

## Studies in Dyeing. I. Effect of Crystal Modification of Disperse Dyes on their Dyeing Behavior

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### Synopsis

Three commercial disperse dyes and a laboratory-synthesized disperse azo dye were converted to different crystal forms. These were characterized by melting point, x-ray diffractograms, and their dyeing behavior on polyester fibers. The different crystal modifications of the same dye were shown to dye polyester fibers (but not polyamide fibers) at different rates and to different fiber saturation values. An attempt has been made to explain these differences based on a thermodynamic approach. An attempt is made to apply the concept of crystal modification of disperse dyes to some of the earlier studies done on dyeing and printing of disperse dyes on polyester and secondary cellulose acetate substrates reported in the literature.

### INTRODUCTION

The dyeing of polyester and polyamide fibers with disperse dyes has attracted considerable attention. In this field, the chemical nature of the dye, the presence of hydrophilic groups, and the polarity of the dyes, molecular size, and particle size of the dye, etc., have been studied.<sup>1-8</sup> Recently, another aspect has been studied by Biedermann.<sup>9,10</sup> He found that the disperse dyes are polymorphic, and he synthesized an azopyrazole disperse dye in five different crystallographic forms and dyed them on cellulose acetate fibers. Each of these forms has a separate dyeing rate and a separate fiber saturation value (0.77-5.5 g dye/100 g fiber). Those forms which have higher fiber saturation values are thermodynamically less stable (metastable). On heating, the metastable form is transformed into a more stable form, especially in an aqueous environment. The practical importance of crystal modification of disperse dyes lies in the fact that a higher color yield of the chemically identical dye may be obtained by modifying the crystal structure or may be adversely affected by the use of an improper dispersing agent during dyeing, especially under high-temperature dyeing conditions.

The present communication deals with the effect of crystal modification of disperse dyes on their dyeing behavior on polyester and polyamide fibers. To effect crystal modification crystallization of the dyes from different organic solvents was employed.

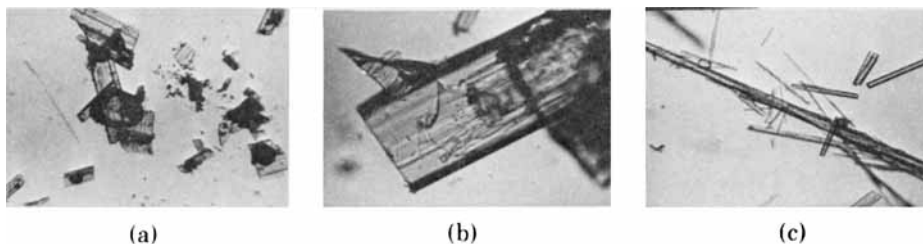


Fig. 1. Photomicrographs of different forms (I, II, and III) of Foron Yellow SE-FL.

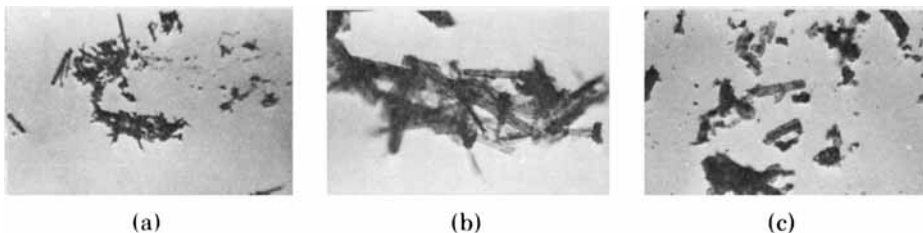


Fig. 2. Photomicrographs of different forms (I, II, and III) of Foron Scarlet S-3GFL.

## EXPERIMENTAL

### Fibers

Terene polyester fiber, manufactured by M/s Chemicals and Fibres of India Ltd., Bombay, was used after Soxhlet extraction with acetone for 8 hr.

Jaykaylon (100 den/20 fil nylon 6) manufactured by M/s J. K. Synthetics Ltd. Kota, India, was used after scouring with 1 g/l. nonionic detergent based on nonylphenol-ethylene oxide condensate and 1.5 g/l. sodium bicarbonate at the boil for 30 min.

### Dyes

The following dyes were used: (1) Foron Yellow SEFL (CI Disperse Yellow 42); (2) Foron Scarlet S-3GFL (CI Disperse Red 54); (3) Celliton Fast Yellow G (CI Disperse Yellow 3); and (4) *p*-nitroaniline  $\rightarrow$  diethylaniline.

The commercial dyes (the first three dyes) were boiled with distilled water along with alum till the dispersion broke. This was followed by filtering and washing the dye free from dispersing agents and electrolytes and drying at  $60^\circ \pm 2^\circ\text{C}$ . They were then Soxhlet extracted with appropriate solvents (benzene, chlorobenzene, and methanol) and crystallized. In some cases, the dye (after removing the dispersing agent and electrolytes) was boiled with distilled water under reflux for 5 hr. The photomicrographs (at magnification of  $200\times$ ) of all these crystal modifications are shown in Figures 1-4. The melting points of the different forms of the dyes were determined in capillary tubes using an electrically heated Toshniwal melting point apparatus and are given in Table I.

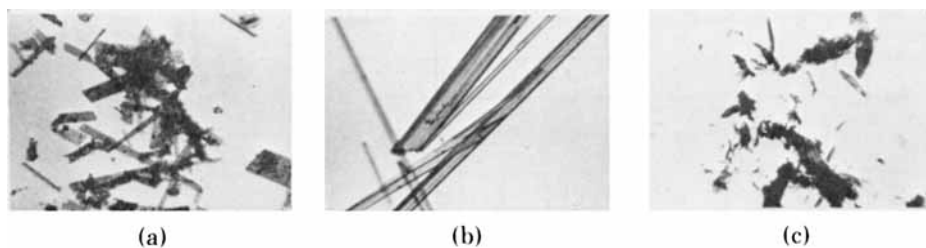


Fig. 3. Photomicrographs of different forms (I, II, and III) of Celliton Fast Yellow G.

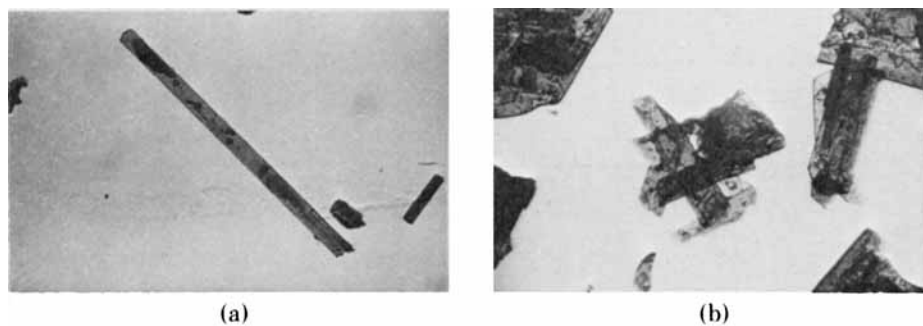


Fig. 4. Photomicrographs of different forms (I and II) of *p*-nitroaniline  $\rightarrow$  diethylaniline.

### X-Ray Spectra

X-Ray diffractograms of the different forms of CI Disperse Yellow 42 and *p*-nitroaniline  $\rightarrow$  diethylaniline were recorded using a Philips 1009 x-ray diffraction unit, while those of the others were recorded using a Philips PWU 1130 x-ray diffraction unit. The source of x-rays in both the units was  $\text{CuK}_\alpha$  radiation. The diffraction patterns have been converted into line diagrams in which the intensity is plotted against  $\theta$  (Figs. 5-8). The appearance of peaks at different  $\theta$  values (forms I, II, and III of Fig. 5; forms I, II, and III of Fig. 6, and forms I and II of Fig. 8) indicate that these are different crystallo-

TABLE I  
Effect of Crystal Modification on the Melting Point of Disperse Dyes

Dye	Crystal form	Method of preparation	Crystal shape	Melting point, °C
Foron Yellow SE-FL	I	benzene-crystallized	thick plate	157
	II	chlorobenzene-crystallized	thick plate	157
	III	methanol-crystallized	needle	155
Foron Scarlet S-3GFL	I	chlorobenzene-crystallized	short needle	150
	II	methanol-crystallized	rectangular	152
	III	preboiled form I	irregular	153
Celliton Fast Yellow G	I	benzene-crystallized	rhombic	196
	II	methanol-crystallized	long needle	196
	III	preboiled form I	irregular	196
<i>p</i> -Nitroaniline $\rightarrow$ Diethyl-aniline	I	methanol-crystallized	hexagonal	149
	II	preboiled form I	plate-like	152

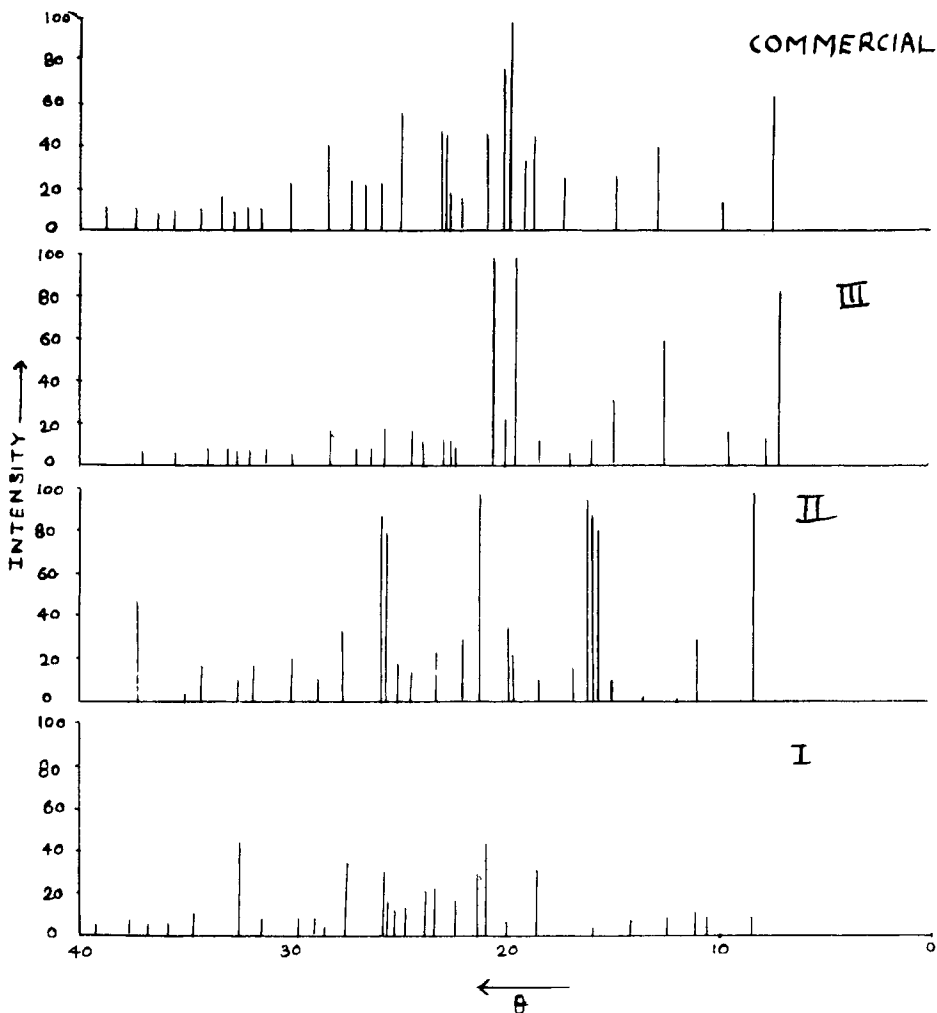


Fig. 5. X-Ray diffractograms (line diagrams) of different forms of Foron Yellow SE-FL.

graphic forms. In the case of Celliton Fast Yellow G, peaks appear at the same  $\theta$  values indicating that forms I, II, and III are not crystallographically different.

### Preparation of Dye Dispersions and Dyeing

Dye dispersions were prepared by grinding 1–2 g of the dye in a rotating stout glass tube containing stainless steel rods. Grinding was carried out for 24–48 hr in the presence of a small amount of an anionic dispersing agent (naphthalene- $\beta$ -sodium sulfonate-formaldehyde condensate). The dispersion was diluted to 500 ml and filtered. The filtrate was used as the dye dispersion. The amount of the dispersing agent in the dyebath was adjusted to 1.5 g/l. by adding further quantities of the dispersing agent. The amount of the dye in the dyebath was taken in such an excess that at the end of the dyeing excess, solid dye remained. The suspended excess dye acted as a reservoir of the dye when the dye concentration in the bath fell below the satu-

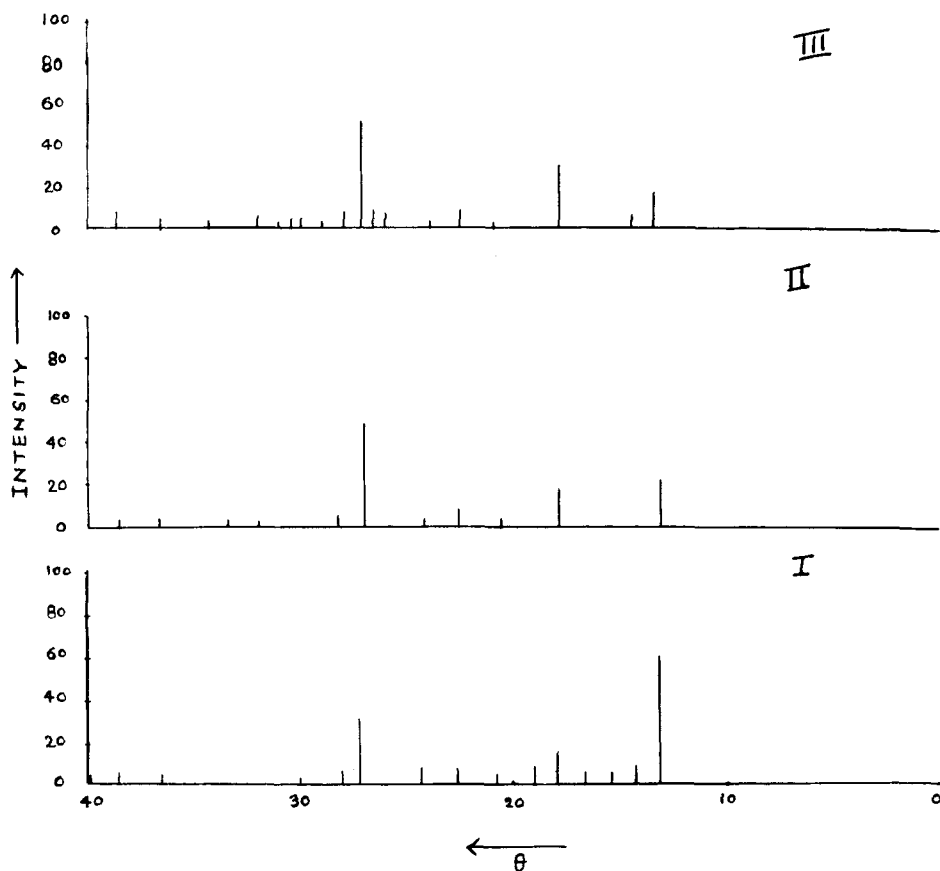


Fig. 6. X-Ray diffractograms (line diagrams) of different forms of Foron Scarlet S-3GFL.

ration value during dyeing. The dyeing apparatus is shown in Figure 9.

The dyeing was carried out in 350-ml Corning glass tubes fitted with rubber bungs into which condensers were inserted. A loop-type stirrer passed through the condenser and was rotated by a small motor. The tubes were placed in an electrically heated constant-temperature water bath. Agitation was periodically interrupted (every 30 min), a small portion of the dyed fiber was withdrawn, and the remainder was dyed further with a fresh dispersion of the dye. This procedure was continued until fiber saturation value was reached. This was followed to avert any possibility of transition of a metastable form of the dye to a more stable one during dyeing.

#### Analysis of Dyed Fiber

After dyeing, the fibers were removed from the dyebath, washed thoroughly in running water, dried, and conditioned at 65% R.H. and at  $30^{\circ} \pm 2^{\circ}\text{C}$ . An accurately weighed quantity (10–100 mg) of the dyed fiber was extracted with a suitable solvent (chlorobenzene for polyester and a 50/50 mixture of chlorobenzene/glacial acetic acid for polyamide fibers) and made of to a

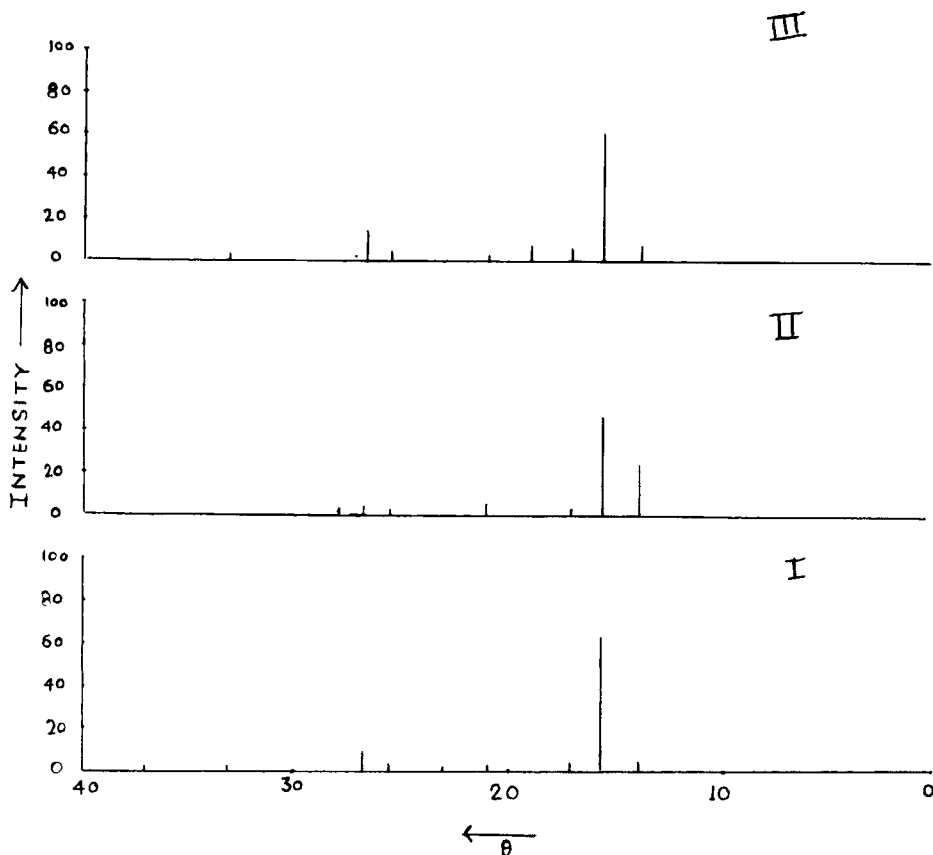


Fig. 7. X-Ray diffractograms (line diagrams) of different forms of Celliton Fast Yellow G.

known volume (10–250 ml). The dye present in this solution was estimated spectrophotometrically using a Hilger Biochem Pattern Absorptiometer. The dye content of the fiber is expressed in g dye/100 g fiber.

## RESULTS

### Dyeing of Polyester Fibers

The three crystalline forms of purified Foron Yellow SE-FL were dyed up to fiber saturation on polyester fibers at the boil from an aqueous bath by the method described above. The rate of dyeing curves are shown in Figure 10.

It is seen that each crystalline form of the dye has a separate fiber saturation value, the numerical values being 0.97, 1.10, and 1.53 g/100 g fiber for forms I, II, and III, respectively. Also, each form of the dye has a separate rate of dyeing, and the forms having higher fiber saturation values have higher dyeing rates. The rate of dyeing curve for the commercial dye Foron Yellow SE FL is also shown in Figure 10 where it is seen that it falls on that of form III.

The rate of dyeing curves for the other three dyes are shown in Figures 11–13. The fiber saturation values of the different forms of all the dyes are given in Table II.

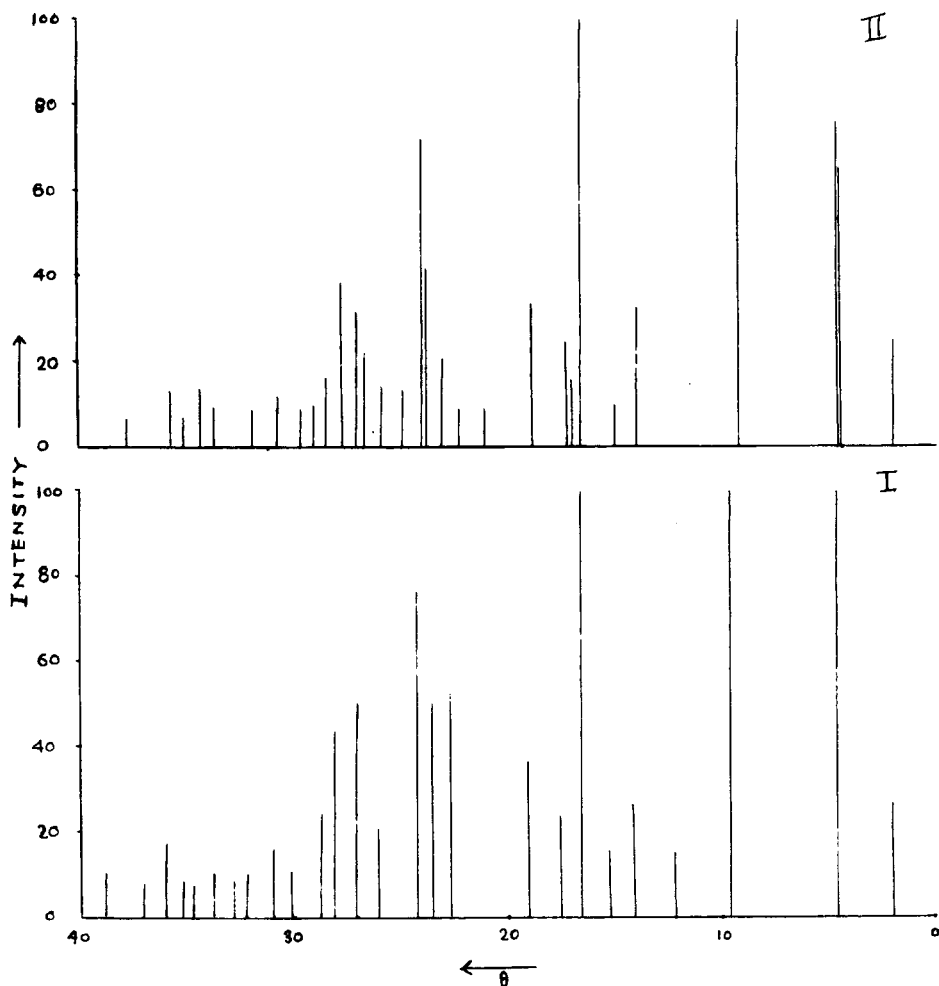


Fig. 8. X-Ray diffractograms (line diagrams) of different forms of *p*-nitroaniline  $\rightarrow$  diethylaniline.

The different forms of the dyes were dyed on polyamide fibers by the method described earlier, but the dyeing was carried out at 75°C. One dye was dyed at the boil also. The fiber saturation values are given in Table III.

## DISCUSSION

During the dyeing of disperse dyes on polyester fibers from an aqueous medium, the dye distribution process comes to a halt when the chemical potential of the dye is the same in both phases. The driving force for the diffusion of the dye is the chemical potential gradient and not the concentration gradient. At the end of the dyeing, the chemical potential of the dye remains the same in both phases. When the dye-solvent system is ideal,

$$\mu = \mu^0 + RT \ln C \quad (1)$$

where  $\mu$  and  $\mu^0$  are the chemical potential and the standard chemical poten-

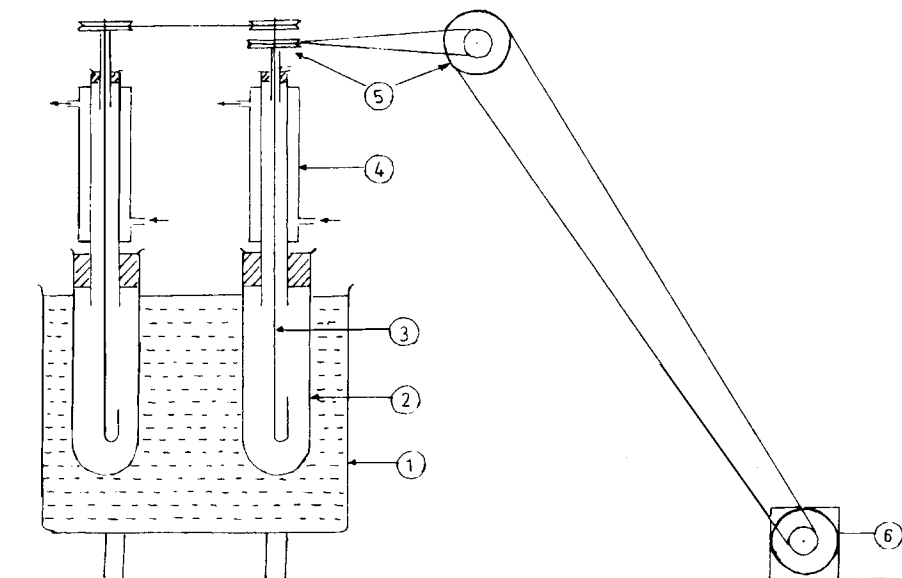


Fig. 9. The dyeing equipment: 1, water bath; 2, dyeing tube; 3, stirrer; 4, condenser; 5, pulleys; 6, motor.

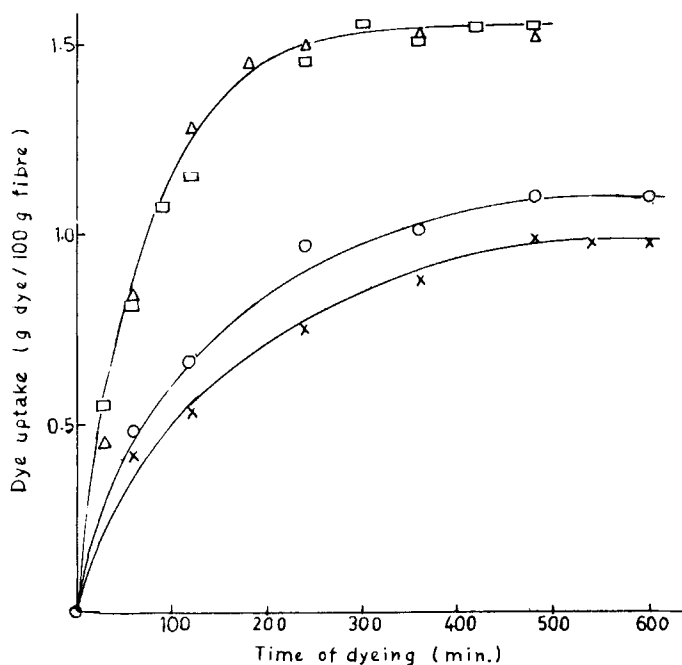


Fig. 10. Dyeing rate curves for the different forms of Foron Yellow SE-FL on polyester fibers at 100°C: (□) commercial dye; (Δ) form III; (○) form II; (×) form I.

tial of the dye in the solvent, respectively;  $R$  is the gas constant;  $T$  is the absolute temperature; and  $C$  is the concentration of the dye in the solvent.

According to the modern theory of dyeing developed by McGregor<sup>12</sup> and Milicevic and McGregor,<sup>13</sup> based on nonequilibrium thermodynamics, the



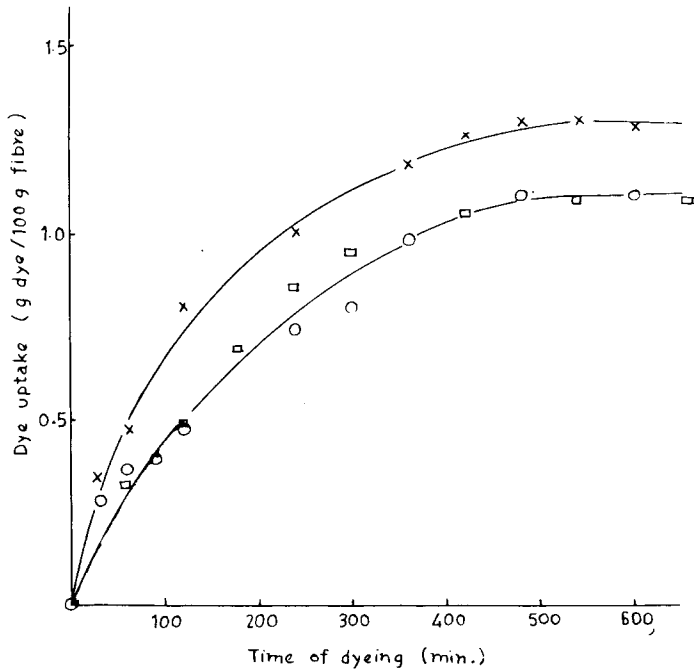


Fig. 11. Dyeing rate curves for the different forms of Foron Scarlet S-3GFL on polyester fibers at 100°C: (x) form I; (o) form II; (□) form III.

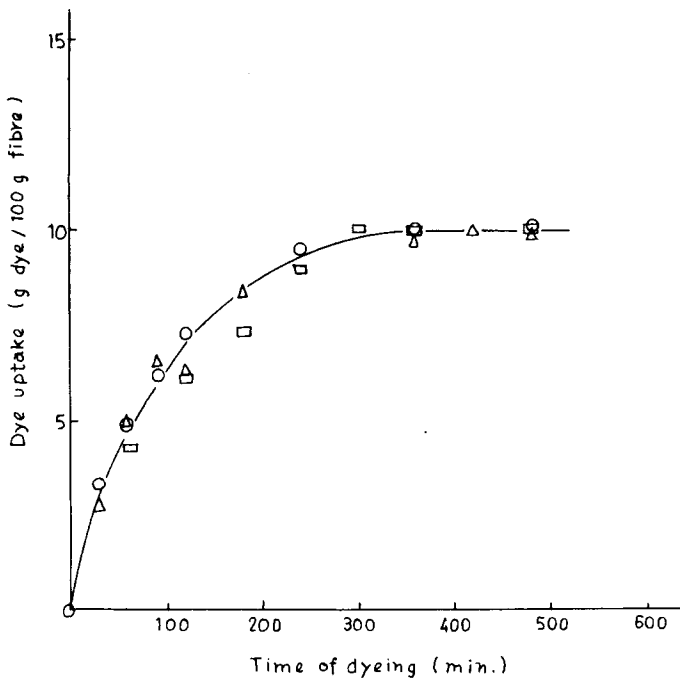


Fig. 12. Dyeing rate curves for the different forms of Celliton Fast Yellow G on polyester fibers at 100°C: (o) form I; (Δ) form II; (□) form III.

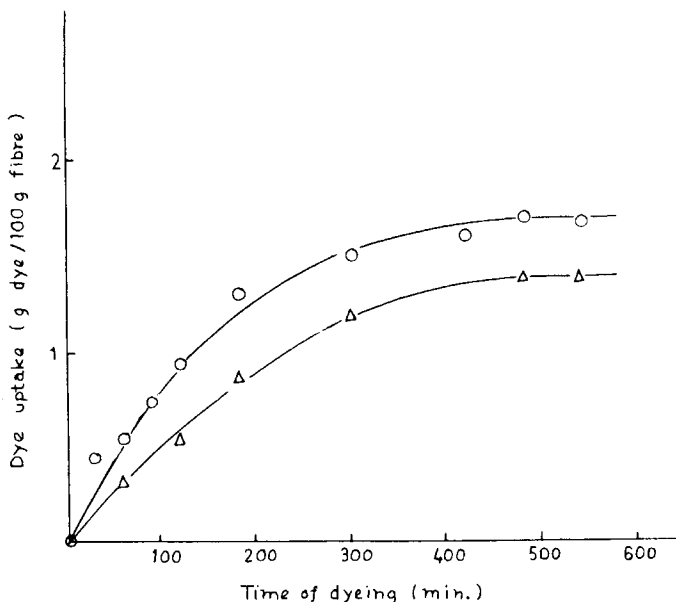


Fig. 13. Dyeing rate curves for the different forms of *p*-nitroaniline  $\rightarrow$  diethylaniline on polyester fibers at 100°C: (O) form I; ( $\Delta$ ) form II.

driving force for the diffusion of a dye in the fiber at any instant is the difference in the chemical potentials ( $-\Delta\mu$ ) of the dye in water ( $\mu_s$ ) and the dye in the fiber ( $\mu_f$ ). This is termed instantaneous affinity or instantaneous driving force of dyeing. As the dyeing continues, more and more dye goes into the fiber and  $-\Delta\mu$  goes on decreasing, and so also is the dyeing rate. At equilibrium, the chemical potentials of the dye in water and in the fiber become equal, the dye transfer comes to a halt, and the chemical potential of the dye in the crystal ( $\mu_c$ ) equals that of the dye in water ( $\mu_s$ ) and the dye in fiber ( $\mu_f$ ). When the dye exists in more than one crystalline form, each form possesses a free energy or chemical potential (free energy/molecule). A crystalline form which is thermodynamically unstable (metastable) has higher free energy (chemical potential) than a stable form.

In the present investigation, the different crystalline forms of the same dye except Celliton Fast Yellow G are found to have different saturation solubilities in the polyester fiber. The x-ray diffraction data of the three forms (I, II,

TABLE II  
Fiber Saturation Values of Different Crystal Forms of Dyes on  
Polyester Fibers at 100°C

Dye	Fiber saturation value, g/100 g fiber			
	I	II	III	Commercial dye
1. Foron Yellow SE-FL	0.97	1.10	1.53	1.55
2. Foron Scarlet S-3GFL	1.30	1.09	1.08	—
3. Celliton Fast Yellow G	10.03	10.00	10.00	—
4. <i>p</i> -Nitroaniline $\rightarrow$ diethylaniline	1.68	1.40	—	—

and III) and the melting point, 196°C (Table I) as well as the same fiber saturation values (Table II) for Celliton Fast Yellow G show that they are really not different crystal forms.

When the different forms of the disperse dyes were dyed on polyamide fibers (nylon 6) at 75°C and 100°C by the same method as used in the dyeing of polyester fibers, fiber saturation was reached in 3–5 hr (Table III).

It is seen that for most of the dyes, the fiber saturation values are independent of the crystal form of the dyes. It may be suggested that since polyamide fibers contain amide groups, it is likely that this results in a strong interaction between the dye and the fiber. If the dye–fiber interaction is very strong, the system may deviate from ideal behavior. In such cases, the relationship between the concentration and the chemical potential is not known. It seems that the relationship is such that there is a little change in the concentration with the change in chemical potential. Therefore, the differences in the chemical potentials due to differences in the crystal structure of the dye may bring about a little change in the concentration of the dye in the fiber. Such minute change may be insignificant. Hence, the effect of crystal modification of disperse dyes on their dyeing behavior on polyamide fibers may be insignificant.

In conclusion, it may be said that crystal modification of disperse dyes has a significant effect on their dyeing behavior on polyester fibers as in the case of secondary acetate reported by Biedermann.<sup>9</sup> The crystalline form in the metastable state gives higher color yield in dyeing than a more stable crystalline form. On heating, a metastable form is transformed into a more stable form, which will lower the color yield as well as the dyeing rate. These two aspects are of paramount importance in commercial dyeing of polyester fibers with disperse dyes. The tendency of transformation of a metastable form to a more stable one will be rapid at higher temperatures, which prevails in high-temperature dyeing (beam dyeing).

Due to this tendency, the color yield as well as the dyeing rate will be decreased. If the presence of a dispersing agent in the dyebath accelerates this tendency of transformation of one form into another, the dyeing rate and color yield are adversely affected. Therefore, in the manufacture of disperse dyes, the crystalline nature, in addition to the chemical nature, of the dye has to be considered seriously. The work on the dyeing of polyester fibers with disperse dyes of different crystal forms at 130°C under high-temperature dyeing conditions is under progress and will be reported later.

TABLE III  
Fiber Saturation Values of Different Crystal Forms of Dyes on  
Polyamide Fibers at 75°C

Dye	Fiber saturation value, g/100 g fiber		
	I	II	III
1. Foron Yellow SE-FL	0.67 (1.11) <sup>a</sup>	0.67 (1.12)	0.67 (1.12)
2. Foron Scarlet S-3GFL	1.15	1.02	1.02
3. Celliton Fast Yellow G	14.4	14.4	14.4
4. <i>p</i> -Nitroaniline → diethylaniline	0.18	0.18	—

<sup>a</sup> The values given in parentheses are those for dyeing carried out at 100°C.

## APPENDIX

## A Note on Earlier Results Reported in the Literature

In view of the results obtained by Biedermann<sup>9</sup> on the effect of crystal modification of a disperse dye on the dyeing of secondary cellulose acetate and also of the results of the present investigation on the dyeing of polyester fibers with disperse dyes of different crystalline forms, it may be possible to apply these results to some of the earlier observations on dyeing studies with disperse dyes reported in literature. Thus, as early as 1942, Vickerstaff and Waters<sup>7</sup> studied the rate of dyeing of 1-methylamino-4-anilinoanthraquinone at 85°C on secondary cellulose acetate in the presence of a dispersing agent. Their results are given in Table IV.

It is significant to note from these results that the dye uptake of the fiber increases with time up to 4 hr of dyeing and then decreases. In order to find out whether the equilibrium was really reached in 4 hr of dyeing, they carried out the dyeing for 24 hr at 85°C by taking different amounts of the dye in the dyebath. Some of their results are given in Table V.

In this case also, a very slight reduction in the quantity of the dye taken up by the fiber is noted in 24 hr of dyeing as compared to that in 4 hr. The small but definite decrease in the dye uptake by cellulose acetate has been attributed to the increase in particle size of the dye which lowered the dye concentration in water, and consequently the dye was desorbed in the water phase. It seems that the crystalline form of the dye used by Vickerstaff and Waters<sup>7</sup> might have been in a metastable state, which in the dyebath at 85°C for a prolonged period might have undergone a phase transition to a more stable form that could dye to a lower uptake by the fiber.

Daruwalla and Limaye<sup>14</sup> purified CI Disperse Violet 1 by crystallizing the dye from acetone and prepared dye samples of various particle size by (1) sublimation, (2) precipitation by sudden addition of water to an acetone solution of the dye, and (3) precipitation by gradual dilution of the acetone solution of the dye with water. These different dye samples were transferred to secondary cellulose acetate film from starch film by steaming. The rate of dye transfer from the starch film to the cellulose acetate film is shown in Figure 14.

It is seen that the rates of transfer of the dye forms prepared under different conditions of precipitation and by sublimation are different. This finding was explained on the basis of different

TABLE IV  
Dyeing of Cellulose Acetate with a Disperse Dye at 85°C<sup>a</sup>

Duration of dyeing, hr	Standard dispersion on fiber, cc
1	12.2
2	14.6
4	15.9
6	15.8
8	15.2

<sup>a</sup> From ref. 7.

TABLE V  
Dyeing of Cellulose Acetate with a Disperse Dye at 85°C with  
Different Starting Dye Concentrations<sup>a</sup>

Standard dispersion in initial dyebath, cc	Standard dispersion on fiber after 4 hr, cc	Standard dispersion on fiber after 24 hr, cc
5	4.83	4.80
20	13.40	13.00
40	15.00	14.70
80	15.70	15.30

<sup>a</sup> From ref 7.

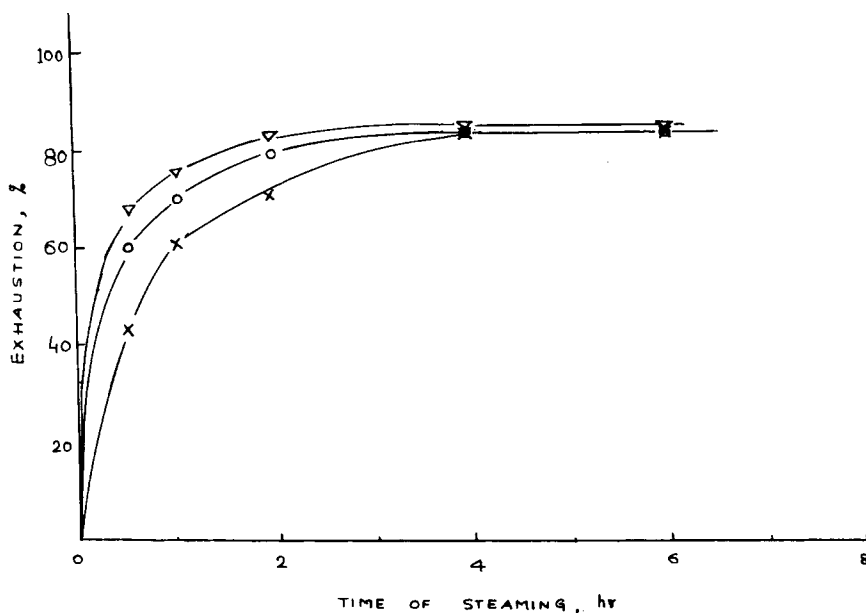


Fig. 14. Dye transfer rates from starch into secondary cellulose acetate during steaming: (▽) rapidly precipitated dye; (O) slowly precipitated dye; (X) sublimated dye.

particle size of the dye forms; the finer the particle size, the higher was the rate of dye transfer because of the higher rate of dissolution. Now it seems that the different forms of the disperse dye used by them might have been in different crystalline forms, which could have different rates of transfer from starch film into cellulose acetate film.

While determining the fiber saturation values of disperse dyes on cellulose acetate, Bird and co-workers<sup>15</sup> referred to the work of Harris, indicating that the presence of a dispersing agent reduced the fiber saturation values of the dye, 2-methoxy-4-nitroaniline  $\rightarrow$  N,N-bis- $\beta$ -hydroxyethyl-aniline. They also found that when *p*-nitroaniline  $\rightarrow$  N,N-bis- $\beta$ -hydroxyethyl-aniline was dyed on cellulose acetate in the presence of Dispersol LC and Lissapol LS, the dispersing agents reduced the fiber saturation values of the dye. It appears that these dyes might have been in a metastable crystalline form which, in the dyebath at 80–90°C and in the presence of the dispersing agents, might have undergone phase transition to a more stable crystalline form, which could lower the fiber saturation value.

McDowell and Weingarten<sup>16</sup> dyed commercial, purified, and preboiled (for 1 hr with water) forms of Dye I (1,4-diamino-2,3-diphenoxyanthraquinone) and Dye II (phenol  $\leftarrow$  *p*-phenylenediamine  $\rightarrow$  phenol) on polyester at 100°C for 150 min and found that in the case of Dye I, the commercial and purified forms had the same rate as well as the same extent of dyeing (1.1 g/100 g fiber), but the preboiled dye had a lower rate of dyeing and lower extent of dyeing (0.5 g/100 g fiber). For Dye II, the purified dye had the highest rate and extent of dyeing (3.8 g/100 g fiber). The preboiled and commercial forms dyed to lower extents (3.2 and 1.8 g/100 g fiber, respectively). The higher dye uptake and higher rate of dyeing may now be attributed to the different crystalline forms of the dyes. When Dye I and three other disperse dyes were dyed for 24 hr at different temperatures (90–140°C), the dye uptake decreased with increase in temperature. This decreased dye uptake might have been due to the fact that at higher temperatures the dye might have undergone a transition to a more stable form that could lower the dye uptake.

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