

〈研究論文(學術)〉

## 에틸렌이민 유도체를 갖는 아조계 분산염료의 염색성에 관한 연구(II) - 나일론 6.6 섬유에의 응용 -

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## A Study on Dyeing Property of Azo Disperse Dyes Containing Ethyleneimine Derivatives Part (II) - Application to 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 나일론 염색 조건의 확립이다.

두 쌍의 염료 A-1/A-2와 D-1/D-2의 최대흡수파장( $\lambda_{max}$ )을 비교할 경우, 아세톤 최대흡수파장( $\lambda_{max}$ )의 차이가 없거나 적어졌다.

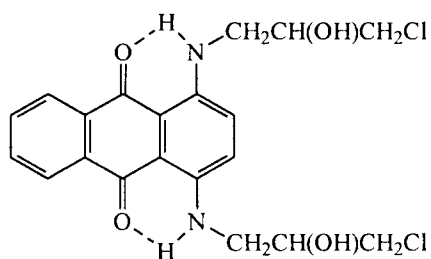
세가지 아지리디닐 모노 아조 염료와 이들 염료의 가수분해 된 형태 그리고 디메틸아닐린계 아조 염료의 나일론 6.6 섬유에 대한 염색 및 견뢰도 성질이 조사되었다.

아지리디닐 염료의 나일론 섬유상의 최대 염착은 pH 5에서 얻어졌으며, 염색된 나일론 섬유에서의 용매 추출의 경우 최소 염료 추출은 pH 8.0-10.0에서 얻어졌다.

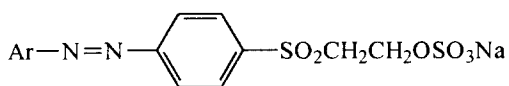
아지리디닐 염료 염색된 나일론 섬유상의 세탁 견뢰도와 광 견뢰도는 염색 시 pH의 증가에 따라 증가 하였으나, pH 8에서의 견뢰도 성질이 pH 10에서와 비교하여 보다 개선되었다. 세가지 아지리디닐 염료와 이들 염료의 가수분해 된 형태 그리고 디메틸아닐린계 아조 염료와 비교해서 나일론 6.6 섬유상에서 보다 개선된 견뢰도를 나타내었고 이는 염료와 섬유간의 공유 결합으로 기인한 것으로 여겨진다.

## 1. Introduction

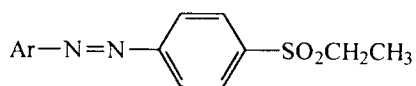
Although disperse dyes can be applied to nylon fibre, owing to their limited build-up and low to moderate fastness properties, the use of these dyes is not popular. Attempts have been made to produce disperse dyes that carried reactive groups and that have the favourable characteristics of both disperse and reactive dyes, namely excellent coverage of substrate irregularities and high wet fastness. In 1958 the Procilyn (ICI) range of reactive disperse dyes were introduced which included chlorohydrin, chlorotriazine or chloroethylaminosulphone reactive groups<sup>1)</sup>; one example of such dyes is CI Reactive Blue 6 (1).



(1)



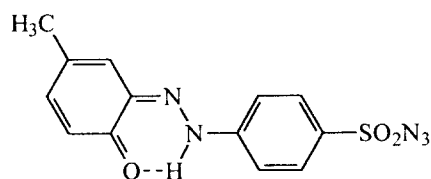
(2)



(3)

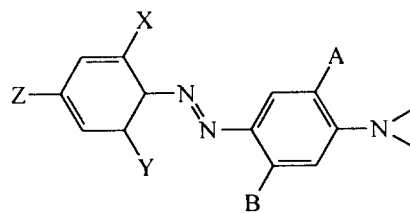
In a study of the dyeing properties of monoazo reactive disperse dyes of general structure(2) on nylon 6.6 fabric, Lo<sup>2)</sup> found that dye exhaustion increased with increasing pH of application in the range pH 5-10 and maximum dye fixation occurred at pH 8. Burkinshaw and Collins<sup>3)</sup> examining the dyeing properties of three reactive disperse dyes

of structure (2) and one monoazo disperse dye of structure (3) on nylon 6.6. These three dyes were shown to exhibit excellent wash fastness on both conventional and microfibre nylon 6.6 at 1/1 standard depth. Dohmyou<sup>5)</sup> demonstrated that sulphonazide disperse dyes(48) were covalently bound to nylon 6.



(4)

Monoazo disperse dyes that contained an aziridinyl terminal group<sup>6, 7)</sup> of general formula (5) were found to yield dyeings of higher wash fastness than conventional disperse dyes of similar structure and Mr on nylon 6.6.



(5)

This type of dye(5) is the subject of the work reported in this paper and was discussed in detail as below.

## 2. Experimental

### 2.1 Dye application

#### 2.1.1 Experimental materials

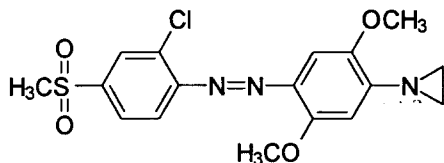
##### 2.1.1.1 Nylon 6.6 fabrics

Commercially available, scoured knitted conventional (78f20, 3.9 dtex<sup>p</sup>; 230.5 g/m<sup>2</sup>) fabrics were used.

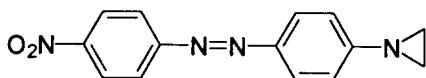
## 2.1.1.2 Dyes

The aziridiny dyes synthesis (A-1, C-1 and D-1) that were used throughout the study were described in previous work<sup>6)</sup> the 2-hydroxyethylaniline azo dyes (A-2, C-2 and D-2) and the N,N-dimethylaniline azo dye synthesis (B-4) were described in my previous work<sup>8)</sup>.

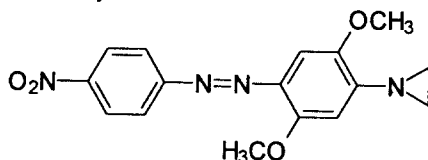
- 2-chloro-4-methanesulphonylaniline 1-(2,5-dimethoxyphenyl)aziridine (Dye A-1)



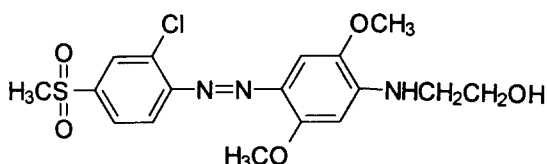
- 4-nitroaniline → 1-phenylaziridine (Dye C-1)



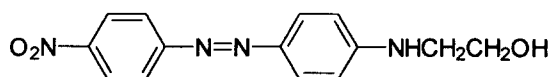
- 4-nitroaniline → 1-(2,5-dimethoxyphenyl)aziridine (Dye D-1)



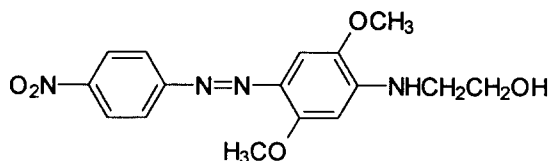
- 2-chloro-4-methanesulphonylaniline → 2,5-dimethoxy-N-β-hydroxyethylaniline (Dye A-2)



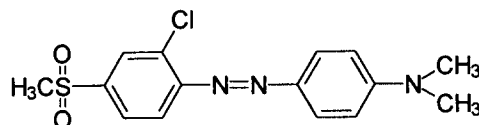
- 4-nitroaniline → N-β-hydroxyethylaniline (Dye C-2)



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



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

2.1.2 Determination of  $\epsilon_{\max}$  values

The  $\epsilon_{\max}$  values of dyes was determined using a Perkin-Elmer Lambda 15 UV/VIS Spectrophotometer.  $1 \times 10^{-1}$  mole of dye was dissolved in 100 ml of acetone with stirring to prepare stock dye solution and an aliquot (20 ml) of stock dye solution was pipetted into another 100 ml of acetone. The dilution of dye was repeated until absorbance of dye-acetone solution was obtained at close to 1 unit value of optical density.  $\epsilon_{\max}$  value was calculated<sup>9)</sup> as follows.

$$A = \epsilon cl$$

where A = absorbance

$\epsilon$  = molar extinction coefficient

c = the concentration of solute (mol./litre)

l = path length through the sample (cm)

When the width of cell, namely, path length through the sample is 1cm and absorbance was observed at  $\lambda_{\max}$ , the molar extinction coefficient ( $\epsilon_{\max}$ ) was obtained from following equation.

$$\epsilon_{\max} = Ac^{-1} \cdot \text{lmol}^{-1}\text{cm}^{-1}$$

## 2.1.2.1 Chemicals and auxiliaries

Commercial samples of Ufoxane 2 (YCL ; UK), 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 labora-

tory 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.

### 2.1.3 Preparation of dye samples

1.0g of dye, 2.0g of dispersing agent (Ufoxane 2) and 100cm<sup>3</sup> of distilled water were placed in a 250cm<sup>3</sup> 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 micro and conventional decitex polyester fabrics and micro and conventional decitex nylon 6.6 fabrics as described in sections 2.1.4 and 2.1.7.

### 2.1.4 Dyeing

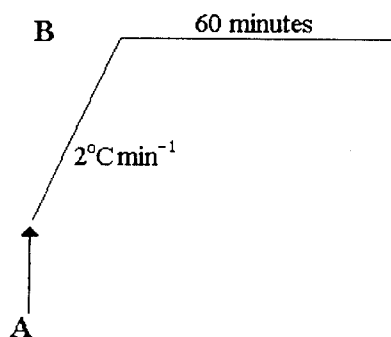


Fig. 1 Dyeing method

A : Fabric (2g) added and dyeing begins at 40°C, B : 98°C for 60 minutes

Dyeing was carried out in sealed, stainless steel dyepots of 200cm<sup>3</sup> 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; 1g l<sup>-1</sup>)

were added to make the volume up to 60cm<sup>3</sup>.

#### 2.1.4.1 Effect of dyeing temperature

Dyeings were carried out using the equipment as described in section 2.1.4. A dye pot was taken out of the dyeing machine after 5 minutes (50°C), 15 minutes (70°C), 20 minutes (80°C), 25 minutes (90°C), 29 minutes (98°C), 39 minutes (98°C), 49 minutes (98°C), 59 minutes (98°C), 69 minutes (98°C), 79 minutes (98°C) and 89 minutes (98°C) from the beginning of the dyeing procedure. The dyed fabrics were rinsed in cold tap water and dried in the open air. The colour strength (K/S) of each dry, dyed fabric was measured as described in section 2.1.8.

#### 2.1.4.2 Dye build-up

Various dyeings (Table 1) using aziridinyl 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 98½ for nylon fabrics in the presence of 1g l<sup>-1</sup> Ufoxane 2 as described in section 2.1.4. 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 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.

#### 2.1.4.3 Effect of pH on build-up

Nylon 6.6 conventional fabrics were dyed (1.0% omf) with the aziridinyl dyes A-1, C-1 and D-1,

Table 1. % omf dye applied to nylon 6.6 fabric

Dye	pH	Nylon 6.6 fabric	
		Conventional decitex	Microfibre
A-1	5.0	0.7, 1.5, 2.0, 2.5%	0.5, 1.0, 1.5, 2.0%
	6.0	0.5, 0.7, 1.0, 1.5, 2.0, 2.5%	—
	8.0	0.5, 0.7, 1.0, 1.3, 1.5, 2.0, 2.5%	0.5, 1.0, 1.5, 2.0%
	10.0	0.5, 0.7, 1.0, 1.3, 1.5, 2.0, 2.5%	0.5, 1.0, 1.5, 2.0%
A-2	5.0	—	0.5, 1.0, 1.5, 2.0%
	6.0	0.5, 1.0, 1.5, 2.0%	—
B-4	5.0	0.5, 0.7, 1.0, 1.5, 2.0%	0.5, 1.0, 1.5, 2.0%
C-1	5.0	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	5.0	0.5, 0.7, 1.0, 1.5, 2.0%	0.5, 1.0, 1.5, 2.0%
D-1	5.0	0.3, 0.5, 0.7, 1.0, 1.3, 1.5%	0.5, 1.0, 1.5, 2.0%
	8.0	0.5, 0.7, 1.0, 1.5, 1.8%	0.5, 1.0, 1.5, 2.0%
	10.0	0.5, 0.7, 1.0, 1.5, 1.8%	0.5, 1.0, 1.5, 2.0%
D-2	5.0	0.3, 0.5, 0.7, 1.0, 1.3, 1.5%	0.5, 1.0, 1.5, 2.0%

the hydrolysed dye A-2 and the N,N-dimethylaniline dye B-4 at pH values of 4 to 12. The dyed nylon 6.6 (2.0 % omf) was rinsed in cold tap water and allowed to dry in the open air. The colour strength of the dyeings was determined as described in section 2.1.8.

#### 2.1.4.3.1 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 (0.026 M) in 1 litre of distilled water. A buffer solution of pH 6 and 6.5 was obtained by dissolution of acetic acid (0.02 M) and sodium acetate (0.17 M) in 1 litre of distilled water; the final pH value was secured by the addition of either 0.1M of acetic acid solution or 0.1M of sodium acetate solution.

#### 2.1.4.3.2 Basic dye bath

Buffer solutions of pH 7, 8, 9 and 10 were obtained by the dissolution of disodium hydrogenphosphate (5g) and potassium dihydrogenphosphate (1g) in 1 litre of distilled water; the approp-

riate pH value was secured by the addition of either 0.1 M aqueous hydrochloric acid or 0.1 M 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 1.0 M/0.1 M aqueous sodium hydroxide solution or 0.1 M aqueous hydrochloric acid to the mixed phosphate buffer solution.

#### 2.1.4.3.3 Dye extraction using DMF

A sample (1.0g) of dyed nylon 6.6 fabric which had been dyed with dye A-1 (1.0% omf; at pH 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and also 12) was extracted using 80cm<sup>3</sup> of DMF at 100°C for 1 hour in a 100cm<sup>3</sup> 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 sec-

tion 2.1.8.

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

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

#### 2.1.4.4 Dyeing of nylon 6.6 fabrics of different amino end group (AEG) content

##### 2.1.4.4.1 Fabric preparation

Nylon 6.6 fabrics (1.0 g) of AEG content 45, 50, 60 and 70 g equiv.g $\times 10^{-6}$  were scoured by subjecting them to the following routine<sup>10)</sup>

- rinse in cold distilled water.
- scour in a solution (distilled water) comprising 1gl<sup>-1</sup> anionic surface-active agent (Sandozin NIE) and 2gl<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> for 30 minutes at 70°C.
- neutralise by treating in a solution of acetic acid (1cm<sup>3</sup>l<sup>-1</sup> glacial) for 10 minutes at room temperature.
- rinse in cold distilled water.
- dry in the open air.

##### 2.1.4.4.2 Dyeing procedure

The dyeing of nylon 6.6 fabrics of various AEG content was carried out under the following conditions :

- 1.0% omf of dye A-1, C-1 or B-4
- pH 8.0
- 1gl<sup>-1</sup> dispersing agent (Ufoxane 2)
- dyeing procedure described in 2.1.4.
- liquor ratio 30 : 1
- rinse in cold distilled water and dry in the open air

The K/S values of the dyed nylon fabrics were measured as described in section 2.1.8.

#### 2.1.4.5 Dyeing nylon 6.6 fabrics using ammonia

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

dyeing at 98C for 1 hour

pH 10 adjusted using NH<sub>4</sub>OH

0.5, 1.0, 1.5, 2.0% omf of dye A-1 (dyeing was repeated to achieve the 1/1 standard depth)

1gl<sup>-1</sup> dispersing agent (Ufoxane 2)

liquor ratio 30 : 1

dyeing procedure was as described in section 2.1.4.

#### 2.1.5 Maximum absorbance ( $\lambda_{max}$ ) of residual dyebaths

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

2cm<sup>3</sup> of dye A-1 stock solution (10 gl<sup>-1</sup>) which was prepared as described in section 2.1.3.

1gl<sup>-1</sup> of dispersing agent (Ufoxane 2)

dyeing procedure described in Fig. 1.

water was added to make the volume up to 60cm<sup>3</sup> pH 5.5

At each sampling position (A to L in Fig. 2), during nylon 6.6 dyeing (pH 5.5), 1cm<sup>3</sup> of the residual dye-bath was pipetted from the dyepot into two, 50cm<sup>3</sup> beakers. DMF was poured into one beaker and ethanol was poured into the other to make a dye aliquot : solvent ratio of 1 : 3. The wavelength of maximum absorbance ( $\lambda_{max}$ ) of the residual dye-bath in both the dyebath-DMF (1 : 3) and dye-bath-ethanol (1 : 3) systems was determined using a Perkin-Elmer Lambda 15 UV/VIS Spectrophotometer.

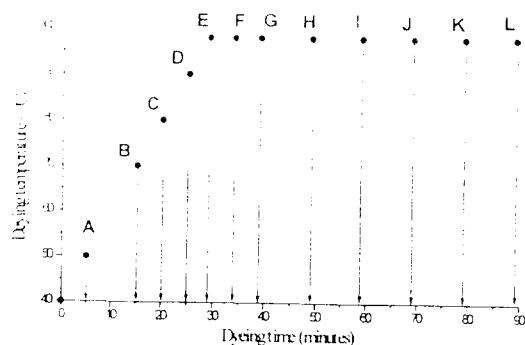


Fig. 2 Sampling positions for  $\lambda_{max}$  analysis during nylon 6.6 dyeing

### 2.1.6 Evaluation of hydrolysis during dyeing

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

2cm<sup>3</sup> of a 10 gl<sup>-1</sup> dye A-1 stock solution was prepared as described in section 2.1.3.

1gl<sup>-1</sup> of dispersing agent (Ufoxane 2)

dyeing procedure described in Fig. 1

water added to make the volume up to 60cm<sup>3</sup>

pH 5.5

Analysis was carried out using a Varian Series 5000 liquid chromatograph equipped with an Apex C18 reverse-phase column using a flow rate of 1.0cm<sup>3</sup> min<sup>-1</sup> 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 20cm<sup>3</sup> portion of the dyebath of dye A-1 and A-2 before dyeing was pipetted into a separating funnel and extracted using 20cm<sup>3</sup> 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 20cm<sup>3</sup> portion of the dyebath of dye A-1 at each sampling position during 'blank' dyeing (Fig. 3) was pipetted into a separating funnel and extracted using 20cm<sup>3</sup> 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 (Fig. 3) was analysed and the percentage area of the resulting peaks for both the aziridinyll and the hydrolysed forms of the dyes were calculated.

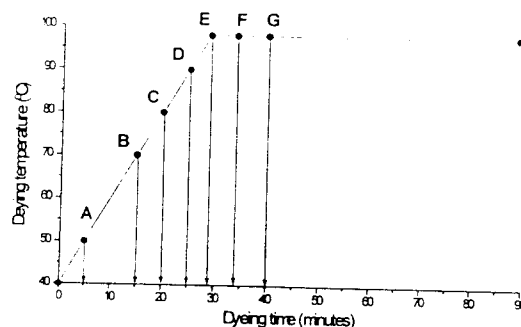


Fig. 3 Sampling positions for HPLC analysis during nylon 6.6 dyeing

In the case of nylon 6.6 dyeing at pH 5.5 (1.0% omf), analysis was carried out of the aziridinyll dye A-1 and the hydrolysed dye A-2 after 5 minutes (50°C ; position A in Fig. 3), 15 minutes (70 °C ; position B), 20 minutes (80°C ; position C), 25 minutes (90°C ; position D), 29 minutes (98 °C ; position E), 34 minutes (98°C ; position F) and 40 minutes (98°C ; position G) from the beginning of dyeing.

### 2.1.7 Standard depth dyeings

Commercially available, scoured, knitted conventional decitex 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 98°C in the presence of 1 gl<sup>-1</sup> Ufoxane 2 at pH 6, 8 and 10 as described in section 2.1.4. At the end of dyeing, 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 nylon 6.6 fabrics was visually compared with the appropriately coloured Society of Dyers and Colourists' matt standard depth shades<sup>11)</sup> in an ICS/Texicon (ICS, UK) viewing cabinet under illuminant D<sub>65</sub>. Dyeings were repeated to achieve a 1/1 standard depth of shade for each of the dye samples on nylon 6.6 fabrics. Some of dyeings which could not be obtained at 1/1 standard depth of shade were examined at 1/6 standard depth.

### 2.1.8 Colour measurement

The reflectance values of the dry, dyed nylon 6.6 fabrics as well as the DMF-extracted dyed nylon 6.6 fabrics were measured using an ICS Micro-match 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<sup>12)</sup> 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.

### 2.1.9 Fastness properties of the dyed samples

#### 2.1.9.1 Wash fastness assessment

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)<sup>13)</sup>

#### 2.1.9.2 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 Application to nylon 6.6 fabric

#### 3.1.1. The $\lambda_{\max}$ of dyed conventional decitex nylon 6.6 fabric

In this study of the dyeing properties of aziridinyl dyes on conventional decitex nylon 6.6 fabric, the colour strength (K/S) of conventional deci-

Table 2.  $\lambda_{\max}$  of dyed conventional decitex nylon 6.6 fabric

Dye	pH	$\lambda_{\max}$ of dyed nylon conventional fabrics		$\lambda_{\max}$ in acetone	
		$\lambda_{\max}$	$\Delta\lambda$	$\lambda_{\max}$	$\Delta\lambda$
A-1	6.0	520	0	448.4	45.6
	8.0	520			
	10.0	520			
A-2	5.0	520		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	540	0	455.2	43.2
	8.0	540			
	10.0	540			
D-2	5.0	540		498.4	



tex nylon 6.6 fabric which had been dyed with both aziridinyl and hydrolysed dyes was measured at the  $\lambda_{\max}$  of the dyeings as described in section 2.1.8 and a comparison was made between the aziridinyl dyes and their hydrolysed counterparts in terms of  $\lambda_{\max}$  of dyeings (Table 2).

In the case of the two pairs of dyes A-1/A-2 and D-1/D-2, there was no difference in  $\lambda_{\max}$  between the aziridinyl dye and its hydrolysed counterpart, although the  $\lambda_{\max}$  of the dyes in acetone for each pair differed. For the C-1/C-2 pair of dyes, a 20 nm difference in max was obtained in the case of dyed conventional decitex nylon 6.6 fabrics, although the difference in  $\lambda_{\max}$  between dye C-1 and C-2 in acetone was 68.4 nm (Table 2).

### 3.1.2 The hydrolysis of aziridinyl dye during dyeing

Although the dyeing temperature used for the nylon 6.6 fabric in this work (98°C) was not as high as that employed in polyester dyeing (130°C), hydrolysis of the aziridinyl dyes (aziridinyl ring opening in water) was observed during nylon 6.6 dyeing as observed during polyester dyeing<sup>8)</sup>. The extent of its hydrolysis of the aziridinyl dye was determined by examining the max variation of the residual dye baths and using HPLC analysis as described in sections 2.1.5 and 2.1.6, respectively.

Examination of the max shift of the residual dye baths of the aziridinyl dye A-1 at pH 5.5 during nylon 6.6 dyeing, in the absence of nylon 6.6 fabric, was carried out as described in section 2.1.5. A blank dyeing was performed in which a dyeing was carried out in the absence of nylon 6.6 fabric; also, the  $\lambda_{\max}$  of the residual dye bath during dyeing was investigated as described in section 2.1.5.

Analysis of the extent of dye hydrolysis using HPLC was carried out during dyeing in the absence of nylon fabric as described in section 2.1.6. In this study, dye was extracted from the residual dye baths using dichloromethane as discussed in section 2.1.6. After the dye had been extracted, dichloromethane was removed using rotary evaporation under vacuum and the dry dye then dissol-

ved in a 50 : 50 acetonitrile : water mixture.

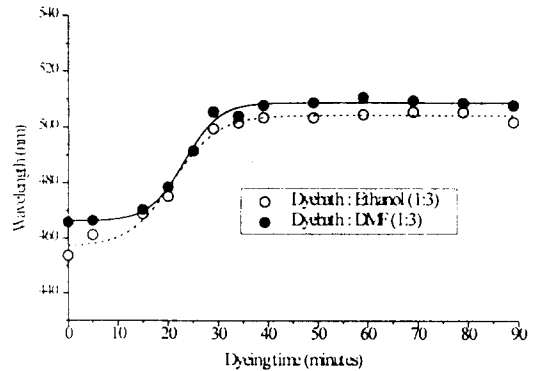


Fig. 4 The variation in  $\lambda_{\max}$  of the residual dye bath of dye A-1 during dyeing in the absence of nylon 6.6 fabric at pH 5.5

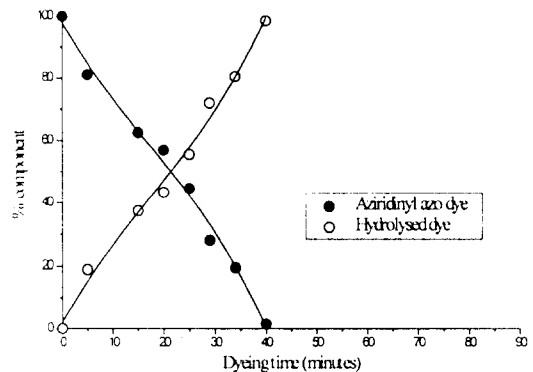


Fig. 5 The extent of hydrolysis of aziridinyl dye A-1 during nylon dyeing at pH 5.5

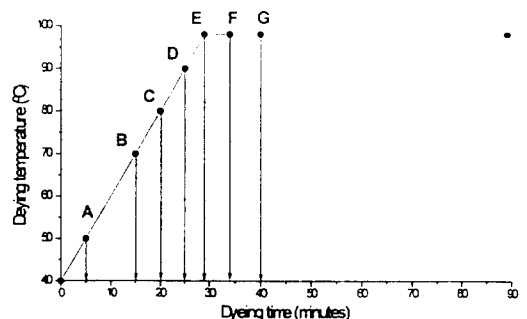


Fig. 6 Sampling positions for HPLC analysis during nylon 6.6 dyeing

Fig. 5 shows that hydrolysis of dye A-1 occurred from the beginning of dyeing at pH 5.5, and was complete after 39 minutes of dyeing (position F in Fig. 6).

Fig. 4 shows the variation in max of the residual dyebath (dye A-1 using DMF or ethanol) during dyeing in the absence of nylon 6.6 fabric with dye A-1 at pH 5.5. The  $\lambda_{\max}$  of dye A-1 increased from 465.8 nm to 505.4 nm; this being similar to the  $\lambda_{\max}$  of dye A-2 in DMF (Fig. 4), after 29 minutes dyeing when the dyeing temperature was increasing to 98°C. When ethanol was employed as co-solvent for the dye, the max of dye A-1 increased from 453.6 nm to 499.4 nm, this being similar to max of dye A-2 after 29 minutes from the start of dyeing, when the dyeing temperature was increasing to 98°C; this particular finding agrees with that secured when DMF had been used as co-solvent for the dye. This investigation of the variation in max of the aziridine dye A-1 during dyeing in the absence of nylon 6.6 fabric (Fig. 4) clearly demonstrated that ring-opening (hydrolysis) of the aziridinyl dye started from the beginning of dyeing at pH 5.5.

### 3.1.3 Dye build-up

The dyeing of conventional decitex nylon 6.6 fabric with dye A-1 at pH 5, 6, 8 and 10 as well as the dyeing with dye A-2 at pH 6 was carried out as described in section 2.1.4.2. In the case of dye C-1 and D-1, dyeing was carried out at pH 5, 8 and 10. Also, in the case of dye C-2 and D-2, dyeing was carried out at pH 5. The dyed fabrics were rinsed in cold tap water, dried in the open air and the colour strength measured as described in section 2.1.8.

It is well known that conventional disperse dyes exhibit poor to moderate build-up on nylon fibres, this being attributable to the ionic, and relatively hydrophilic nature of the substrate.

Fig. 7 shows the build-up of dyes A-1, A-2

and B-4 on conventional decitex nylon 6.6 fabric when applied at pH 6.0.

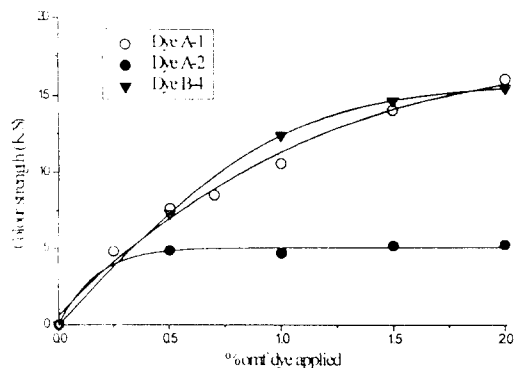


Fig. 7 Build-up of dyes A-1, A-2 and B-4 on conventional decitex nylon 6.6 fabric at pH 6.0

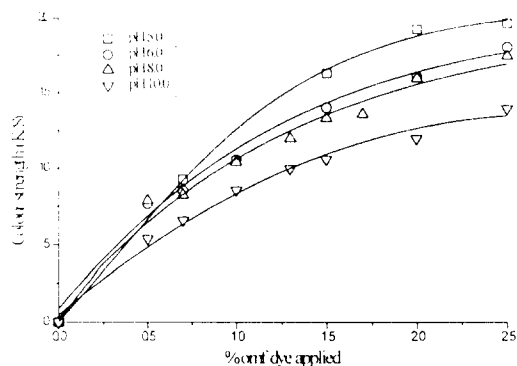


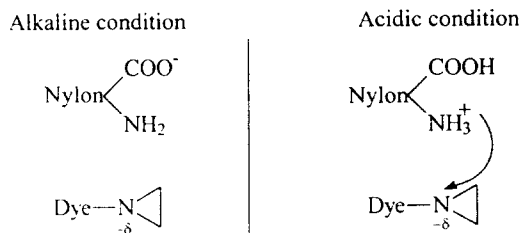
Fig. 8 Build-up of dye A-1 on conventional decitex nylon 6.6 fabric at various pH

When the concentration of dye was increased to 0.5%, build-up of dye A-2 reached a constant value (Fig. 7) which may be due to the substantivity of dye A-2 towards nylon 6.6 fibre being low. Fig. 7 also reveals that dyes A-1 and B-4 exhibited good build-up at pH 6.0, this being greater than that of dye A-2; also, the shape of the build-up curves of dyes A-1 and B-4 were similar. Furthermore, Fig. 7 clearly implies, from the gradients of the curves obtained, that dye build-up would continue to increase with further increase in con-

centration of dyes A-1 and B-4 applied at pH 6.0.

Fig. 8 shows the build-up of dye A-1, when applied at pH 5, 6, 8 and 10 decreased with increasing pH of application. This finding may be due to the characteristics of nylon 6.6 which has two kinds of ionic dye-site<sup>14)</sup>, namely anionic carboxylic groups and cationic amino groups. Thus, the charge on the nylon fibre surface changes changing depending on the pH of dyebath. In the case of the dyeing of nylon fibre with the aziridinyl dye under alkaline conditions, the substantivity of the dye, which contains a nucleophilic amino group, towards the negatively charged nylon 6.6 fibre surface could be low (Fig. 9).

Fig. 10 illustrates the build-up of the aziridinyl dye C-1 and the 2-hydroxyethyl dye C-2. Clearly, the build-up of dye C-2 on conventional decitex nylon fibre was much higher than that of dye C-1; this finding may be attributable to the substantivity of dye C-2 towards nylon being higher than that of dye C-1 as well as the marked hydrophobic character of C-1 which may have resulted in poor dispersion of dye being achieved. Also, the low tinctorial strength of dye C-1 may have contributed to the findings displayed in Fig. 10.



Aziridinyl dye contains nucleophilic amine

Fig. 9 Possible interactions between nylon and aziridinyl dye

In the case of dye C-1, build up decreased with increasing pH (Fig. 11). A comparison was made of the build-up on conventional decitex nylon 6.6 fabrics of dyes D-1 and D-2 at pH 5 (Fig. 12). Fig. 12 reveals that the poor build-up characteristic of aziridinyl dye D-1 was lower than that of the hydrolysed dye, D-2; This may be due to the substantivity of dye D-2 towards nylon fibre being

higher than that of D-1.

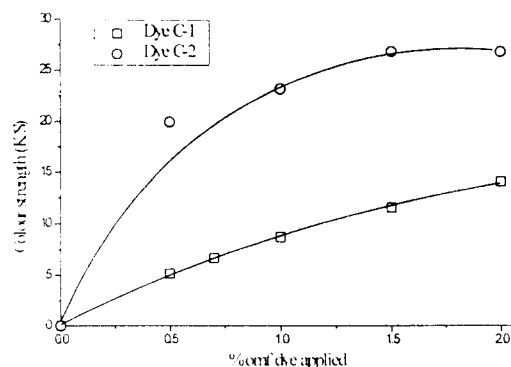


Fig. 10 Build-up of dyes C-1 and C-2 on conventional decitex nylon 6.6 fabric at pH 5.0

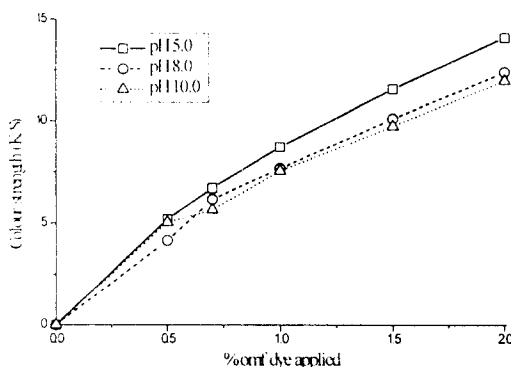


Fig. 11 Build-up of dye C-1 on conventional decitex nylon 6.6 fabric at pH 5, 8, and 10

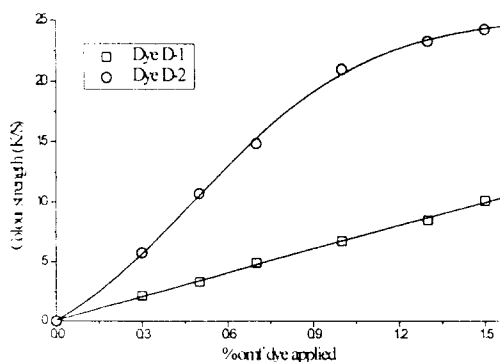


Fig. 12 Build-up of dyes D-1 and D-2 on conventional decitex nylon 6.6 fabric at pH 5.0

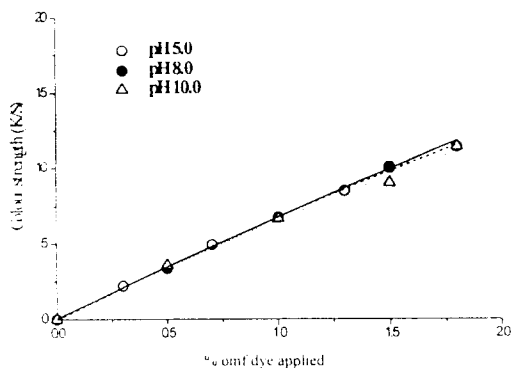


Fig. 13 Build-up of dye D-1 on conventional decitex nylon 6.6 fabric at various pH

Fig. 13 shows the build-up of the aziridiny dye D-1, when applied at pH 6, 8 and 10 from which it is evident that dye build-up on conventional decitex nylon 6.6 fibre decreased slightly with increasing pH of application.

#### 3.1.4 Effect of pH

Investigation of pH effect on colour strength of conventional decitex nylon 6.6 fabric which had been dyed with dye A-1, A-2, B-4, C-1 and D-1 was carried out as described in section 2.1.4.3. Dyed conventional decitex nylon 6.6 fabrics were rinsed in cold tap water and allowed to dry in the open air. The effect of pH on the colour strength of fabric dyed with the aziridiny dyes, the 2-hydroxyethylaniline dye and the N,N'-dimethylaniline dye are given in Fig. 14 to Fig. 16.

In the case of the conventional disperse dye (B-4) and the 2-hydroxyethyl-aniline dye (A-2), the colour strength achieved was independent of pH as shown in Fig. 14. In contrast, the colour strength of dye A-1 on conventional decitex nylon 6.6 fabrics (Fig. 15) was affected by pH; in the case of dyeings carried out at pH values lower than 5, the colour strength of the nylon was low and the hue and chroma of the dyeings changed significantly at pH values of 2 to 5.

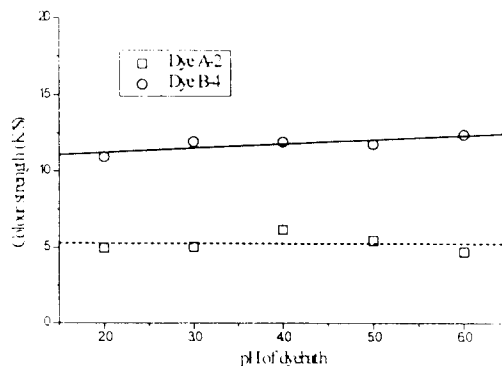


Fig. 14 Effect of pH on the colour strength of conventional decitex nylon 6.6 fabric which had been dyed with dye A-2 and B-4 (1.0% omf)

Table. 3 The effect of pH on shade, hue and chroma of conventional decitex nylon 6.6 fabric which had been dyed with dye A-1 (at pH values of 2.0 to 5.0, 2.0 % omf dye applied)<sup>1</sup>

pH of dyebath	L*	a*	b*	c*	h°
2.0	62.9	29.87	26.18	39.72	41.23
3.0	48.53	50.15	16.77	52.88	18.49
4.0	40.68	54.23	17.61	57.02	17.99
5.0	39.24	55.37	17.94	58.20	17.95

<sup>1</sup>Under illuminant D<sub>65</sub> 10° standard observer.

At pH 5.0, maximum colour strength on conventional decitex nylon 6.6 fabric was achieved (Fig. 15); however, the aziridiny dye is very susceptible to hydrolysis at pH 5. At pH values of 5 to 12, the colour strength of dyeings of A-1 decreased with increasing pH (Fig. 15).

When the effect of pH on the colour strength of the three aziridiny dyes A-1, C-1 and D-1 on conventional decitex nylon 6.6 is considered, the reduction in colour strength that accompanied an increase in pH was most marked in the case of dye A-1. This finding may be due to A-1 (IOR

value 0.691) being more hydrophilic than the two other dyes (IOR value of C-1 : 0.571, IOR value of D-1 : 0.615)<sup>8)</sup>.

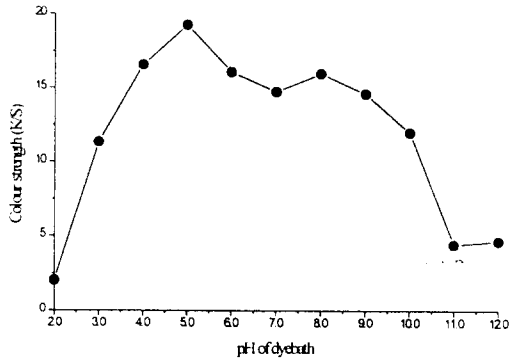


Fig. 15 Effect of pH on the colour strength of conventional decitex nylon 6.6 fabric dyed with dye A-1 (2.0% omf)

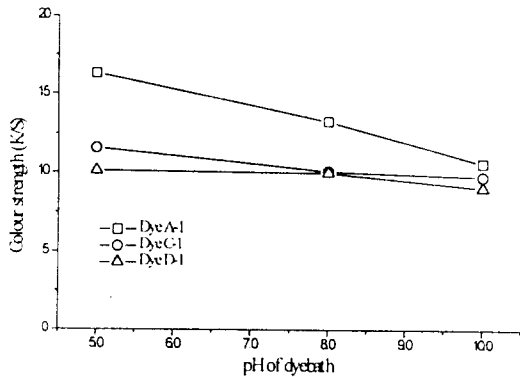


Fig. 16 Effect of pH on the colour strength of conventional decitex nylon 6.6 fabric dyed with the three aziridinyl dyes A-1, C-1 and D-1 at 1.5 % omf

### 3.1.5 Solvent extraction

Conventional decitex nylon 6.6 fabric, which had been dyed with the aziridinyl dye A-1 at pH 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12, was extracted using DMF under reflux at 100C for 1 hour as

described in section 2.1.4.3.3.

A comparison was made of the colour strength of the nylon fabric that had been dyed with A-1 at various pH values before and after DMF extraction (Fig. 17). The extent of dye that was stripped from the dyed fabric was calculated as described in section 2.5.3.3.3 (Fig. 18).

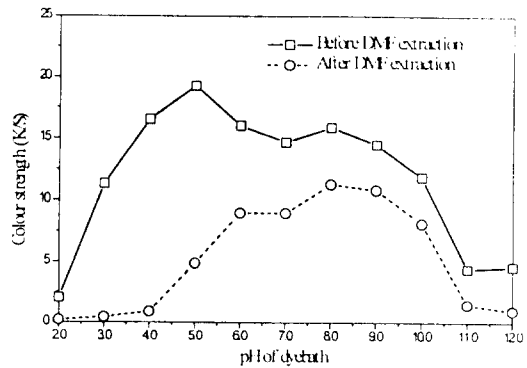


Fig. 17 Comparison of the colour strength of conventional decitex nylon 6.6 fabric which had been dyed with 2.0 % omf A-1 at various pH values before and after DMF extraction

Fig. 17 shows the maximum colour strength of the solvent extracted dyeings which had been dyed with A-1 was obtained at pH values of 8 to 9, whereas the maximum colour strength of dyeings before DMF extraction was obtained at pH 5. These findings imply that dye-fibre fixation was favoured at pH values of 8 to 9. Thus, these results show that dyeing with the aziridinyl dye A-1 under alkaline condition (pH 8 to 9) is suitable for the dyeing of nylon 6.6 conventional decitex fibre in pale to medium depths to excellent fastness standards.

Table 4 shows the nature of both the polyamide and the aziridinyl dye A-1 under different pH values. It can be considered that the polyamide is negatively charged at pH higher than 9 and the aziridinyl dye, which contains the nucleophilic aziridinium ion, is stable. Thus, it can be postulat-

Table 4. The nature of nylon 6.6 and hydrolysis of aziridinyl dyes

pH of dyebath	nature of nylon 6.6	Aziridinyl dye
Strongly acidic conditions (<2)	$^+H_3N$ —(CH <sub>2</sub> ) <sub>6</sub> —NH—CO—(CH <sub>2</sub> ) <sub>4</sub> —COOH	Completely hydrolysed
Weakly acidic and neutral conditions (3–7)	$^+H_3N$ —(CH <sub>2</sub> ) <sub>6</sub> —NH—CO—(CH <sub>2</sub> ) <sub>4</sub> —COO <sup>-</sup>	Partially hydrolysed
Alkaline conditions (>9)	H <sub>2</sub> N—(CH <sub>2</sub> ) <sub>6</sub> —NH—CO—(CH <sub>2</sub> ) <sub>4</sub> —COO <sup>-</sup>	Stable

ed that the extent of the adsorption and dye-fibre fixation decreases with increasing pH above 9 due to the low substantivity of the aziridinyl dye towards the fibre under such alkaline conditions (Fig. 17).

The extent of dye that was stripped from the dyed fabric was calculated as described in section 2.1.4.3.3 DMF extraction of the dye from dyed conventional decitex nylon 6.6 fabric demonstrated that minimum dye stripping was achieved when the dye had been applied at pH values of 8 to 10 (Fig. 18). Thus, maximum dye-fibre fixation and excellent wet fastness properties are expected in this pH range. This finding concurs with that of other workers who observed that maximum fixation of reactive disperse dyes on nylon occurred at pH 8<sup>15), 16), 17)</sup>.

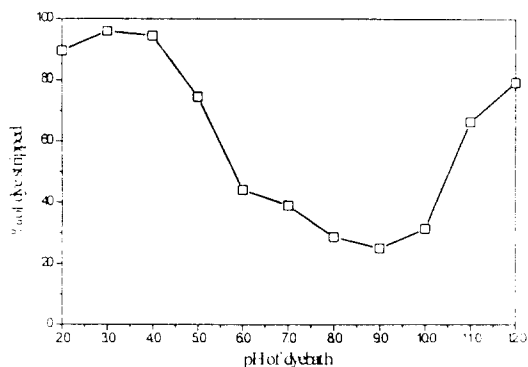


Fig. 18 The extent of dye stripped from conventional decitex nylon 6.6 fabric which had been dyed with A-1 at various pH values

### 3.1.6 Effect of amino end group

In the polymerisation process of polyamide, a small amount of a monocarboxylic acid (commonly acetic acid) is added in order to control the molecular mass of the polymer, thus nylon fibre contains terminal carboxylic acid groups together with a small number of terminal amino groups. The presence of these end groups has a very important effect on the dyeing of the fibre with acid dyes<sup>18)</sup> and, generally, the rate of dyeing and equilibrium uptake of acid dyes increases with increasing amino end group content<sup>19)</sup>. Peters<sup>20)</sup> showed that the uptake of certain anionic dyes exhibited a stoichiometric relationship to the amino end group content of nylon fibres. In the case of non ionic disperse dyes, however, dye uptake on nylon fibre is not influenced by amino end group (AEG) content since the dyeing mechanism involved can be assumed as being one of solid solution as with other hydrophobic fibres<sup>21)</sup>. Thus, because variation of the AEG content of nylon fibre does not affect the uptake of disperse dyes, if the adsorption mechanism of aziridinyl dyes on nylon fibre is assumed to be the same as an ionic dye, then uptake of the dyes will be affected by the AEG content of the fibre. In contrast, if uptake of the aziridinyl dye is unaffected by AEG variation then the mechanism of a adsorption of the dye can be assumed to mirror that of a disperse dye.

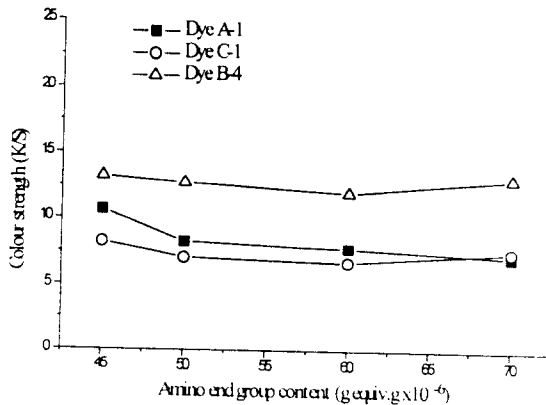


Fig. 19 Effect of amino end group on the colour strength of dyed conventional decitex nylon 6.6 fabric (pH 8 ; 1.0 % omf)

The investigation of the effect of AEG on the colour strength of conventional decitex nylon 6.6 fabrics which had been dyed with the conventional disperse dye B-4 and the aziridiny dyes A-1 and C-1, was carried out as described in section 2.1.4.4. The fabrics which had been dyed with A-1, B-4 and C-1 were rinsed in cold tap water and dried in the open air.

1.0 % omf of aziridiny azo dyes A-1, C-1 and the N,N'-dimethylaniline azo dye (B-4) were applied to conventional decitex nylon 6.6 fabrics of 45, 50, 60 and 70 g equiv.g<sup>6</sup> AEG at pH 8, since these conditions had been shown (Fig. 19) to result in optimum dye-fibre fixation as described in section 2.1.4.4.

Clearly, none of the three dyes used were affected by AEG variation (Fig. 19). Therefore, the adsorption mechanism of the aziridiny dyes on

nylon fibre can be proposed as being that of conventional non ionic disperse dyes. Thus, this finding supports the fact that the observed decrease in colour strength that accompanied an increase in pH of application (sections 3.1.3. and 3.1.4) was not due to the dyeing behaviour of the aziridiny dye but due to the ionic nature of the nylon fibre.

### 3.1.7 Standard depth dyeing

Standard depth dyeings were obtained in order to carry out the wash and light fastness testing of conventional decitex nylon 6.6 fabric that had been dyed with the aziridiny dyes A-1, C-1 and D-1, the 2-hydroxyethylaniline dyes A-2, C-2 and D-2 and the N,N-dimethylaniline dye B-4. The dye concentrations required to achieve standard depths on conventional decitex nylon 6.6 fabrics are given in Table 5.

At pH values of 5 to 10, as the build-up of the aziridiny dyes decreased with increasing pH of dyeings as mentioned before, it follows that the amount of the aziridiny dyes required to obtain the standard depth on conventional decitex nylon 6.6 fabric should have increased as the pH of dyeing was increased, as indeed was observed (Table 5). Owing to the poor build-up of the dye A-2 it was possible to achieve only a 1/6 standard depth dyeing on conventional decitex nylon 6.6 fabric rather than a 1/1 standard depth.

### 3.1.8 Wash fastness assessment

The wash fastness of standard depth dyeings on nylon 6.6 (section 3.1.7) was carried out according to the ISOC06/C2 (60°C, 30 minutes) and

Table 5. Dye concentration (% omf) required to give standard depth dyeings on conventional decitex nylon 6.6 fabric

Dye	A-1				A-2	C-1	C-2			D-1	D-2			
pH	5.0	7.0	8.0	10.0	5.0	5.0	5.0	8.0	10.0	5.0	5.0	8.0	10.0	5.0
Concentration required (%)	1.3	1.7	1.8	1.9	0.4	0.4	0.3	0.4	0.45	0.3	1.5	1.55	1.6	0.4
	(1/1)	(1/1)	(1/1)	(1/1)	(1/6)	(1/1)	(1/1)	(1/1)	(1/1)	(1/1)	(1/1)	(1/1)	(1/1)	(1/1)

ISOC06/C4 (95°C, 30 minutes) test methods as described in section 2.1.9.1.

As previously mentioned, owing to the poor build-up of dye A-2, it was possible only to achieve a 1/6 standard depth dyeing of conventional decitex nylon 6.6 fabric rather than the 1/1 standard depth. Thus, the difference in wash-fastness observed between dyes A-1 and A-2 is very marked in the case of colour change 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 1/6 standard depths shown in Table 6 and Table 7

Table 6 also demonstrates that the wash fastness of the N,N'-dimethylaniline azo dye (B-4) was similar to that of A-1 which had been applied at pH 10. However, slightly higher wash fastness was found for the aziridinyl dyes C-1 and D-1 over the hydrolysed dyes C-2 and D-2.

The wash fastness of the aziridinyl dyes was expected to be highest at pH 8; however, this was not observed using the ISOC06/C2 test method. Table 6 shows that the wash fastness of A-1, when dyeing was carried out at pH 8, was slightly higher than that obtained when the dye had been applied at pH 5, 7 and 10 in the case of staining of acetate, cotton and nylon 6.6 adjacent fabrics. The wash fastness of dye C-1 when applied at pH 8 was slightly higher than that achieved, when dyeing had been carried out at pH 5 and 10, in the case of staining of nylon 6.6 adjacent fabric. For D-1, the wash fastness of dyeing at pH 8, in the case of staining of acetate and nylon 6.6, was slightly higher than that of the dyeing at pH 5 and 10. In order to obtain a clearer picture of the fastness of the dyes, a more severe wash test method (ISOC06/C4) was also used as described in section 2.1.9.1.

Table 7 also shows the results of the ISOC06/C4 test method (95°C 30 minutes). In the case of the three aziridinyl dyes A-1, C-1 and D-1, highest

Table 6. Colour fastness to washing (ISOC06/C2) of standard depth dyeings

Dye	pH	Colour depth	Ch	Adj	Ac	Co	Ny	PET	Acry	Wo
A-1	5.0	1/1	4/5	2/3	2	4/5	2	5	5	3/4
	7.0	1/1	4/5	3	2/3	4/5	2/3	5	5	4
	8.0	1/1	4/5	3	3	5	3	5	5	4
	10.0	1/1	4/5	3	2/3	5	3	5	5	4
A-1*	10.0	1/1	4/5	3	2/3	5	3	5	5	4
A-2	5.0	1/6	4/5	3	3	5	3	5	5	4
B-4	5.0	1/1	4/5	3	2/3	4/5	3	4	5	3/4
C-1	5.0	1/1	4	3/4	4	5	3/4	5	5	5
	8.0	1/1	4/5	4	4	5	4	5	5	5
	10.0	1/1	4/5	4	4	5	3/4	5	5	5
C-2	5.0	1/1	3	3	3	4/5	3	5	5	4/5
D-1	5.0	1/1	4/5	3	3	5	3	5	5	4/5
	8.0	1/1	4/5	3/4	3/4	5	3/4	5	5	4/5
	10.0	1/1	4/5	3/4	3	5	3	5	5	4/5
D-2	5.0	1/1	4/5	3	2/3	4/5	3	5	5	4/5

\*Dyeing with ammonia solution



wash fastness was achieved when dyeing had been carried out at pH 8 (Table 7). The difference in wash fastness between dyes A-1 and A-2 is very marked in the case of colour change. 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 1/6 standard depths shown in Table 7.

Table 7 also illustrates that the wash fastness of the N,N'-dimethylaniline azo dye (B-4) was much lower than that of A-1 which had been applied at pH 8 in the case of the colour change and slightly lower in the case of staining of adjacent acetate, polyester and wool fabrics. The wash fastness of the conventional decitex polyester fabric which had been dyed with dyes C-1 at pH 8 was much higher than that of dye C-2 in the context of colour change and staining of adjacent acetate, nylon 6.6 and slightly higher in the case of staining of polyester, acrylic and wool fabric. This find-

ing may supports that the dye C-1 became covalently bound to nylon 6.6 by action of aziridiny group since dye C-1 does not have any substituent in its molecular structure except for the aziridiny ring, whereas dye C-2 has a terminal hydroxyethyl group. Thus, the wash fastness of dyed conventional decitex nylon 6.6 fabric was improved by the presence of aziridiny ring in dye C-1. The wash fastness of the hydrolysed dye D-2 was much lower than that of the aziridiny dye D-1 in terms of change of colour and staining of adjacent acetate, nylon, acryl fabrics ; indeed, the difference in colour change is very clear.

Although variation in application pH did not have a significant effect on wash fastness, some improvement was obtained at pH 8. The dyeings which had been dyed with dye A-1 using ammonia did not give any improvement in wash fastness property (Table 6 and Table 7).

### 3.1.9 Light fastness assessment

The light fastness of conventional decitex nylon 6.6 fabric which had been dyed with the aziridi-

Table 7. Colour fastness to washing (ISOC06/C4) of standard depth dyeings

Dye	pH	Colour depth	Ch	Adj	Ac	Co	Ny	PET	Acry	Wo
A-1	5.0	1/1	3/4	2	1/2	4/5	1/2	4	4	3
	7.0	1/1	3/4	2/3	2	4/5	2	4	4	3/4
	8.0	1/1	4/5	3	2	4/5	2	4	4	3/4
	10.0	1/1	3	2	2	4/5	2	3/4	3/4	3
A-1*	10.0	1/1	3/4	2	2	4/5	2	3/4	3/4	3
A-2	5.0	1/6	2	2/3	2	5	2	5	4/5	3
B-4	5.0	1/1	1	2	1/2	4/5	2	4	4	3
C-1	5.0	1/1	3/4	3/4	4	5	3/4	4/5	4/5	4/5
	8.0	1/1	4	3/4	4	5	3/4	4/5	4/5	4/5
	10.0	1/1	4	3/4	4	5	3	4	4/5	4
C-2	5.0	1/1	1/2	2	2/3	5	1/2	4	4	4
D-1	5.0	1/1	3/4	2	2	4/5	1/2	4	4	3/4
	8.0	1/1	4/5	2/3	2/3	4/5	2	4	4	3/4
	10.0	1/1	3	2/3	2/3	4/5	2	3	4	3
D-2	5.0	1/1	1/2	2	2	4/5	1/2	4	3/4	3/4

\*Dyeing with ammonia solution

nyl 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 2.1.9.2.

It was found (Table 8) that the lightfastness of dyeings of the three aziridinyl dyes A-1, C-1 and D-1 was higher than their hydrolysed forms and the N,N'-dimethylaniline azo dye (B-4).

Dyeings which had been dyed with dye A-1 using ammonia solution displayed the same light fastness as dyeings of A-1 carried out without ammonia; thus ammonia did not impart any improvement to light fastness.

**Table 8. Lightfastness of dyed conventional decitex nylon 6.6 fabric**

Dye	% omf	pH	Colour depth	Light Fastness
A-1	1.3	5/0	1/1	5
	1.8	8.0	1/1	6
	1.9	10.0	1/1	6
A-1*	2.2	10.0	1.1	5
A-2	0.4	5.0	1/6	4
B-4	0.4	5.0	1/1	3-4
C-1	0.3	5.0	1.1	4
	0.4	8.0	1/1	4-5
	0.45	10.0	1/1	4-5
C-2	0.3	5.0	1/1	3-4
D-1	1.5	5.0	1/1	3-4
	1.55	8.0	1/1	4
	1.6	10.0	1/1	4
D-2	0.4	5.0	1/1	2

### 3.2 Conclusions

When nylon 6.6 fabrics which had been dyed with aziridinyl azo dyes were extracted with boiling DMF, no dye was removed by the solvent. In contrast, when nylon 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.

This observations implied that the aziridinyl dyes were either covalently bound to or had undergone dimerisation within nylon 6.6 fibres.

The optimum pH for the dyeing of nylon fibre with aziridinyl disperse dyes was 8 to 9 since dyeings obtained at these pH values displayed greatest resistance to extraction with DMF. These finding imply that dye-fibre fixation was favoured at pH 8 to 9.

Adsorption of the aziridinyl dyes was found to be completely unaffected by variation in the AEG of conventional nylon 6.6. This shows that the dyes behave as conventional disperse dyes in terms of the mechanism of their adsorption on to nylon 6.6. As it is generally accepted that, in the case of conventional disperse dyes, the mechanism of their adsorption on to all hydrophobic fibres is identical, it can be postulated that the mechanism of the adsorption of the disperse aminoazobenzene dyes containing ethyleneimine ring on nylon 6.6 fibres is the same as that on polyester.

The wash fastness of aziridinyl dyes on conventional nylon 6.6 was higher than that of the hydrolysed forms of the dyes and the N,N-dimethylaniline dye (B-4); thus, it appears that the aziridinyl dyes may be covalently bound to the fibre or that dimers may have been formed during dyeing.

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