

## Relation between Chemical Structure of Yellow Disperse Dyes and Their Lightfastness

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**Abstract:** Five yellow disperse dyes were synthesized and their dyeing, fastness and photodegradation behaviors were investigated. It was found that dyes derived from phenylindole and N-alkylaminobenzene showed dye uptake directly proportional to the dye concentration, but the build-up of dyes derived from carbazole and pyridone were not good. The wavelength at maximum absorption, molar extinction coefficient, and the tendency to the photodegradation were strongly dependent on the electron donating ability of the coupling component. The dye, whose coupling component was phenylindole, possessed the excellent dyeing properties and the high degree of lightfastness. UVA had an effect on the inhibition of the photodegradation especially for the easily photodegradable dyes.

**Keywords:** Lightfastness, Disperse dye, Coupling components, Phenylindole, UVA

### Introduction

Factors affecting lightfastness of dye are known to be the energy distribution of light, the chemical structure of dye and fiber, the concentration of dye in fiber, the amount of water, temperature and the presence of auxiliaries such as ultraviolet absorbing agents (UVA)[1]. The reaction mechanism of photodegradation of dyes has been widely studied, it has been found that azo dyes will either undergo photooxidation or photoreduction reactions depending very much on the nature of the polymer and the atmosphere[2,3]. Photoreduction essentially produces a hydrazo compound and eventually disproportionation gives substituted anilines, and is more predominant in reductive environments, while the oxidative photofading of azo dyes is attributed to the active participation of singlet oxygen. These two reactions have been consistently proposed in the literature[4,5].

The major textile fibers used in automotive interiors and seats are polyester, nylon, acryl and wool. Recently polyester fibers have gained a bigger share at the expense of nylon fibers. This is partly attributable to the good photostability of dyed polyester fabric and the lack of suitable lightfastness improvers for nylon fabrics[6]. It is generally accepted that polyester fiber dyed with disperse dyes shows relatively high lightfastness compared with other fibers, and that the polyester-disperse dye system is useful and practical in cases where high lightfastness is required[7].

The very high level of lightfastness of fabric used for automotive seats is required because automotive is exposed to daylight and the temperature of the inside of automotive with closed window becomes very high at summer, accelerating the rate of photofading of dyes. Hence major dye manufacturers have been trying to develop disperse dyes having excellent lightfastness. The best method to enhance

the photostability of polyester dyed with disperse dyes is to use dyes very resistant to the photofading. Recently, coupling components such as N,N-dialkylaniline substituted with cyano group, pyridone, phenylindole, diaminopyridine, carbazole and benzotriazole derivatives are known to be used for the production of dyes having high lightfastness[8]. Also, UVAs, especially benzotriazoles for polyester fabric, are often employed during dyeing in order to improve the lightfastness[9].

The purpose of this study is to investigate dyeing, fastness and photofading behaviors of yellow disperse dyes synthesized from different coupling components, and to elucidate the relation between chemical structure and lightfastness of disperse dyes.

### Experimental

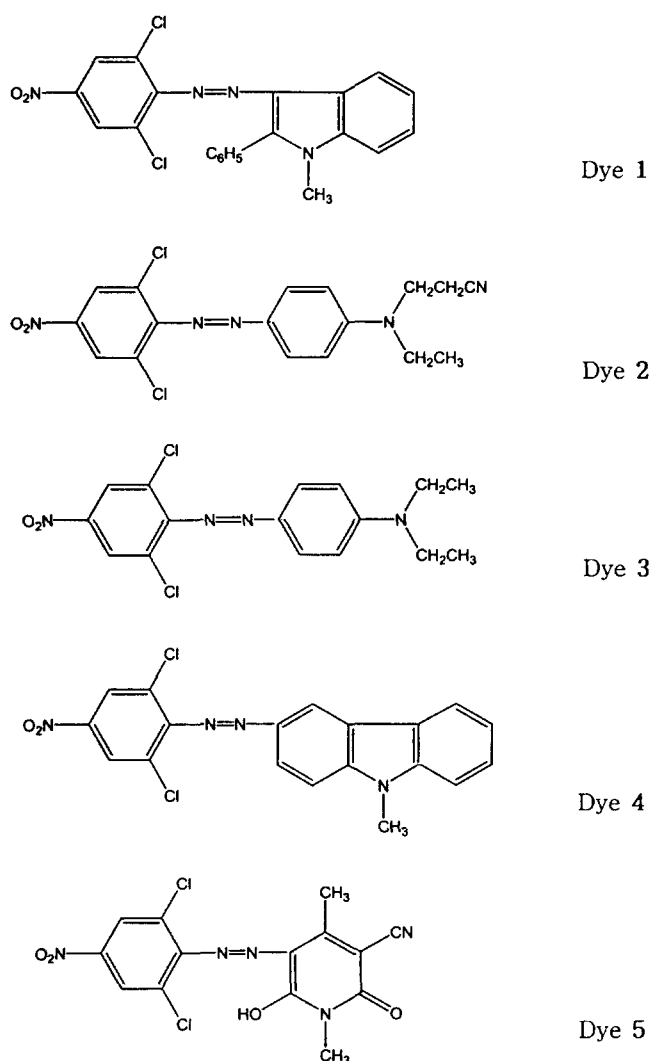
#### Synthesis of Yellow Disperse Dyes

2,6-dichloro-4-nitroaniline was used as a diazo component. Phenylindole, N-cyanoethyl-N-ethylaniline, N,N-diethylaniline, carbazole, pyridone were purchased and used as coupling components without further purification.

The solution of the coupling component was made using either 1:5 acid (propionic acid/acetic acid) or 5% H<sub>2</sub>SO<sub>4</sub>. Diazotization was performed by the addition of nitrosylsulfuric acid to the solution of the diazo component in 96% H<sub>2</sub>SO<sub>4</sub>. The coupling reaction was done by the slow addition of the diazonium salt solution to the coupling solution at 5°C. When the coupling reaction is completed, the dye precipitate was collected after the addition of reaction mixture to water, and pure dye was obtained through the recrystallization in methanol. Structures of the dye synthesized are shown in Figure 1.

Although chemical structure of dyes was confirmed by 400 MHz <sup>1</sup>H-NMR (Bruker) and FTIR (Jasco), the analytical results are not included in the paper because the chemical

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**Figure 1.** Chemical structure of five disperse dyes synthesized.

structure of dye, which is derived from the known diazo and coupling component, is evident.

### Dyeing Process

Scoured conventional polyester fabric (75 d/36 f, plain weave, 100×89/inch) was used as a substrate.

Purified dye and dispersing agent (weight ratio 1:2) were milled to dye dispersions whose particle size were in the range of 0.3-0.5  $\mu\text{m}$ , using glass beads and mechanical stirrer. Dyeing was carried out in the sealed dyepot (Labomat, Mathis), pH was adjusted to 4.5 by adding acetic acid, and a liquor ratio was 30:1. Temperature was raised from 50°C to 130°C, and dyeing was continued at 130°C for 60 minutes, then the temperature was reduced to 80°C. Dyed polyester fabric was reduction cleared in an aqueous solution containing sodium hydroxide (2 g/l) and sodium hydrosulphite (2 g/l) at 80°C using a liquor ratio 50:1 for 20 minutes, and

rinsed. The dyed fabric was heatsetted at 180°C for 30 seconds.

For the dyeing with UVA (benzotriazole derivative, Cibatex APS), 2% owf UVA was added to the dye bath, and the same dyeing process was used.

### Determination of Dye Uptake

The dye absorbed by the fiber was extracted using N,N-dimethylformamide (DMF) at 100°C. The optical density of the extract was determined on UV-VIS spectrophotometer (UV-160A, Shimadzu). Calibration curves plotted with pure dyes were used to calculate the amount of absorbed dye from the optical density values and expressed in terms of mg of dye/g of fiber.

### Measurements of Fastness and Photodegradation

Fastness to washing, heat, and rubbing were measured using AATCC 61 IIA, AATCC 117 III, and AATCC 8 methods respectively.

Photofading was performed on Ci 35A (Atlas) according to AATCC 16E method. The dyed fabric was exposed to Zenon arc light for 20, 40, 60, and 80 hr, then the color change were evaluated by the color difference ( $\Delta E$ ) using a Color-Eye 3100 (Macbeth).

## Results and Discussion

### Wavelength at Maximum Absorption

It is known that the higher is the polarity of the dye, the longer is wavelength at maximum absorption ( $\lambda_{\text{max}}$ ), and that the polarity of the monoazo disperse dye is directly proportional to the electron donating ability of the coupling component and the electron withdrawing ability of the diazo component. In this study, the difference in  $\lambda_{\text{max}}$  comes exclusively from the electron donating ability of the coupling component because all dyes were synthesized using 2,6-dichloro-4-nitroaniline as the diazo component.

$\lambda_{\text{max}}$  and molar extinction coefficient were measured from the DMF solution of the synthesized dyes, and listed in Table 1. Dye 3 has the longest  $\lambda_{\text{max}}$ , 449 nm, because nitrogen atom of the coupling component being bonded to the two ethyl groups, is forming N,N-diethylaniline which is very powerful electron donating group. Dye 2's  $\lambda_{\text{max}}$  is 432 nm, shorter than Dye 3 by 17 nm since the presence of a

**Table 1.**  $\lambda_{\text{max}}$  and molar extinction coefficient of disperse dyes

Dye	$\lambda_{\text{max}}$ (nm)	molar extinction coefficient (l/mole·cm)
1	407	16,380
2	432	23,660
3	449	24,910
4	404	16,570
5	430	19,180

cyano group, which withdraws the electron density from N,N-diethylaniline, results in the hypsochromic shift. Dyes **1** and **4** possess the shortest  $\lambda_{\max}$ , 407 nm and 404 nm respectively, because the electron donating ability of the coupling component, where nitrogen atom is a part of the aromatic ring and does not have two non-bonding electrons, diminishes a lot.

The molar extinction coefficient is dependent on the coplanarity and the polarizability of the dye, and it is usually getting higher as  $\lambda_{\max}$  increases[10]. The magnitude of the molar extinction coefficient of five dyes in Table 1 can be said to follow the general trend of azo dye.

### Dyeing Properties

The amounts of absorbed dye were determined by extracting with DMF from fabrics dyed at 0.25, 0.5, 1, and 2% owf concentrations, and shown in Figure 2. Generally, the amount of absorbed dye increases with increasing the dye concentration. Dyes **1**, **2**, and **3** show good build-up profiles, but dye uptake of Dyes **4** and **5** are not sufficient. The amount of absorbed Dye **4** at 2% owf is quite similar to that at 1% owf, and those for Dye **5** are lower than other dyes at all dye concentrations.

It is interesting to note that the remarkable difference in dye uptake between Dyes **1** and **4**, whose chemical structures seem to be very similar to each other. The reason of the lower dye uptake of Dye **4** as compared with that of Dye **1** might be the spatial arrangement of the benzene ring. In the case of Dye **1**, the benzene ring is skewed and not coplanar

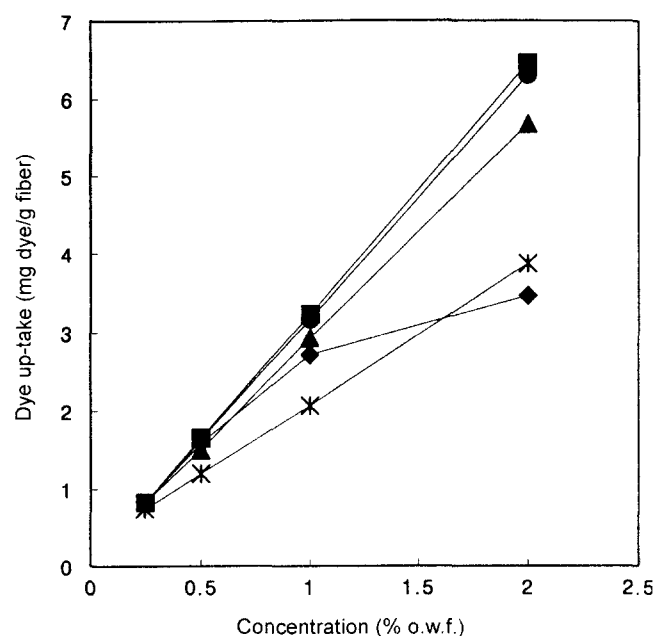
with indole moiety due to the steric hindrance, but the corresponding benzene ring in Dye **4** is a part of the big hetero aromatic system, resulting in a big planar structure. Assuming that the degree of relaxation of physical structure of polyester is same during the dyeing process, the diffusion of the dye which has the big planar region becomes so difficult that the amount of dye uptake decreases. Other example of slow diffusion of dye having the big planar structure is benzodifuranone disperse dye whose maximum dyeing temperature(135~140°C) is higher than normal disperse dyes to ensure the better penetration of dye into the fiber.

### Relation between Chemical Structure and Photofading of Disperse Dyes

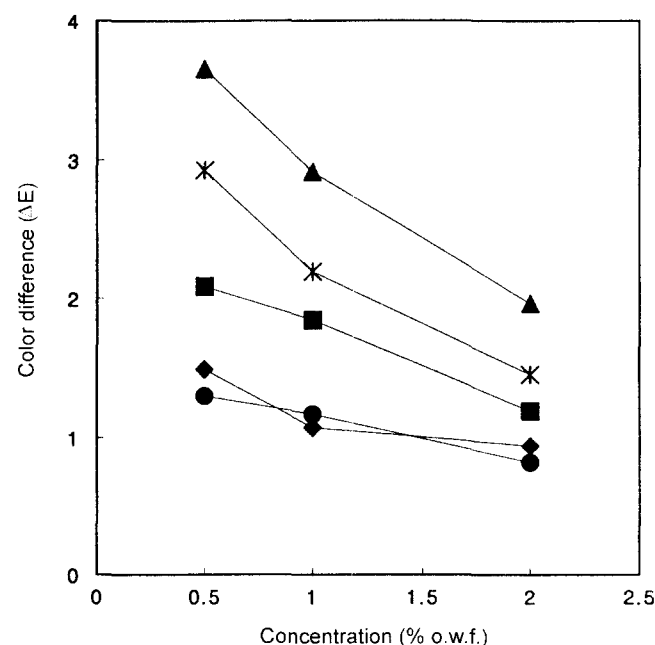
Grades of fastness of polyester fabric dyed at 1% owf are shown in Table 2. The rubbing fastness are excellent for all dyes, and the fastness to washing and heat are good to excellent except Dye **3**. The grade of lightfastness for the

**Table 2.** Color fastness of polyester fabric dyed with yellow dyes

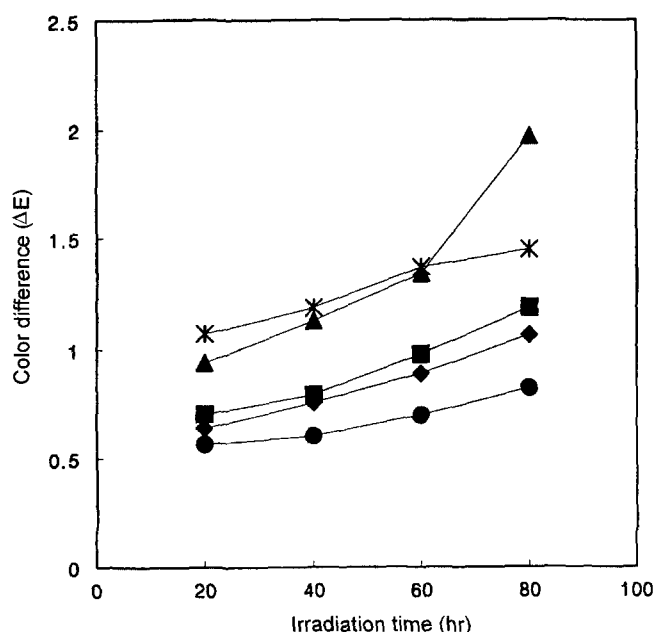
Dye	Washing		Light		Heat		Rubbing	
	staining		color change		staining		staining	
	PET	cotton	none	UVA	PET	cotton	dry	wet
<b>1</b>	5	5	4-5	4-5	4	4-5	5	5
<b>2</b>	5	4	4	4-5	4	4-5	5	5
<b>3</b>	5	3-4	3	3-4	2-3	3-4	5	5
<b>4</b>	5	5	4	4-5	4-5	4-5	5	5
<b>5</b>	5	5	4-5	4-5	4-5	4-5	5	5



**Figure 2.** Variation of the amount of absorbed dyes as a function of the concentration of dye, ●: Dye 1, ■: Dye 2, ▲: Dye 3, ◆: Dye 4, \*: Dye 5.



**Figure 3.** Variation of color difference of polyester fabric after 80 hr irradiation as a function of dye concentration, ●: Dye 1, ■: Dye 2, ▲: Dye 3, ◆: Dye 4, \*: Dye 5.



**Figure 4.** Variation of color difference of polyester fabric dyed at 2% owf as a function of irradiation time, ●: Dye 1, ■: Dye 2, ▲: Dye 3, ◆: Dye 4, \*: Dye 5.

fabric dyed without UVA is 4-5 for Dyes 1 and 5, 4 for Dyes 2 and 4, 3 for Dye 3, respectively, and the addition of UVA improves by half grade for Dyes 2, 3, and 4.

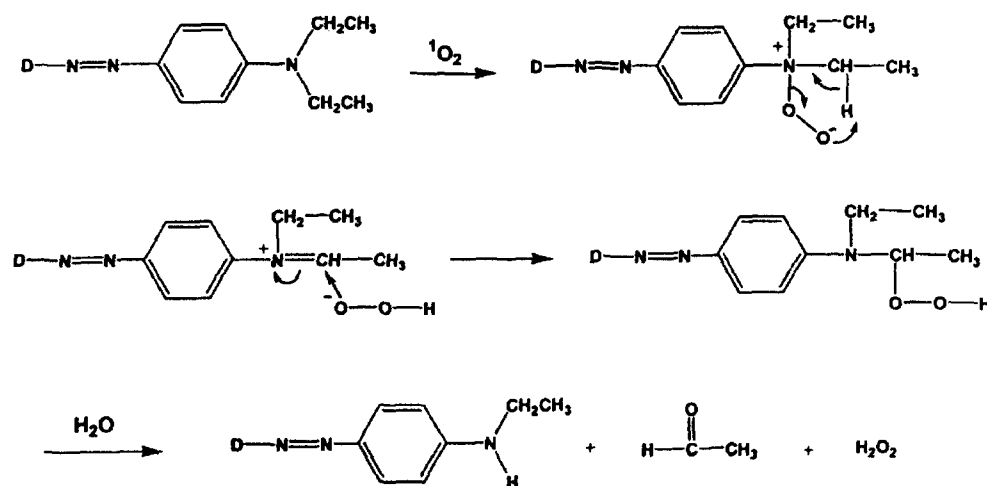
$\Delta E$  of the dyed fabric between before and after Zenon arc exposure is measured as a function of the dye concentration and the exposure time in order to investigate the extent of photofading precisely, and shown in Figures 3 and 4. Based on these experimental results, it can be said that resistance to photofading is in the order of Dye 1, Dye 4, Dye 2, Dye 5, and Dye 3. It is also found that  $\Delta E$  of polyester fabric after 80 hr exposure becomes smaller as the dye concentration increases from 0.5% owf to 2% owf, and that  $\Delta E$  of

polyester fabric dyed at 2% owf is getting larger as the irradiation time increases.

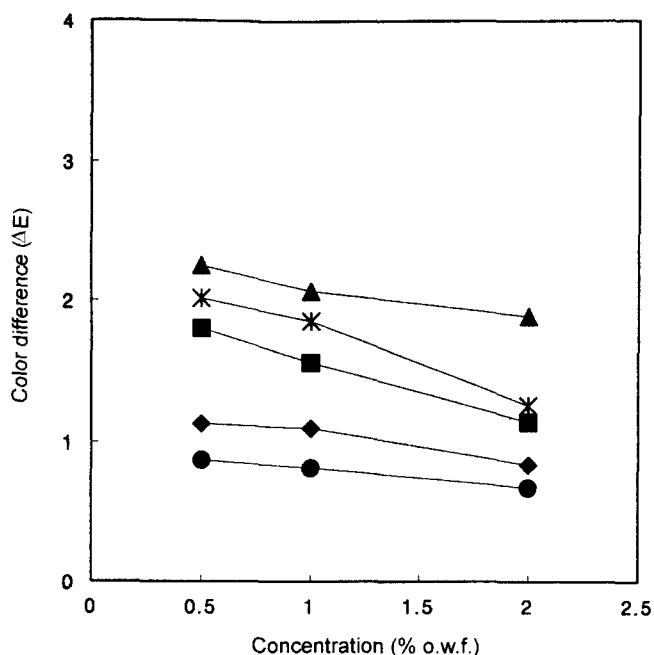
Assuming that disperse dyes are photodegraded through reduction reaction, a dye, which derived from a coupling component having good electron donating ability, can accumulate the electron density on the nitrogen atom of azo group, and tends to abstract hydrogen atom easily from the polymer. If a dye is photofaded through another possible mechanism like N-dealkylation as depicted in Scheme 1[2], a dye, derived from a coupling component having good electron donating ability, also has higher tendency to be attacked by singlet oxygen.

Considering these photodegradation mechanisms, we try to find relation between chemical structure and photofading of disperse dyes. Dye 3, which shows the fastest rate of photodegradation, has the highest possibility of N-dealkylation due to the two ethyl group attached to nitrogen atom. The cyano group in Dye 2 can withdraw the electron density from the nitrogen atom, resulting in the slow photofading than Dye 3. In the case of Dyes 1 and 4, two electrons on the nitrogen atom participates in the heterocyclic aromatic ring system and are quite stabilized, then the ability of electron donating is non or little, and subsequently resistance to photofading becomes high. Hence it can be said that a disperse dye derived from a coupling component which can donate a greater amount of electron density are photodegraded at a fast rate through the reduction or the N-dealkylation, and that a disperse dye which have a nitrogen atom in the heterocyclic ring are photofaded slowly.

Figure 5 shows  $\Delta E$  values measured from fabrics dyed with UVA. As compared with Figure 3,  $\Delta E$  values become smaller, indicating UVA inhibits the photodegradation. It is reported that the 316 nm UV degraded the dyed polyester maximally[11]. According to this report, 316 nm UV degrade polyester first, then the dye on the fiber, and the fading of dye on the fiber is governed predominantly by the



**Scheme 1.** Mechanism of N-dealkylation.



**Figure 5.** Variation color difference of polyester fabric dyed with UVA at 80 hr irradiation, ●: Dye 1, ■: Dye 2, ▲: Dye 3, ◆: Dye 4, \*: Dye 5.

degradation products of the polymer. The UVA used in this study absorbed strongly the 316 nm UV and can prohibit the degradation of polyester and dye considerably.

### Conclusions

It can be concluded on the basis of the dyeing, fastness and photodegradation behaviors of five yellow disperse dyes as follows:

1. The dyeing properties of dyes derived from phenylindole and N-alkylaminobenzene are excellent, but those from carbazole and pyridone are not good.

2. The wavelength at maximum absorption, molar extinction coefficient, and the tendency to the photodegradation are

strongly dependent on the electron donation ability of the coupling component.

3. The dye, whose coupling component is phenylindole, possesses the excellent dyeing properties and the high degree of lightfastness.

4. The UVA have an effect on the inhibition of the photodegradation especially for the easily photodegradable disperse dyes.

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