2.2.3.4. The colour strength (K/S) of each dry, dyed fabric was measured as described in section 2.2.8.

2.2.3.1.1 Dye extraction using DMF

A sample(1.0g) of reduction cleared polyester fabric which had been dyed with dye A-1 and removed after 10 minutes(80°C), 20 minutes(100°C), 30 minutes(120°C), 35 minutes(130°C), 50 minutes (130°C), 65 minutes(130°C), 80 minutes(130°C) and 95 minutes(130°C) dyeing was extracted using 80cm³ of DMF at 100°C for 1 hour in a 100cm³ round-bottom flask equipped with a condenser. At the end of extraction, the dyed sample was rinsed thoroughly in cold tap water and allowed to dry in the open air. The K/S of the extracted dyeing was determined as described in section 2.2.8.

2.2.3.2 Dye build-up

Various dyeings using aziridiny azo dyes(A-1, C-1 and D-1), hydrolysed dyes(A-2, C-2 and D-2) and the *N,N'*-dimethylaniline azo dye(B-4) were carried out at 130°C for polyester in the presence of 1g l⁻¹ Ufoxane 2 as described in section 2.2.3.

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

Table 1. % omf dye applied to polyester fabric

Dye	pH	Polyester fabric	
		Conventional decitex	Microfibre
A-1	6.0	0.3, 0.5, 0.75, 1.0, 1.5%	0.5, 1.0, 1.5, 2.0%
	8.0	0.3, 0.5, 0.75, 1.0, 1.5%	0.5, 1.0, 1.5, 2.0%
	10.0	0.3, 0.5, 0.75, 1.0, 1.5%	0.5, 1.0, 1.5, 2.0%
A-2	6.0	0.3, 0.5, 0.75, 1.0, 1.5%	0.5, 1.0, 1.5, 2.0%
C-1	6.0	0.5, 0.4, 0.5, 0.6, 1.0, 1.5%	0.5, 0.7, 1.0, 1.5, 2.0%
	8.0	0.5, 0.4, 0.5, 0.6, 1.0, 1.5%	0.5, 0.7, 1.0, 1.5, 2.0%
	10.0	0.5, 0.4, 0.5, 0.6, 1.0, 1.5%	0.5, 0.7, 1.0, 1.5, 2.0%
C-2	6.0	0.5, 0.4, 0.5, 0.6, 1.0, 1.5%	0.3, 0.5, 0.7, 1.0, 1.5, 2.0%
D-1	6.0	0.3, 0.4, 0.5, 0.6, 1.0, 1.5%	0.5, 1.0, 1.5, 2.0%
	8.0	0.3, 0.4, 0.5, 0.6, 1.0, 1.5%	0.5, 1.0, 1.5, 2.0%
	10.0	0.3, 0.4, 0.5, 0.6, 1.0, 1.5%	0.5, 1.0, 1.5, 2.0%
D-2	6.0	0.5, 1.0, 1.5%	0.5, 1.0, 1.5, 2.0%

by the dissolution of disodium hydrogenphosphate (5g) and potassium dihydrogenphosphate(1g) in 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.

2.2.3.3 Effect of pH on build-up

Polyester conventional fabrics were dyed(1.0% omf) with the aziridiny dyes A-1, C-1 and D-1, the hydrolysed dye A-2 and the *N,N'*-dimethylaniline dye B-4 at pH values of 4 to 12. The dyed polyester was rinsed with cold tap water and reduction cleared as described in section 2.5.3.4. The colour strength of the dyeings was determined as described in section 2.2.8.

2.2.3.3.1 Acidic dye bath

Buffer solutions of pH 4, 4.5, 5 and 5.5 were prepared by the dissolution of acetic acid(0.0042 M) and sodium acetate(0.026M) in 1 litre of distilled water. A buffer solution of pH 6 and 6.5 was obtained by dissolution of acetic acid(0.02M) and sodium acetate(0.17M) in 1 litre of distilled water ; the final pH value was secured by the addi-

tion of either 0.1M of acetic acid solution or 0.1M of sodium acetate solution.

2.2.3.3.2 Basic dye bath

Buffer solutions of pH 7, 8, 9 and 10 were obtained by the dissolution of disodium hydrogenphosphate(5g) and potassium dihydrogenphosphate(1 g) in 1 litre of distilled water ; the appropriate pH value was secured by the addition of either 0.1M aqueous hydrochloric acid or 0.1M aqueous sodium hydroxide solution to the mixed phosphate buffer solution. Buffer solutions of 11 and 12 were obtained by the dissolution of disodium hydrogenphosphate(5g) and potassium dihydrogenphosphate(1g) in 1 litre of distilled water and then, secured by the addition of either 1.0M/0.1M aqueous sodium hydroxide solution or 0.1M aqueous hydrochloric acid to the mixed phosphate buffer solution.

2.2.3.3.3 Dye extraction using DMF

A sample(1.0g) of reduction cleared polyester fabric which had been dyed with dye A-1(1.0% omf ; at pH 4, 4.5, 5, 5.5, 6, 6.5, 7, 8, 9, 10, 11 and also 12) was extracted using 80cm³ of DMF at 100°C for 1 hour in a 100cm³ round-bottom flask

equipped with a condenser. At the end of extraction, the dyed sample was rinsed thoroughly in cold tap water and allowed to dry in the open air and the colour strength of the extracted dyeing determined as described in section 2.5.8.

In order to estimate the extent of dye that was stripped from the dyed fabric by solution extraction, the % dye stripping(% δ) was calculated as follows :

$$\% \delta = \frac{K/S \text{ before stripping} - K/S \text{ after stripping}}{K/S \text{ before stripping}} \times 100$$

2.2.3.4 Reduction clearing

Dyed polyester was reduction cleared by stirring in an aqueous solution containing 2gl^{-1} sodium hydroxide(pellet), 2gl^{-1} sodium dithionite and 1gl^{-1} Sandozin NIE at 70°C 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.

2.2.4 Maximum absorbance(λ_{max}) of residual dyebaths

A 'blank dyeing' was performed in which a dyeing was carried out in the absence of fabric as follows.

- 2cm^3 of dye A-1 stock solution (10gl^{-1}) which was prepared as described in section 2.5.2
- 1gl^{-1} of dispersing agent(Ufoxane 2)
- dyeing procedure described in Fig. 2
- water was added to make the volume up to 60cm^3
- pH 4, 6 and 7

At each sampling position(A to K in Fig. 3), during the polyester dyeing(pH 4, 6 and 7), 1cm^3 of the residual dyebath was pipetted from the dye-pot into two, 50cm^3 beakers. DMF was poured into one beaker and ethanol was poured into the other to realise a dye aliquot : solvent ratio of 1 : 3. The wavelength of maximum absorbance(λ_{max}) of the residual dyebath in both the dyebath-DMF(1 : 3)

and dyebath-ethanol(1 : 3) systems was determined using a Perkin-Elmer Lambda 15 UV/VIS Spectrophotometer as follows.

- a calibration plot was carried out using blank solvent(DMF or ethanol) using 1cm path length reference and sample cells.
- the sample cell, which had been cleaned with blank solvent(DMF or ethanol), was filled with the residual dyebath-solvent (DMF or ethanol).
- an absorbance spectrum of the sample was obtained in the visible region(400 to 760nm).
- the wavelength of maximum absorbance (λ_{max}) of the residual dyebath both in dyebath-DMF(1 : 3) and dyebath-ethanol(1 : 3) was determined and the absorbance spectrum in the visible region obtained.

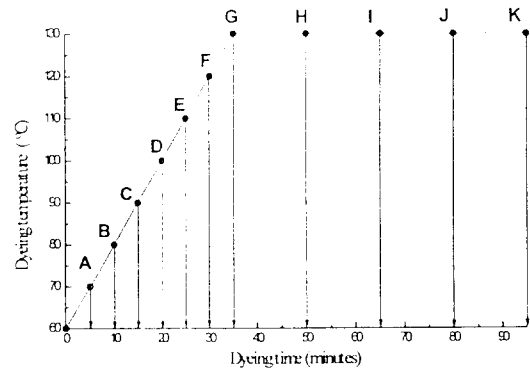


Fig. 3 Sampling positions for λ_{max} analysis during polyester dyeing

2.2.5 Dye extraction using dichloroacetic acid and acetone

A sample(1.0g) of reduction cleared, conventional decitex polyester fabric which had been dyed with dyes A-1, C-1 and D-1(1.0% omf ; pH 10) was dissolved in 80cm^3 dichloroacetic acid at $35\text{-}40^\circ\text{C}$ with stirring for 10 minutes and the precipitated material then collected by filtration under vacuum.

The precipitated material obtained was placed in 80°C acetone in a 100cm^3 round bottom flask bea-

ker and the acetone mixture stirred for 10 minutes at room temperature. The precipitated material was separated by filtration under vacuum, washed with acetone and dried in the open air. The colour of both the dried, precipitated material and the acetone was noted.

2.2.6 Evaluation of hydrolysis during dyeing

A blank dyeing was performed in which a dyeing was carried out in the absence of fabric as follows.

20cm³ of a 10 gl⁻¹ dye A-1 stock solution was prepared as described in section 2.2.2.

- 1gl⁻¹ of dispersing agent(Ufoxane 2)
- dyeing procedure described in Fig. 2
- water added to make the volume up to 60cm³
- pH 4, 10 and 12

Analysis was carried out using a Varian Series 5000 liquid chromatograph equipped with an Apex C18 reverse-phase column using a flow rate of 1.0cm³ min⁻¹ and 50 atmospheres pressure. The ion-pair system used comprised a 0.25% aqueous solution of cyclohexamine phosphate in distilled water and 99.8% HPLC grade acetonitrile.

A 20cm³ portion of the dyebath of dye A-1 and A-2 before dyeing was pipetted into a separating funnel and extracted using 20cm³ dichloromethane. The dichloromethane was removed using rotary evaporation under vacuum and the residual dye was then dissolved in a 50 : 50 acetonitrile : water mixture. The extracted dyes in the 50 : 50 acetonitrile : water mixture as described above were analysed and the retention time of the dyes A-1 and A-2 were used as a reference for the analysis of residual dyebaths obtained during blank dyeing.

A 20cm³ portion of the dyebath of dye A-1 at each sampling position during blank dyeing was pipetted into a separating funnel and extracted using 20cm³ dichloromethane. The dichloromethane

was removed using a rotary evaporation under vacuum and the residual dye dissolved in a 50 : 50 acetonitrile : water mixture. The extracted dye from the residual dyebath at each sampling position during blank dyeing was analysed and the percentage area of the resulting peaks for both the aziridinyl and the hydrolysed forms of the dyes were calculated.

During polyester dyeing at pH 4(1.0% omf), analysis was carried out of the aziridinyl dye A-1 and the hydrolysed dye A-2 after 5 minutes(70°C), 10 minutes(80°C), 15 minutes(90°C) and 17.5 minutes(100°C) from the beginning of dyeing. For polyester dyeing at pH 10(1.0% omf), analysis was carried out of the aziridinyl dye A-1 and the hydrolysed dye A-2 after 5 minutes(70°C), 15 minutes(90°C), 25 minutes(110°C), 30 minutes(120°C), 35 minutes(130°C), 50 minutes(130°C) and 95 minutes(130°C) from the beginning of dyeing. For polyester dyeing at pH 12(1.0% omf), analysis was carried out of the aziridinyl dye A-1 and the hydrolysed dye A-2 after 15 minutes(90°C), 20 minutes(100°C), 30 minutes(120°C), 35 minutes(130°C), 65 minutes(130°C), and 95 minutes(130°C) from the beginning of dyeing.

2.2.7 Standard depth dyeings

Commercially available, scoured, knitted conventional decitex polyester fabric was 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°C, in the presence of 1gl⁻¹ Ufoxane 2 at pH 6, 8 and 10 as described in section 2.2.3. At the end of dyeing, the dyed polyester fabric was rinsed thoroughly in cold tap water, reduction cleared as described in section 2.2.3.4. and dried in the open air.

The depth of shade of each of the dyed polyester was visually compared with the appropriately coloured Society of Dyers and Colourists matt standard depth shades¹⁰⁾ in an ICS/Texicon(ICS, UK)

viewing cabinet under illuminant D₆₅. Dyeings were repeated to achieve a 1/1 standard depth of shade for each of the dye samples on polyester fabrics. Some of dyeings which could not be obtained at 1/1 standard depth of shade were examined at 1/3 standard depth.

2.2.8 Colour measurement

The reflectance values of the dry, reduction cleared, dyed polyester fabrics as well as the DMF-extracted dyed polyester fabrics were measured using an ICS Micromatch 2000 colour measurement system under the following viewing conditions :

- illuminant D₆₅ ;
- 10° standard observer ;
- UV component included ;
- specular component excluded.

The CIELab coordinates and Kubelka-Munk (K/S) values¹¹⁾ 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.

2.2.9 Fastness properties of the dyed samples

2.2.9.1 Wash fastness assessment

Rinsed and reduction cleared, dyed polyester 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)¹²⁾

2.2.9.2 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°C
- Relative humidity : 60%
- Exposure time : 24 hours

3. Results and Discussion

3.1 λ_{\max} values and colour strength (ϵ_{\max}) for dye samples in acetone

The λ_{\max} values and the colour strength (ϵ_{\max}) of each dyes used in acetone were determined as described in section 2.1.4. λ_{\max} values of the aziridinyl azo dyes in acetone displayed hypsochromic shifts compared with analogous N, β -hydroxyethylaniline azo dyes. The λ_{\max} values and the colour strength(ϵ_{\max}) of each dye sample are given in Table 2.

3.2 The IOR values of dye samples

IOR(inorganic/organic) values, which were used to estimate the hydrophilicity/hydrophobicity^{13,14)} of the dye samples, were found to be as follows (Table 3).

Table 3 shows that each of the hydroxyethyl azo dyes was more hydrophilic than the corresponding aziridinyl azo dyes. The IOR value of poly-

Table 2. λ_{\max} values and colour strength (ϵ_{\max}) for dye samples in acetone

Dye	A-1	A-2	C-1	C-2	D-1	D-2
λ_{\max}	448.4	494.0	388.4	456.8	455.2	498.4
ϵ_{\max}	2.03	3.18	1.12	1.57	1.99	1.39

Table 3. The IOR values emax values of dye samples

Dye	A-1	A-2	B-4	C-1	C-2	D-1	S-2
IOR	0.691	0.929	0.658	0.571	0.857	0.615	0.872

ter was calculated as $0.7^{13,14}$ and thus, the IOR values of dyes A-1 and were closest to that of polyester.

3.3 Application to conventional decitex polyester fabric

In this study of the dyeing properties of the aziridinyl dyes on conventional decitex polyester fabric, TLC was used to show that the ball-mill finishing of aziridinyl azo disperse dyes in the presence of a dispersing agent, as described in section 2.2.2., had no deleterious effect on the dyeing behaviour of the dyes⁶. The dyeing of conventional decitex polyester fabric was carried out as described in section 2.2.3.

3.3.1 Possible Components of Dye-bath during Dyeing

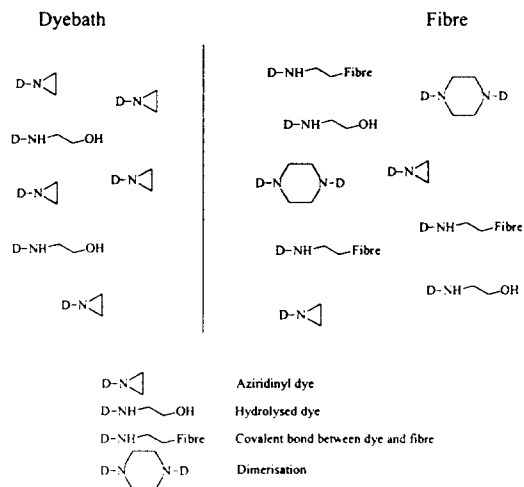


Fig. 4 Possible components present in the dyebath and dyed fibre

Theoretically, the dyebath can comprise the aziridinyl azo dye and its hydrolysed counterpart,

the latter having been produced during dyeing. Thus, the fabric will be able to adsorb both types of dye (Fig. 4).

In terms of the polyester fabric, it is possible that, during dyeing, the aziridinyl dye may become covalently bound to the substrate⁶. Also, it is possible that dimerisation may occur⁶ in the dyebath and that this dimerised form of the dye is substantive towards the fabric; furthermore, the dyed material can be considered to contain hydrolysed dye. This situation is depicted in Fig. 4.

3.3.2 The λ_{max} of dyed conventional decitex polyester fabric.

The colour strength(K/S) of conventional decitex polyester fabric which had been dyed with both aziridinyl and hydrolysed dyes was measured at the λ_{max} of the dyeing as described in section 2.2.8. and a comparison made between the aziridinyl dyes and their hydrolysed counterparts in terms of the λ_{max} of the dyeings (Table 4).

In the case of the two pairs of dyes A-1/A-2 and D-1/D-2, there was no λ_{max} difference between the aziridinyl dye and its hydrolysed counterpart, even though the λ_{max} of the dyes in acetone solution for each pair differed.

For the C-1/C-2 pair of dyes a 20nm difference in λ_{max} was obtained in the case of dyed conventional decitex polyester fabrics, although the difference in λ_{max} between dye C-1 and C-2 in acetone solution was 68.4nm.

As mentioned, during dyeing, it is possible that the polyester fibre adsorbed the aziridinyl dye, its hydrolysed form as well as the dimerised form of the dye. Also, it is possible that the aziridinyl dye was bound covalently to the fibre as described above.

Table 4. Comparison of the λ_{\max} of dyed conventional decitex polyester fabrics and of the dye in acetone

Dye	pH	λ_{\max} of dyed conventional decitex polyester fabric		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	

3.3.3 The hydrolysis of aziridinyl azo dyes

The aziridinyl ring is very susceptible to opening by the attack of water or acid due to strain in the aziridine ring and the nucleophilicity of the amino nitrogen ion. Hydrolysis of aziridinyl dyes (aziridinyl ring opening in the water) was observed during polyester dyeing, the extent of hydrolysis of the aziridinyl dye was determined by examining the λ_{\max} variation of the residual dyebaths and the HPLC analysis as described in sections 2.2.4. and 2.2.6., respectively.

3.3.3.1 The λ_{\max} shift of residual dyebaths

Generally, the λ_{\max} of a commercial disperse dye does not change during polyester dyeing because the structure of the dye has not changed. In contrast, the λ_{\max} of an aziridinyl disperse dye changes during dyeing because of ring opening of the dye. Examination of the λ_{\max} shift of the residual dyebaths of the aziridinyl dye A-1 at pH 4, 6 and 7 and the hydrolysed dye A-2 during polyester dyeing, in the absence of polyester, was car-

ried out as described in section 2.2.4.

When the residual dyebaths were examined, the λ_{\max} of the aziridinyl dyes in the dyebath had changed (Fig. 5); at the end of dyeing, the λ_{\max} of the aziridinyl dyes was found to be very similar to that of the hydrolysed dye.

Table 5. The λ_{\max} of the dyebaths (dye A-1 and A-2) before dyeing

Dye	Dyebath:DMF(1:3)	Dyebath:Ethanol(1:3)
A-1	460.4	452.0
A-2	510.6	502.4

The λ_{\max} of the dyebath (dye A-1 and A-2) before dyeing are given in Table 5. Fig. 5 shows the variation in the λ_{\max} of the residual dyebaths (dye A-1 and A-2 using DMF) during polyester dyeing at pH 6.0. Clearly, the λ_{\max} of A-2 ($\lambda_{\max} = 510.6\text{nm}$) did not change throughout dyeing which can be attributed to the molecular structure of dye A-2 having not changed during dyeing.

In contrast, the λ_{\max} of dye A-1 increased from 460.4nm to 508.0nm, which was similar to the λ_{\max} of dye A-2 in DMF (Table 5) after 35 minutes from the beginning of dyeing when the dyeing temperature was increasing to 130°C.

Fig. 6 shows the variation in the λ_{\max} of the residual dye bath during dyeing in the absence of polyester fabric, with dye A-1 at pH 4.0, 6.0 and 7.0. It is evident that when 'blank' dyeing had been carried out at pH 4.0, the λ_{\max} of the residual dye bath increased from 460.4nm to 509.0nm which was similar to the λ_{\max} of A-2 in DMF (Table 5) after 15 minutes from the start of dyeing, when the dyeing temperature was increasing to 90°C. In the case of dyeing at pH 6.0, the λ_{\max} increased from 460.4nm to 508.0nm after 35 minutes dyeing and, when dyeing was carried out at pH 7.0, the λ_{\max} of the residual dye bath increased from 460.4 nm to 507.6nm after 50 minutes dyeing when the dyeing temperature was increased to 130°C.

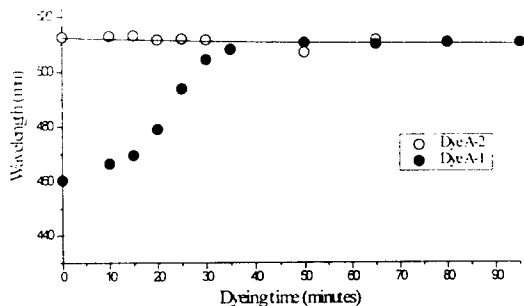


Fig. 5 The variation in the λ_{\max} of the residual dye baths of dye A-1 and A-2 during dyeing in the absence of polyester fabric at pH 6.0 (Dye bath : DMF 1 : 3)

Fig. 7 shows the variation in λ_{\max} of the residual dye baths when ethanol (dye bath : ethanol 1 : 3) was employed as co-solvent for the dye during dyeing in the absence of polyester fabric with dye A-1 at pH 4.0, 6.0 and 7.0. When blank dyeing had been carried out at pH 4.0, the λ_{\max} of the

residual dye bath increased from 452.0nm to 504.2 nm this being similar to the λ_{\max} of the hydrolysed dye A-2 (Table 5) after 15 minutes dyeing when the dyeing temperature increased to 90°C. This finding agrees with that secured when DMF had been used as co-solvent for the dye (Fig. 6). In the case of dyeing at pH 6.0, the λ_{\max} increased from 452.0nm to 501.4nm after 35 minutes dyeing and, when the dyeing was carried out at pH 7.0, the λ_{\max} of the residual dye bath increased from

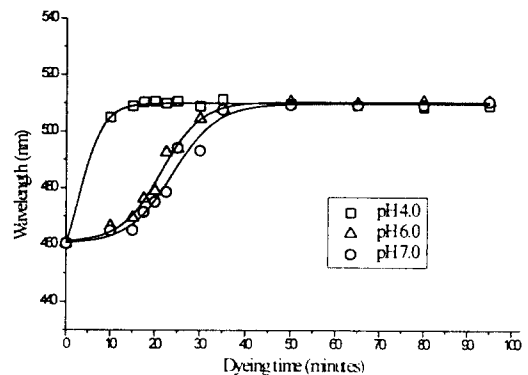


Fig. 6 Variation in λ_{\max} of the residual dye baths (dye A-1) during dyeing in the absence of polyester fabric (residual dye bath : DMF 1 : 3)

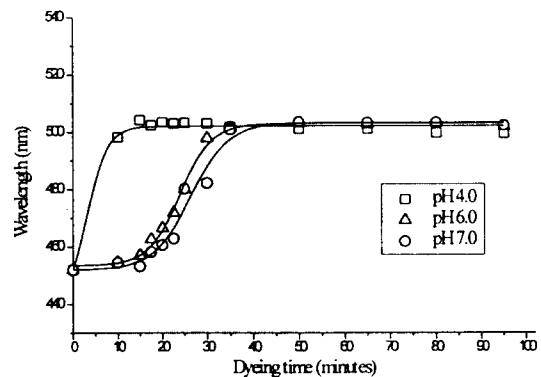


Fig. 7 The variation in λ_{\max} of the residual dye baths (dye A-1) during dyeing in the absence of polyester fabric (residual dye bath : ethanol 1 : 3)

452.0nm to 503.4nm after 50 minutes dyeing(130°C). These results agree with those obtained when DMF had been used as co-solvent(Fig. 6).

This investigation of the variation in λ_{max} of the aziridine dye A-1 during dyeing in the absence of polyester fabric(Fig. 6, Fig. 7) clearly demonstrated that ring-opening(hydrolysis) of the aziridinyl dye started from the beginning of dyeing at pH 4, 6 and 7.

3.3.3.2 HPLC analysis of residual dye-baths

In order to analyse the residual dyebaths obtained during dyeing with the aziridinyl dyes in the absence of polyester fabric, using HPLC, as described in section 2.2.6., a correct solvent that would extract the dye from the residual aqueous dyebath was needed. The solubility of both the aziridinyl dye A-1 and its hydrolysed form(A-2) in the selected solvent had to be considered, otherwise the proportion of dyes A-1 and A-2 that were extracted from the residual dyebaths would differ.

In this study, dye was extracted from the residual dyebaths using dichloromethane as described in section 2.2.6. After the dye had been extracted, the dichloromethane was removed using rotary evaporation under vacuum and the dry dye then dissolved in a 50 : 50 acetonitrile : water mixture.

The HPLC chromatographs of the aziridinyl dye (A-1) and the hydrolysed dye (A-2) before dyeing are shown in Fig. 8 and 9. The retention time(RT) of the two dyes was found to be 6.39 for the aziridinyl dye A-1(Fig. 8) and 5.37 for the hydrolysed dye A-2 (Fig. 9).

During polyester dyeing at pH 10, the peaks for the aziridinyl dye A-1 and the hydrolysed dye A-2 after 5 minutes(70°C), 15 minutes(90°C), 25 minutes(110°C), 30 minutes(120°C), 35 minutes(130°C), 50 minutes(130°C) and 95 minutes(130°C) from the beginning of dyeing were recorded and some of the results are presented in Figures 11 to 13.

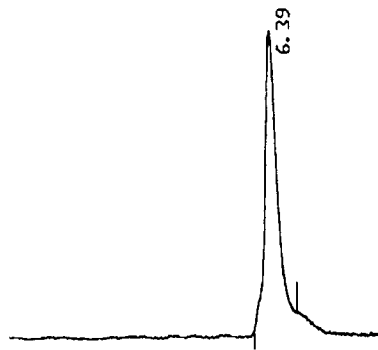


Fig. 8 Chromatograph of the aziridinyl dye A-1 prior to dyeing

Peak #	Retention time (minutes)	Area %	Area
1	6.39	100	279267
Total		100	279267

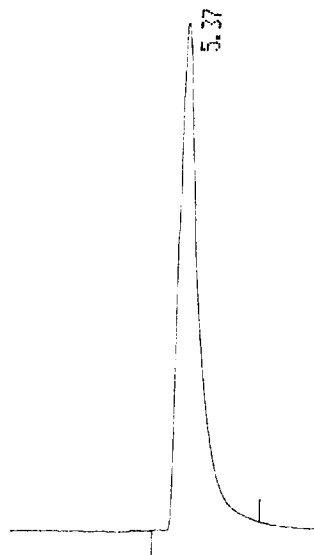


Fig. 9 Chromatograph of the hydrolysed dye A-2 prior to dyeing

Peak #	Retention time (minutes)	Area %	Area
1	5.37	100	437973
Total		100	437973

In the residual dyebath at 110°C was found one peak for the hydrolysed dye of RT 5.34(% area ; 59.3) and another peak for the aziridinyl azo dye of RT 6.39(% area ; 40.7). Thus, when the dyeing temperature had been increased to 110°C over 25 minutes, 59.3% of the aziridinyl dye had been hydrolysed(Fig. 10). At 120°C(after 30 minutes dyeing), one peak for the hydrolysed dye of RT 5.37(% area ; 74.02) and another peak for the aziridinyl azo dye of RT 6.45(% area ; 25.98) were found (Fig. 11). Therefore, 74.02% of the aziridinyl azo dye had been hydrolysed when the dyeing temperature had reached 120°C(i.e. after 30 minutes dyeing).

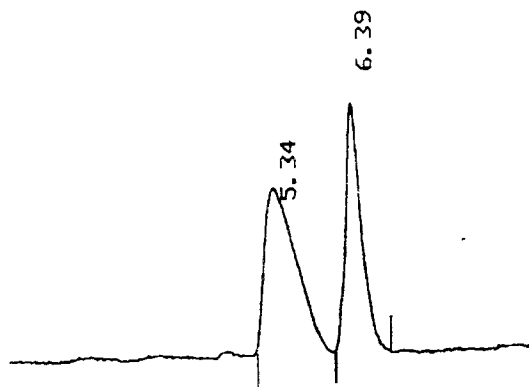


Fig. 10 Chromatograph of residual dyebath at 110°C(25 minutes) during blank dyeing at pH 10.0(position C)

Peak #	Retention time (minutes)	Area%	Area
1	5.34	59.30	86828
2	6.39	64.70	59594
Total		100	146422

Fig. 12 shows only one peak for the hydrolysed dye of RT 5.37 from which it is evident that the aziridinyl dye had been completely hydrolysed after 35 minutes dyeing at pH 10. At the sampling positions of 130°C, 50 and 95 minutes, one peak for the hydrolysed dye of RT 5.24 and 5.77 was

observed.

From the results of the λ_{max} variation discussed in the previous section(3.3.3.1.), it can therefore be concluded that the dye underwent hydrolysis, the extent of which increased with increasing time (and temperature) of dyeing.

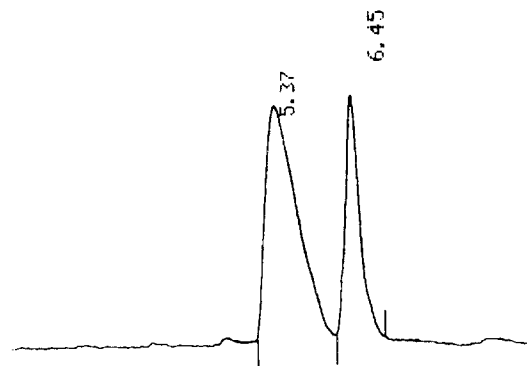


Fig. 11 Chromatograph of residual dyebath at 120°C(30 minutes) during blank dyeing at pH 10.0(position D)

Peak #	Retention time (minutes)	Area%	Area
1	5.37	74.02	185014
2	6.45	25.98	64938
Total		100	249952

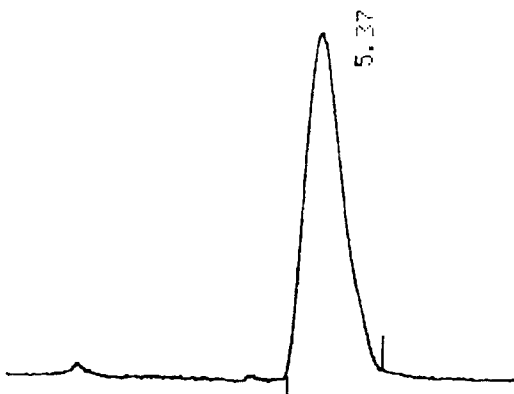


Fig. 12 Chromatograph of residual dyebath at 130°C(35 minutes) during blank dyeing at pH 10.0(position E)

Peak#	Retention time (minutes)	Area%	Area
1	5.37	100	214938
Total		100	214938

Hence, when the aziridinyl dye A-1 was applied to conventional decitex polyester fabric at pH 10, complete hydrolysis of the dye occurred after 35 minutes dyeing.

Analysis of the extent of dye hydrolysis using HPLC was also carried out during dyeing at pH 4.0 and 12.0 ; the results are shown in Fig. 13 to Fig. 15.

Fig. 13 shows that hydrolysis occurred rapidly in the early stages of dyeing at pH 4.0 and that all the aziridinyl dye was completely converted into its hydrolysed form after 17.5 minutes as the dyeing temperature was increasing to 95°C. In the case of dyeing at pH 10, dye hydrolysis also occurred from the beginning of dyeing and all the aziridinyl dye was completely hydrolysed after 35 minutes when the dyeing temperature was increasing to 130°C (Fig. 14) ; this finding is the same as that previously recounted in section 3.3.3.1. Thus, during dyeing at pH 10, there was an opportunity for the fibre to adsorb the aziridinyl dye for 35 minutes while the dyeing temperature was increasing to 130°C.

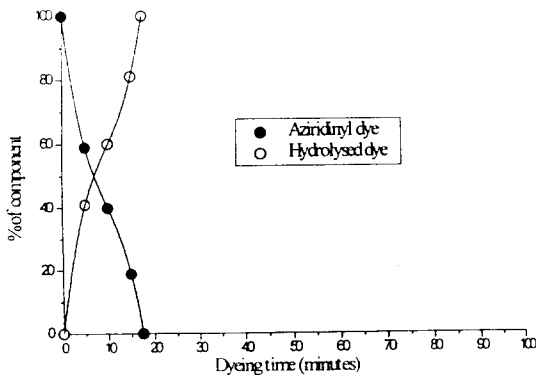


Fig. 13 The extent of hydrolysis of dye A-1 during polyester dyeing at pH 4.0

In the case of dyeing at pH 12, hydrolysis of dye A-1 occurred very slowly compared with that at pH 4 and 10 ; indeed, the aziridinyl dye existed until the end of dyeing(Fig. 15), a total of 95 minutes.

Clearly, these findings reveal that the aziridinyl dye was completely converted into its hydrolysed form after 17.5 minutes(95°C) at pH 4, after 35 minutes(130°C) at pH 10 and after 95 minutes(130°C) at pH 12.

Thus, dyeing at pH 12 appears to offer the greatest opportunity for the dye to react with the polyester fibre and thus to achieve highest dye-fibre fixation efficiency. However, it was considered that dyeing at pH 12 might damage(hydrolyse) the polyester fibre at the high temperature (130°C) used and it was therefore decided that dyeing at pH

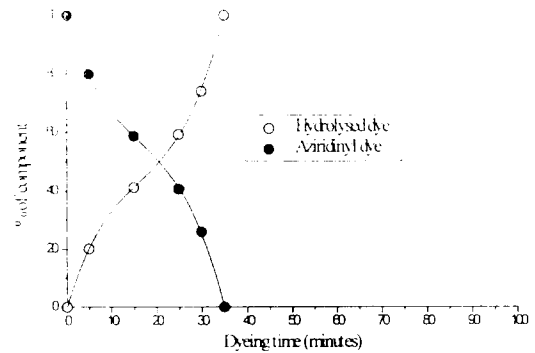


Fig. 14 The extent of hydrolysis of dye A-1 during polyester dyeing at pH 10.0

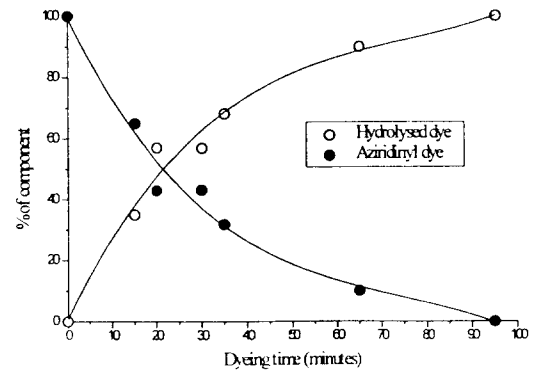


Fig. 15 The extent of hydrolysis of dye A-1 during polyester dyeing at pH 12.0

12 would not be used in the subsequent evaluation of the build-up and fastness properties of the dyes.

3.3.4 The variation in colour strength during polyester dyeing before and after solvent extraction

1.0% omf of the aziridiny dye A-1 as well as 1.0% omf of the hydrolysed form of the dye(A-2) was applied to scoured, conventional decitex polyester fabric using the method described in section 2.2.3.1.. The dyed fabrics were rinsed in cold tap water and dried in the open air and the colour strength(K/S) measured as described in section 2.2.8.

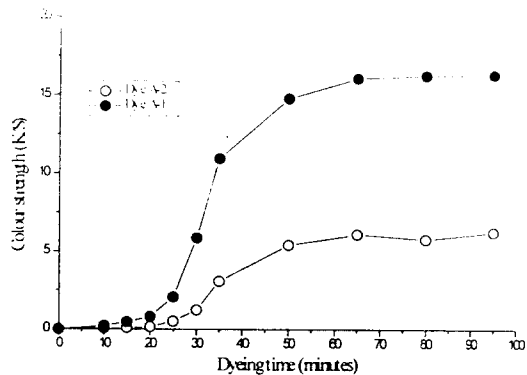


Fig. 16 The variation of colour strength of dyed conventional decitex polyester fabric with dyes A-1 and A-2 during dyeing at pH 6.0(1.0% omf)

Fig. 16 shows the variation in colour strength of A-1 and A-2 as a function of dyeing time. Although the tinctorial strength (ϵ_{\max}) in acetone of the 2-hydroxyethyl azo dye (A-2) was higher than that of aziridiny azo dye (A-1) (Table 2) the colour strength obtained for dye A-2 on conventional decitex polyester fabric was much lower than that achieved using the aziridiny azo dye. Clearly, the saturation level of A-2 was much lower than that of A-1; also, the rate of uptake of dye A-2 was found to be lower than that of dye A-1 (Fig. 16).

Dye A-2 has an IOR value of 0.929 whilst that of dye A-1 is 0.691 (IOR value of polyester 0.7) and the Mr of A-2 is 18 units greater than that of A-1. Therefore, the findings that the saturation level of A-2 was much lower than that of A-1 and that the rate of dyeing of dye A-2 was slower than that of dye A-1 may be due to the substantivity of the 2-hydroxyethyl aniline azo derivative A-2 towards polyester being lower than that of the aziridiny azo dye.

Fig. 17 shows the variation of colour strengths of the aziridiny dye A-1 both before and after DMF extraction as a function of dyeing time when dyeing was carried out at pH 4 and also pH 6. From the results of the study of the hydrolysis of aziridine dyes during dyeing (Section 3.3.3.) using HPLC, the residual dyebath obtained for dye A-1 when dyeing at pH 4.0 showed that all of the aziridiny dye was converted into its hydrolysed form in the early stages of dyeing (Section 3.3.3., Fig. 6, Fig. 7 and Fig. 13). Thus the variation of colour strength of dye A-1 at pH 4.0 was similar to that of A-2 which has low substantivity towards polyester fabric (Fig. 16 and Fig. 17).

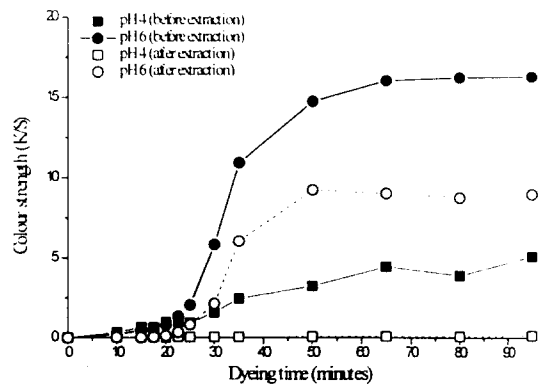


Fig. 17 The variation of colour strength of conventional decitex polyester fabric dyed with dye A-1 during dyeing (1.0% omf); before and after DMF extraction)

The colour strength of dye A-1, when dyeing was carried out at pH 4, after dye extraction using DMF reveals that all of the dye on the dyed polyester fabric was removed by solvent extraction and, therefore, that dye-fibre fixation did not occur during dyeing at this particular pH.

Previously, it was shown that when dyeing had been carried out at pH 6.0, the aziridinyl dye was completely hydrolysed when the dyeing temperature had reached 130°C after 35 minutes dyeing (Section 3.3.3.1, Fig. 6 and Fig. 7). Thus, the saturation value of the dye on polyester fabric at pH 6 was much higher than that of pH 4.0 (Fig. 17). The colour strength of the DMF-extracted dyeing of A-1, when dyeing was carried out at pH 6.0, demonstrates that about half of the adsorbed dye was removed by the solvent and thus, that dye-fibre fixation occurred during dyeing (Fig. 17).

Fig. 17 also shows that, when dyeing had been carried out at pH 6, the colour strength of the solvent extracted dyeing of A-1 reached a constant value at about 50 minutes. When the fact that the hydrolysis of dye A-1 was completed after 35 minutes dyeing as described in section 3.3.3 is considered, it can therefore be proposed that dye-fibre

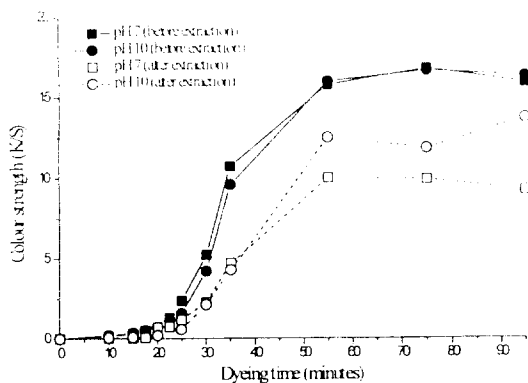


Fig. 18 The variation of colour strength of conventional decitex polyester fabric dyed with dye A-1 during dyeing (1.0 % omf ; before and after DMF extraction)

reaction did not occur after 50 minutes dyeing. Results for the dyeing of conventional decitex polyester fabric with dye A-1 at pH 7.0 and also pH 10.0 are shown in Fig. 18.

Although the colour strength of the fabric which had been dyed at pH 7 before DMF extraction was similar to that of the fabric which had been dyed at pH 10, after DMF extraction, the K/S of the fabric dyed at pH 10 was higher than that of the fabric which had been dyed at pH 7. The analysis of dye hydrolysis, when dyeing was carried out at pH 7 and 10, showed that complete hydrolysis of dye A-1 occurred after 35 minutes dyeing (130°C) (Fig. 7 and Fig. 14). However, the finding that Fig. 18 shows that the colour strength of the fabric dyed at pH 10 was higher than that of the fabric dyed at pH 7 after DMF extraction may be due to pH 10 favouring dye-fibre reaction.

Previously, Fig. 15 revealed that at pH 12, hydrolysis of dye A-1 occurred very slowly and the aziridinyl dye (A-1) existed until the end of the dyeing after 95 minutes dyeing. This is reflected in the finding (Fig. 19) that the difference in colour strength of polyester fabric during dyeing at pH 12 before and after DMF extraction was smaller

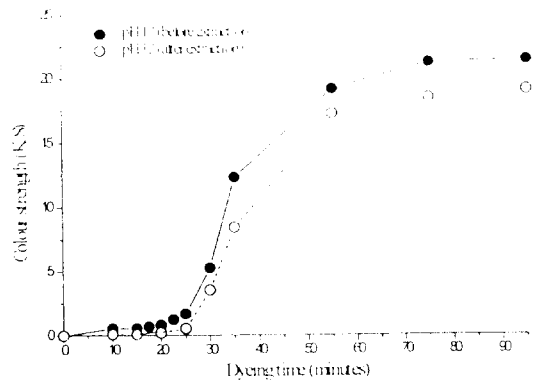


Fig. 19 The variation of colour strength of conventional decitex polyester fabric dyed with dye A-1 during dyeing (1.0 % omf ; before and after DMF extraction)

than that at pH 4, 6, 7 and 10. The extent of dye uptake, when dyeing was carried out at pH 12, was also higher than that of dyeings carried out at lower pH values.(Fig. 17, Fig. 18 and Fig. 19). In conclusion, the extent of fixation of the aziridinyl azo dye (A-1) to conventional polyester fibre was in the order :

$$\text{pH } 4 \ll \text{pH } 6 < 7 < 10 \text{ pH } 12$$

3.3.5 Dye-build-up

Table 2 and Table 3 show the inorganic/organic values, the λ_{max} and the molar extinction coefficient(ϵ_{max}) in acetone of both the three aziridinyl azo dyes and the three 2-hydroxyethylaniline azo dyes under consideration. It is evident that all three hydrolysed azo dyes absorbed bathochromically compared to the aziridinyl dyes and the aziridinyl azo dyes were more hydrophobic than the hydrolysed dyes ; of the six dyes, C-1 was the most hydrophobic.

In the case of dyeing polyester with dye A-1 at pH 6.0, 8.0 and 10.0, it can be considered that the dye A-1 will be present in the dyebath in both the aziridine and hydrolysed form (A-2). If the solubilities of dyes A-1 and A-2 in polyester were similar, then the saturation values of this dye mixture may exceed the sum of the solubilities of dye A-1 and A-2 due to interaction between the two dyes. However, it can be argued that there will not be any synergistic effect¹⁵⁾ because the two types of dye have different solubilities in polyester, as reflected in the different IOR values of the dyes. Thus the two forms of the dye cannot form mixed crystals that would result in abnormal adsorption behaviour¹⁶⁾.

The dyeing of conventional decitex polyester fabric with dye A-1 at pH 6, 8 and 10 as well as dyeing with dye A-2 at pH 6 was carried out as described in section 2.2.3.2.. Fig. 20 shows the build-up of dyes A-1 and A-2 on conventional decitex polyester fabrics. When the concentration of

dye was increased up to 1.0%, the build-up of dye A-2 reached a constant value(Fig. 20) which may be due to the substantivity of dye A-2 towards polyester fibre being low. Fig. 20 also reveals that the shape of the build-up curve of dye A-1 at each of the three pH values 6 and 10 was similar. Furthermore, the dye exhibited good build-up at pH 6, 8 and 10, this being much greater than that of dye A-2. Fig. 20 clearly implies, from the gradients of the curves obtained, that dye build-up would continue to increase with further increase in concentration of dye A-1 applied at pH 6 and 8 whereas at pH 10, build-up would not continue to increase for applied dye concentrations in excess of 2.0% omf.

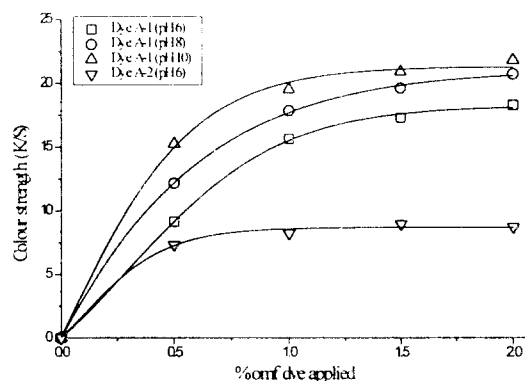


Fig. 20 Build-up of dyes A-1 and A-2 on conventional decitex polyester fabric

Fig. 21 shows the build-up of dyes C-1 and C-2 on conventional decitex polyester fabrics. The build-up of C-1 increased with increasing pH of application as had been observed for dye A-1(Fig. 20). However, the build-up of dye C-2 was higher than that of C-1, at both pH values. This finding may be due to the substantivity of C-2 being higher than that of C-1 as well as the marked hydrophobic character of C-1 (Table 3 ; IOR value 0.571) which may have resulted in a poor dispersion of dye being achieved. Also, the low tinctorial strength (ϵ_{max}) of dye C-1 (Table 3 ; IOR value 0.857) may

have contributed to the findings displayed in Fig. 21.

Fig. 22 shows the build-up profiles of dyes D-1 and D-2 on conventional decitex polyester fabric from which it is evident that the build-up profiles of D-1 at pH 6, 8 and 10 were higher than that of D-2 at pH 6. This observation may be due to the higher tinctorial strength(ϵ_{max}) of D-1 as well as the fact that the IOR value of D-1 was closer than that of D-2 to that of the polyester fibre(0.7 for polyester, 0.615 for D-1, 0.872 for D-2). In other words, the substantivity of D-1 towards the polyester fibre was higher than that of D-2. The build-up profiles of dyes D-1 and D-2 were similar to those of dyes A-1 and A-2.

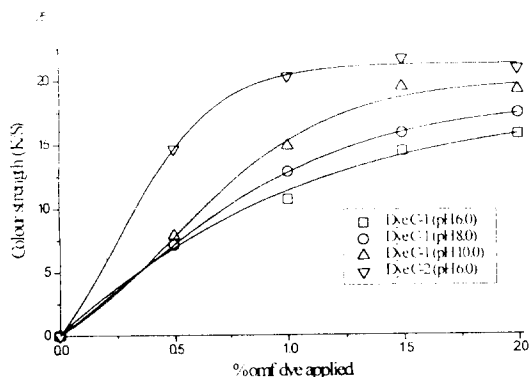


Fig. 21 Build-up of dyes C-1 and C-2 on conventional decitex polyester fabric

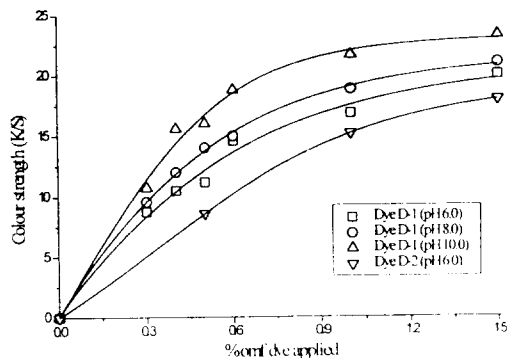


Fig. 22 Build-up of dyes D-1 and D-2 on conventional decitex polyester fabric

3.3.6 Effect of pH

The results presented in sections 3.3.3., 3.3.4. and 3.3.5. revealed that the higher the pH of dyeing, the lower was the extent of hydrolysis of the aziridinyl dyes during dyeing and the higher was the build-up of the aziridinyl dyes on conventional decitex polyester fabrics.

The dyeing of conventional decitex polyester fabric with dyes A-1, A-2, B-4, C-1 and D-1 at various pH values was carried out as described in section 0. Fig. 23 to Fig. 25 show the variation in colour strength as a function of application pH for 1.0% omf dyeings.

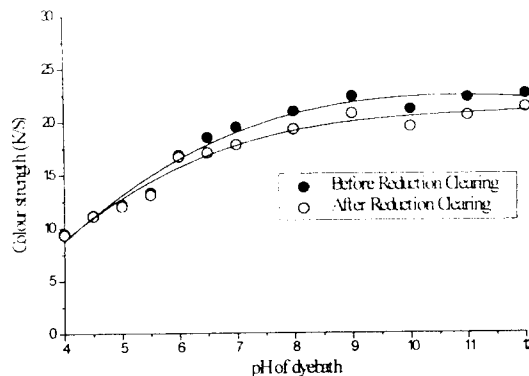


Fig. 23 Effect of pH on the colour strength of conventional decitex polyester fabric dyed with dye A-1(1.0% omf)

When a comparison of the colour strength of conventional decitex polyester fabric which had been dyed with A-1 both before and after reduction clearing was made(Fig. 23), the colour strength of the reduction-cleared and non reduction-cleared fabrics increased with increasing pH of application. Thus, dye fibre reaction increased with increasing pH of application.

The colour strength of the 2-hydroxyethylaniline azo dye (A-2) and the *N,N'*-dimethylaniline azo dye (B-4) were independent of pH whereas that of the aziridinyl dyes A-1, C-1 and D-1 increased

with increasing pH of application(Fig. 24 and Fig. 25).

In the case of dye A-1, the extent of this increase in colour strength that accompanied an increase in dyeing pH was greater than the other aziridinyl azo dyes C-1 and D-1. This finding may be due to the substantivity of A-1 being higher than C-1 and D-1 because the IOR value of A-1(0.691) was closer to that of the polyester fibre(OR=0.7) than that of the two other aziridinyl dyes(OR of dye C-1=0.571 and dye D-1=0.615). The results

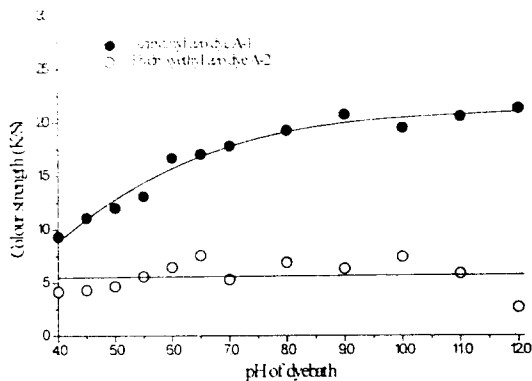


Fig. 24 Effect of pH on the colour strength (K/S) of conventional decitex polyester fabric dyed with dye A-1 and A-2(1.0% omf)

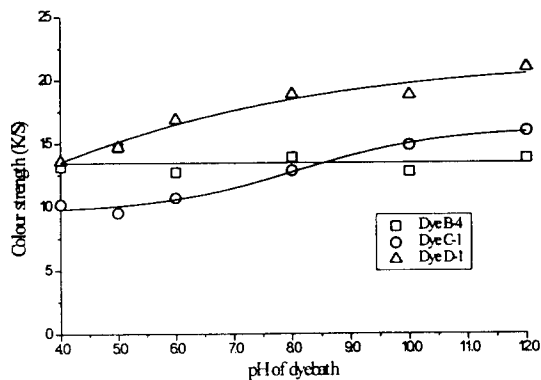


Fig. 25 Effect of pH on the colour strength of conventional decitex polyester fabric dyed with dye B-4, C-1 and D-1(1.0% omf)

clearly demonstrate that the application to polyester of the aziridinyl dyes is favoured by high pH values.

3.3.7 Solvent extraction

In order to investigate whether the aziridinyl disperse dyes became covalently bound to polyester fibre, dyeings were solvent extracted. Two approaches were used.

Firstly, a 1g sample of reduction cleared, conventional decitex polyester fabric which had been dyed with the aziridinyl azo dyes A-1, C-1 or D-1, was dissolved in 80cm³ dichloroacetic acid at 35~40°C and the precipitated material collected by drowning out into acetone at room temperature¹⁷⁾. The precipitated material was separated from acetone by filtering under vacuum and, after additional washing with acetone, was dried in the open air as described in section 2.2.5.. This revealed that the precipitated polyester, which had been dyed with A-1, C-1 or D-1 and dissolved in dichloroacetic acid, was deeply coloured after drowning out into acetone whilst the acetone was only weakly coloured or even colourless. Additional washing of the precipitated polyester with acetone did not release any further colour from the substrate. By way of contrast, this procedure was repeated using a corresponding sample of fabric that had been dyed with the hydrolysed dyes A-2, C-2 or D-2 as well as *N,N'*-dimethylaniline azo dye (B-4) as described in section 2.2.5.. It was observed that the precipitated polyester, which had been dyed with the dyes A-2, C-2, D-2 and B-4, released colour into the acetone with the result that the precipitated material was either very pale coloured or colourless whilst the acetone was deeply coloured. These findings therefore imply that in the case of the aziridinyl dyes (A-1, C-1 and D-1) the dyes were covalently bound to the substrate whereas the non-aziridinyl derivatives(A-2, C-2, D-2 and B-4) were simply bound to the substrate by

physical forces of interaction.

Secondly, conventional decitex polyester fabric, which had been dyed with the aziridinyl dye A-1 at pH 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 9, 10, 11 and 12, was extracted using DMF by refluxing at 100°C for 1 hour as described in section 2.2.3.3.3. The solvent extracted polyester fabric, which had been dyed at pH values higher than 6, was deeply coloured and the DMF solvent only very weakly coloured or colourless at the end of extraction. However, in the case of dyeings carried out at pH values lower than 6, the solvent was deeply coloured whilst the polyester fabric was either colourless or very pale at the end of extraction. Therefore, when polyester dyeing was carried out at higher than pH 6, it is evident that the aziridinyl dye (A-1) became covalently bound to the fibre.

A comparison was made of the colour strength of conventional decitex polyester fabric that had been dyed with A-1 at various pH values before and after DMF extraction (Fig. 26) and the extent of dye that was stripped from the dyed fabric calculated as described in section 2.5.3.3.3 (Fig. 27).

Fig. 26 demonstrates that the colour strength of the solvent extracted fabric which had been dyed with A-1 increased with increasing pH. Also, it is clear that the solvent extracted dyeings at pH 4, 4.5, 5, 5.5, 6 were either colourless or very weakly coloured whilst dyeings carried out at pH higher than 6 was deeply coloured. These findings may be due to the aziridinyl dye at pH lower than 5 being completely hydrolysed in the early stages of dyeing as mentioned in section 3.3.3. (Fig. 27). As Fig. 27 shows, half of dye was removed from polyester fabric which had been dyed with A-1 at pH 6 and 26% dye was removed from fabric which had been dyed with A-1 at pH 7 by solvent extraction. In the case of dyeings at pH 9, 10 and 11, around 15% of the dye was removed; dyeing at pH 12 resulted in around 10% of the dye being stripped (Fig. 27).

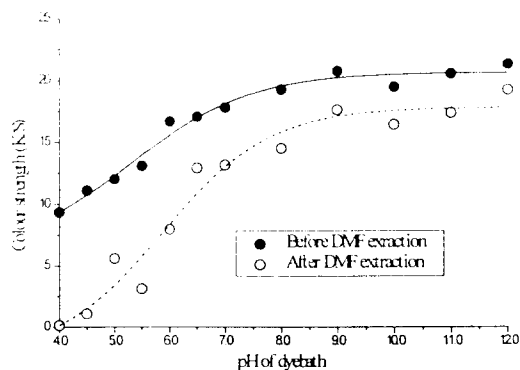


Fig. 26 Comparison of the colour strength of conventional decitex polyester fabric which had been dyed with 1.0% omf A-1 at various pH values before and after DMF extraction

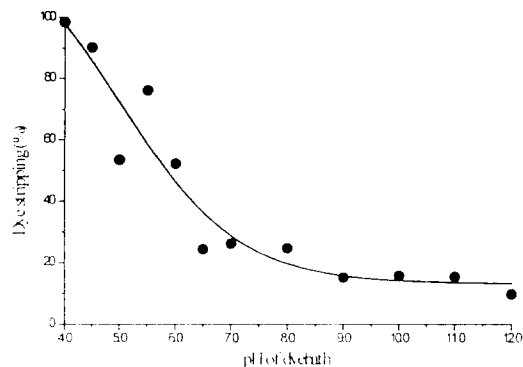


Fig. 27 The extent of dye stripped from conventional decitex polyester fabric which had been dyed with 1.0% omf A-1 at various pH values

It is evident that the higher the pH of application, the lower was the extent of dye stripped by solvent extraction. This finding may be due to dye-fibre fixation being favoured by the higher pH of application and also by the higher pH having stabilised the tertiary aziridinium ion in the aziridinyl azo dye which retarded hydrolysis (aziridinyl ring opening in water). In the case of the *N,N'*-dimethyl-aniline azo dye (B-4) and the 2-hydroxyethyl-aniline azo dye (A-2), complete dye stripping occurred after dye extraction using DMF, clearly

showing that none of these dyes was covalently bound to the fibre.

3.3.8 Standard depth dyeing

The dye concentrations required to achieve a standard depth on conventional decitex polyester fibre are given in Table 6. As the build-up of the aziridinyl dyes increased with increasing pH of dyeing as mentioned before, it follows that the amount of the aziridinyl dyes required to obtain the standard depth on conventional decitex polyester fabric should have decreased as the pH of dyeing was increased, as indeed was observed (Table 6).

Table 6. Dye concentration(% omf) required to give standard depth dyeings for conventional decitex polyester fabric

Dye	pH	Concentration(% omf)
A-1	6.0	1.4(1/1)
	8.0	1.1(1/1)
	10.0	0.7(1/1)
A-2	6.0	1.4(1/3)
B-4	6.0	0.7(1/1)
A-1	6.0	0.8(1/1)
	8.0	0.7(1/1)
	10.0	0.6(1/1)
C-2	6.0	0.3(1/1)
D-1	6.0	0.55(1/1)
	8.0	0.5(1/1)
	10.0	0.4(1/1)
D-2	6.0	1.6(1/1)

3.3.9 Washfastness assessment

Evidence that the aziridinyl dye was covalently bound to polyester fibre was obtained from the results of the solvent extraction of conventional decitex polyester fabric which had been dyed with aziridinyl azo dyes. Further evidence to support this proposition is provided by the wash-fastness

results of the aziridinyl dyes A-1, C-1 and D-1 on the substrate.

The washfastness of standard depth dyeings (section 3.3.8) on polyester was carried out according to the ISOC06/C2 (60°C, 30 minutes) and ISOC06/C4, (95°C 30 minutes) methods, as described in section 2.2.9.1.

Owing to the poor build-up of dye A-2, it was possible only to achieve a 1/3 standard depth dyeing of conventional decitex polyester fabric rather than the 1/1 standard depth secured using dye A-2. Thus, the difference in wash-fastness observed between dyes A-1 and A-2 is very marked in the case of staining of adjacent acetate, nylon 6.6 and wool since, in view of the well known fact that wash-fastness decreases with increasing depth of shade, if it had been possible to obtain 1/1 standard depths using dye A-2, it can be anticipated that the fastness to washing of such dyeings would have been much lower than that secured for the 1/3 standard depths shown in Table 7. Table 7 also demonstrates that the wash fastness of the *N,N'*-dimethylaniline azo dye (B-4) was lower than that of A-1 which had been applied at pH 10. However, the anticipated higher wash fastness of the aziridinyl dyes C-1 and D-1 over the hydrolysed dyes C-2 and D-2 was not found.

The wash fastness of the aziridinyl dyes was expected to increase with increasing pH of application. However, this was not observed using the ISOC06/C2 test method. Table 7 shows that the wash fastness of A-1, when dyeing was carried out at pH 10, was slightly higher than that obtained when the dye had been applied at pH 6 and 8 in the case of staining of acetate and nylon 6.6 adjacent fabrics. The wash fastness of dye C-1 which had been applied at pH 10 was slightly higher than that of the dye, when dyeing had been carried out at pH 6 and 8, in the case of staining of nylon 6.6 adjacent fabric. In the case of D-1, the wash fastness of dyeing at pH 8, in the case

Table 7. Colour Fastness to Washing(ISOC06/C2) of Standard Depth Dyeings¹

Dye	%	pH	Colour depth	Ch	Adj	Ac	Co	Ny	PET	Acry	Wo
A-1	1.4	6.0	1/1	5	5	4/5	5	4/5	5	5	5
	1.1	8.0	1/1	5	5	4/5	5	4/5	5	5	5
	0.7	10.0	1/1	5	5	5	5	4/5	5	5	5
A-2	1.4	6.0	1/3	5	5	3/4	5	3/4	5	5	4/5
B-4	0.7	6.0	1/1	5	5	4/5	5	4/5	5	5	5
C-1	0.8	6.0	1/1	5	5	4/5	5	4	5	5	5
	0.7	8.0	1/1	5	5	4	5	4	5	5	5
	0.6	10.0	1/1	5	5	4/5	5	4/5	5	5	5
C-2	0.3	6.0	1/1	5	5	4/5	5	4/5	5	5	5
D-1	0.55	6.0	1/1	5	5	4/5	5	4	5	5	5
	0.5	8.0	1/1	5	5	4/5	5	4/5	5	5	5
	0.4	10.0	1/1	5	5	4/5	5	4/5	5	5	5
D-2	1.6	6.0	1/1	5	5	4/5	5	4/5	5	5	5

¹ Ch : Colour Change ; Adj : Staining of adjacent conventional polyester ; Ac : Acetate ; Co : Cotton ; Ny : Nylon 6.6 ; Acr : Acryl ; Wo : Wool.

of staining of nylon 6.6, was slightly higher than that of the dyeing at pH 6. These findings may be due to the conditions of the ISOC06/C2 test method not being severe enough to give the anticipated difference in fastness. Thus, a more severe test method(ISOC06/C4) was also used as described in section 2.2.9.1.

Table 8 shows the results of the ISOC06/C4 test method(95°C 30 minutes). The difference in wash fastness between dyes A-1 and A-2 is very marked in the staining of adjacent acetate, nylon 6.6 and wool. When it is remembered that wash fastness decreases with increasing depth of shade then if it had been possible to obtain 1/1 standard depths using dye A-2, it can be anticipated that the fastness to washing of such dyeings would have been much lower than that secured for the 1/3 standard depths shown in Table 8. Table 8 also illustrates that the wash fastness of the *N,N'*-dimethylaniline azo dye (B-4) was lower than that of A-1 which had been applied

at pH 10 in the case of the staining of adjacent acetate, polyester, acrylic and wool fabrics. The wash fastness of the conventional decitex polyester fabric which had been dyed with dyes C-1 at pH 10 was higher than that of dye C-2 in the context of staining adjacent acetate and nylon 6.6. The wash fastness of the hydrolysed dye D-2 was much lower than that of the aziridinyl dye D-1 in terms of change of colour and staining of all of the adjacent fabrics; indeed, the difference in staining of acetate and nylon 6.6 fabrics is very clear.

In the case of the three aziridinyl dyes A-1, C-1 and D-1, highest wash fastness was achieved when dyeing had been carried out at pH 10.

Table 8 clearly demonstrated that the wash fastness of the aziridinyl dyes (A-1, C-1 and D-1) was higher than their hydrolysed counterparts (A-2, C-2 and D-2).

Thus, the wash fastness results obtained show that the higher the pH of dyeing, the higher the fastness to washing.

Table 8. Colour Fastness to Washing (ISOC06/C4) of Standard Depth Dyeings²

Dye	%	pH	Colour depth	Ch	Adj	Ac	Co	Ny	PET	Acry	Wo
A-1	1.4	6.0	1/1	5	5	3/4	5	3	5	5	4
	1.1	8.0	1/1	5	5	3/4	5	3	5	5	4
	0.7	10.0	1/1	5	5	4	5	4	5	5	4/5
A-2	1.4	6.0	1/3	5	5	2/3	5	2/3	5	5	4
B-4	0.7	6.0	1/1	5	4/5	3/4	5	4	4/5	4/5	4
C-1	0.8	6.0	1/1	5	4/5	3/4	4/5	3	4/5	4/5	4
	0.7	8.0	1/1	5	4/5	4	5	3	4/5	5	4
	0.6	10.0	1/1	5	4/5	4/5	5	3/4	4/5	5	4/5
C-2	0.3	6.0	1/1	5	4/5	3/4	5	3	4/5	5	4/5
D-1	0.55	6.0	1/1	5	4/5	3/4	4/5	3/4	5	5	4/5
	0.5	8.0	1/1	5	4/5	4	5	4	4/5	5	5
	0.4	10.0	1/1	5	5	4/5	5	4	5	5	5
D-2	1.6	6.0	1/1	4/5	4/5	3	4/5	2/3	4/5	4/5	3/4

². Ch : Colour Change ; Adj : Staining of adjacent conventional polyester ; Ac : Acetate ; Co : Cotton ; Ny : Nylon 6.6 ; Acr : Acryl ; Wo : Wool.

3.3.10 Fastness to light

The light fastness of conventional decitex polyester fabric which had been dyed with the aziridinyl dyes (A-1, C-1 and D-1), the hydrolysed dyes (A-2, C-2 and D-2) and the *N,N'*-dimethylaniline azo dye (B-4) was determined according to the ISO B02 method as described in section 2.2.9.2.

Table 9 shows that the fastness to light of the aziridinyl dyes tended to increase with increasing pH of application. The lightfastness of dyeings of the aziridinyl three dyes (A-1, C-1 and D-1) was higher than that of their hydrolysed forms (A-2, C-2 and D-2) ; also, the fastness to light of the *N,N'*-dimethylaniline azo dye (B-4) was higher than that of many of the other dyes assessed.

4. Conclusion

When the λ_{max} of aziridinyl dyes and *N*, β -hydroxyethylaniline dyes in acetone were compared, the λ_{max} of the aziridinyl dye displayed hypsoch-

romic shifts compared with the analogous *N*,-hydroxyethylaniline azo dyes.

Table 9. Light fastness of standard depth dyeings on conventional decitex polyester fabric

Dye	%	Colour Depth	pH	Light Fastness
A-1	1.4	1/1	6.0	4
	1.1	1/1	8.0	4-5
	0.7	1/1	10.0	5
A-2	1.4	1/3	6.0	2
B-4	0.7	1/1	6.0	5
C-1	0.8	1/1	6.0	4-5
	0.7	1/1	8.0	5
	0.6	1/1	10.0	6
C-2	0.3	1/1	6.0	3-4
D-1	0.55	1/1	6.0	3
	0.5	1/1	8.0	3
	0.4	1/1	10.0	4
D-2	1.6	1/1	6.0	2

The build-up and wash fastness of the aziridinyl dyes on conventional decitex polyester fabrics increased with increasing pH of application over the pH range 4 to 12 at 130°C due to the stability of aziridinyl dyes increasing with increasing pH. However, as dyeing polyester at pH 12 was considered to present a practical problem in view of the known susceptibility of the fibre to saponification under high temperature alkaline dyeing conditions, further dyeing was carried out at pH 10.

The following observations implied that the aziridinyl dyes were either covalently bound to or had undergone dimerisation within polyester fibres.

(a) DMF extraction

When polyester and nylon fabrics which had been dyed with aziridinyl azo dyes were extracted with boiling DMF, no dye was removed by the solvent. In contrast, when polyester fabrics which had been dyed with non-aziridinyl dyes were extracted using DMF, dye was removed and the resulting dyeings were either colourless or very weakly coloured.

(b) Dissolution and re-precipitation.

Precipitated polyester fibre, which had been dyed with aziridinyl disperse dyes and dissolved in dichloroacetic acid, was deeply coloured after drowning out into acetone.

The colour strength of dyeings on conventional polyester which had been reduction-cleared and non reduction-cleared, increased with increasing pH of application.

The wash fastness of aziridinyl dyes on conventional 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 aziridinyl dyes in terms of their wash fastness properties was emphasised when fastness testing was carried out at 95°C rather than 60°C. These findings imply that the aziridinyl dyes may be covalently bound to the fibre or that dimers may

have been formed during dyeing and agree with Burkinshaw and Hallas work⁶⁾ which showed that aziridinyl dyes displayed higher wash fastness than non-aziridinyl disperse dyes of similar structure.

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