

Dyeing Properties of 4-Amino-4'-fluorosulfonylazobenzene Disperse Dyes and their 4'-nitro Analogues on PET

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1. Introduction

Azo disperse dyes containing a fluorosulfonyl group are hydrolysed under alkaline condition by SN2 mechanism, and pseudo first-order kinetics were determined by analysis of the dye hydrolysis under alkaline conditions using HPLC. Also, the use of a fluorosulfonyl containing disperse dye showed a reasonable level of build up, excellent wash fastness and offers the option of alkali clearance to achieve high wash fastness, replacing reductive clearing and particularly sodium hydrosulfite, which places a very high BOD on conventional disperse dyeing effluent and the generates aromatic amines.

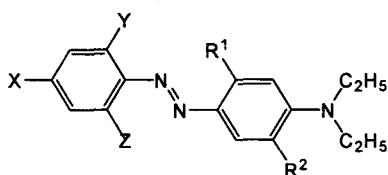
In this study, dyeing properties of 4-(N,N-diethylamino)-4'-fluorosulfonyl azobenzene disperse dyes and their 4'-nitro analogues on PET were investigated in a comparative manner.

2. Experimental

The synthesis of 4-(N,N-diethylamino)-4'-fluorosulfonylazobenzene disperse dyes has been described in the previous work. In order to synthesize 4-(N,N-diethylamino)-4'-nitroazobenzene disperse dyes, the same procedure was repeated except that in place of substituted amines containing fluorosulfonyl group, and the substituted amines containing a nitro group as diazo components were used. The dyes 1-6 that were used throughout the study were given in Table 1.

Synthesized dyes were formulated to be applied to PET. The composition comprises dispersing agent (Diwatex, 40 % on the weight of the dye), wetting agent (Sandozin NIE Liquid, 1 drop) and dye (1.0 % on the weight of water) in 100 ml of water that is buffered at pH 4.0 to 4.5. Dye dispersions were prepared by milling the composition mixture with glass beads in an aqueous medium for 1 week until the mean particle size was $\sim 1 \mu\text{m}$. Dyeing PET fabrics were dyed in a laboratory using a dyeing machine (Ahiba, Datacolour International) at a liquor ratio of 30:1. 60 ml of dyebath was prepared with the formulated dyes and a dispersing agent (Lyocol RDN Liquid 1.0 ml/l) and adjusted to pH 4.5. Then, PET fabric (2.0 g) was immersed in the dyebath for 60 min at 130 °C. The percentage of dyebath exhaustion on PET was estimated colorimetrically by extracting the dyed fabric with DMF under reflux at boiling point for 5 min and measuring the absorbance value of extracted dye using a UV/Visible-spectrophotometer (Kontron uvikon).

Table 1. Alkali-clearable azo disperse dyes containing a fluorosulfonyl group



Dye	X	Y	Z	R1	R2
1a	FO ₂ S	H	H	H	H
1b	NO ₂	H	H	H	H
2a	FO ₂ S	H	H	H	CH ₃
2b	NO ₂	H	H	H	CH ₃
3a	FO ₂ S	NO ₂	H	H	H
3b	NO ₂	NO ₂	H	H	H
4a	FO ₂ S	NO ₂	H	H	CH ₃
4b	NO ₂	NO ₂	H	H	CH ₃
5a	FO ₂ S	NO ₂	Cl	H	H
5b	NO ₂	NO ₂	Cl	H	H
6a	FO ₂ S	NO ₂	Cl	H	CH ₃
6b	NO ₂	NO ₂	Cl	H	CH ₃

3. Results and discussion

In the dyeing of PET fiber, 4'-fluorosulfonyl derivatives which contain the p-fluorosulfonyl group in the diazo component showed lower exhaustion (%) values and higher build-up properties than that of 4'-nitro analogues, probably due to their lower hydrophobicity.

Depending on the substituents of the diazo and coupling components, the color of dyeings was changed from reddish orange to reddish purple as indicated in Figure 1. Trends in the hues of the dyeings were generally consistent with those observed for absorption maxima of the dyes in ethanol solution. Dyes 4 and 5 are relatively dull compared to dyes 1, 2, and 3 as shown in Figure 1. The results are due to the steric hindrance at the azo link to broaden visible absorption peaks.

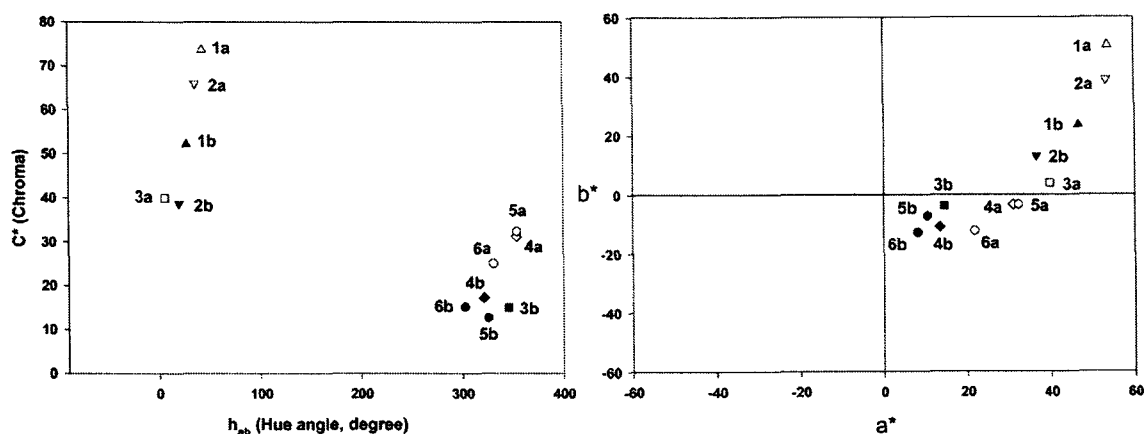


Fig. 1. Comparison of color properties on PET fabrics with 4'-fluorosulfonyl derivatives and 4'-nitro derivatives at 1.0 %owf dye concentration.

As expected, the 4-(N,N-diethylamino)-4'-nitroazobenzene dye was bathochromic on PET relative to its 4'-fluorosulfonyl analogues, owing to greater electron withdrawing power of nitro group. However, the 4'-nitro derivatives are relatively dull compared to the 4'-fluorosulfonyl analogues as shown in Figure 1. These trends in the colorimetric properties are consistent with their spectral properties in solvent. Also, the reasonable linear correlations can be found between chroma values of the dyed samples and the half-band width (in EtOH) of the synthesized dyes; the sharper the half-band width of the dyes, the brighter was the color of dyed PET.

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