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Fundamental Studies of Solvent Dyeing with Tetrachloroethylene. II. The Diffusion of 1,4-Diaminoanthraquinone in Nylon 6

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Synopsis. The diffusion and sorption of 1,4-diaminoanthraquinone in nylon 6 were investigated using a cylindrical film-roll. The diffusion of the penetrant in nylon 6 from the aqueous dyebath was much faster than that from the tetrachlororoethylene (TCE) dyebath. The surface concentration from water was larger than that from TCE. The water added to the TCE dyebath accelerated the diffusion of the penetrant in nylon 6.

Solvent dyeing with halogenated hydrocarbons, especially tetrachloroethylene (TCE), has attracted considerable attention, and many publications on this subject have appeared in the recent literature.[1-6] In the solvent dyeing of poly(ethylene terephthalate) (PET) with disperse dyes, the diffusion from the TCE dyebath is faster than that from the aqueous one,[7] and the partition coefficient in the TCE system becomes smaller than in the aqueous system, as the solubility of dye in TCE is larger than that in water.[1]

In a previous paper, some comparisons of the diffusion of disperse dyes in PET have been made between the systems of water and of TCE.[7] The results obtained have confirmed the above facts and have shown that TCE affected the properties of PET. The glass transition temperature, T_g, of PET has been reduced and disperse dyes have been diffused into PET at lower temperatures than 80 °C.

In this paper, some comparisons will be made between the systems of water and TCE in the diffusion and sorption behavior of 1,4-diaminoanthraquinone in nylon. The effect of water added to the TCE dyebath will also be studied.

Experimental

Films. Biaxial oriented nylon 6 film (Emblem, Unitica Co., Ltd.) was used. It was cut 4 cm wide and 55 cm long, scoured with hot water, and heat-set at 95 °C in water for 24 hr. The film was wound so tightly on a glass tube (ϕ=1 cm) in the same solvent of the dyebath that there were no bubbles between the consecutive layers. The thickness of these films was measured by a thickness gage (Peacock Upright Dial Gage, Ozaki Manufacturing Co., Ltd.) to be 30.0 μm.

Chemicals. 1,4-Diaminoanthraquinone, supplied by Nippon Kayaku Co., Ltd., was crystallized by aqueous acetic acid and dried in a vacuum dryer for more than a week. The absence of impurities was checked by thin-layer chromatography. TCE of a technical grade (Toa Gosei Kagaku Kogyo Co., Ltd.) was used throughout without purification.

Diffusion and Sorption. The diffusion experiments were carried out in a 500 ml or 100 ml diffusion bottle with a reflux condenser. The dyeing conditions are shown in Table 1. Diffusion was carried out after the solution equilibrium of penetrant has been reached in the dyebath. After diffusion, the optical densities of the respective layers at the wavelength of 605 nm were measured by means of a Shimadzu MPS-50L Recording Spectrophotometer. The optical density of the penetrant on film was confirmed to obey Beer's law. The diffusion coefficient and surface concentration were calculated by the method of Sekido-Matsui from the concentration profile obtained experimentally.[8] The surface concentration was assumed to be equal to the equilibrium sorption.

Results and Discussion

The concentration profiles in the substrate are shown in Figs. 1—3. The plots are superimposed by a

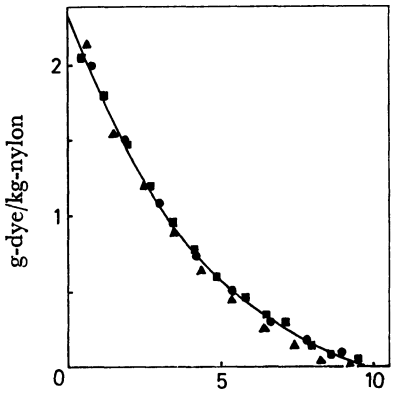

Fig. 1. Diffusion profile in nylon 6 from the water dyebath at 80 °C. (diffusion time, ■: 300 min, ▲: 180 min, ●: 120 min)

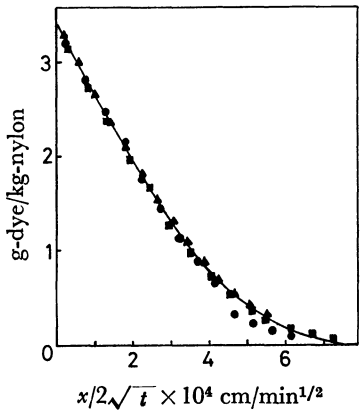

Fig. 2. Diffusion profile in nylon 6 from the 100 ml TCE+1.0 ml water dyebath at 80 °C. (diffusion time, ▲: 1050 min, ●: 720 min, ■: 600 min)

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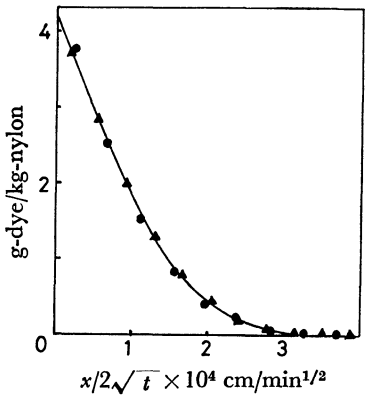

Fig. 3. Diffusion profile in nylon 6 from the 100 ml TCE+0.3 ml water dyebath at 80 °C. (diffusion time, ▲: 1260 min, ●: 900 min)

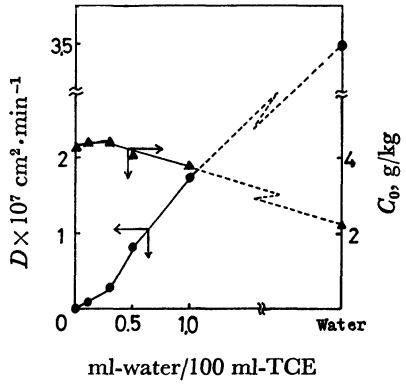

Fig. 4. The effect of water added to the TCE dyebath on the surface concentration C_0 and diffusion coefficient D in nylon 6 at 80 °C.

Boltzmann transformation ($x/2\sqrt{t}$), where x is the diffusion distance and where t is the time. These figures show that the dyeing system (nylon 6+water and/or TCE+dye) does not change during diffusion, even when more water than solubility in TCE was added, and that the diffusion obeys Fick's law. The diffusion coefficients from water were 300 times larger than those from TCE (Table 1). As the concentration in the aqueous dyebath was much smaller than that in the TCE one, the partition coefficient from the aqueous dyebath was larger than that from the TCE one.

The effect of additive water to the TCE dyebath is shown in Fig. 4. The diffusion coefficients increased with an increase in the additive water. The effect on the surface concentration was small. The solubility of water in TCE at 80 °C is estimated to be about 0.08 g in 100 ml of TCE.[9] The essential effect of such excess water is not clear.

Table 1. Diffusion in nylon 6 at 80 °C

Dyebath composition			Time of diffusion hr	Diffusion coefficient cm²/min
TCE ml	Water ml	Dye g		
0	500	0.1	2	3.79×10^{-7}
			3	3.57
			5	3.75
100	1.0	0.1	10—17.5	1.76×10^{-7}
	0.5		10—21	8.55×10^{-8}
	0.3		15—21	2.90
	0.1		20	1.04
	0		168	1.13×10^{-9}

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