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Note

Thin-layer chromatography of disperse dyes on polyamide sheets

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Disperse dyes are being increasingly used in the man-made fibre industry, particularly with polyester fibres. The finished commercial products are usually blends of two or more dye components resulting either from side reactions during the synthesis of the dyes, or introduced into the ready dye as shading components. A knowledge of the heterogeneity of the finished commercial products is essential both for their industrial application and for comparing dyes of different manufacturers and of different trade names. Analytical control carried out at considerable speed and high sensitivity has proved to be an effective means for the control of industrial dye synthesis.

The possibilities of using different chromatographic methods for a better solution of the analytical control of dyes, including disperse dyes, have been investigated extensively in recent years. The best results were achieved by using thin-layer chromatography (TLC) on silica gel plates with different solvent systems, was discussed by Dousheva *et al.*¹. TLC methods have since developed considerably and achieved exceptional acceleration and sensitivity by using polyamide sheets as the carrier. There are no data, however, on the use of this carrier in the dye industry.

The application of TLC with micropolyamide sheets for control of the heterogeneity of disperse dyes was studied in this work. Tests were made with different solvent systems on 18 dyes produced by four companies.

EXPERIMENTAL

TLC was performed with appropriate attention to the necessary conditions for reproducibility of the chromatograms using micropolyamide sheets produced by Schleicher & Schüll (Dassel, F.R.G.), cut to 3 × 3 cm in size. The sheets were used without activation; after use they were washed with acetone-85% formic acid (9:1) and dried with warm air. When cleaned in this way, the sheets can be used at least ten times.

The following organic solvents were tested both singly and in combination: *n*-heptane, *n*-hexane, light petroleum, toluene, benzene, chlorobenzene, chloroform, dichloroethane, diethylether, ethyl acetate, 1,4-dioxane, acetone, ethanol, methanol and formamide.

The following solvents were used in the systems showing optimal separation after being purified as described. Benzene (purum) was shaken continuously with concentrated sulphuric acid (10:1) for 30 min. After washing with water, 2 *M* sodium carbonate solution and water, the benzene was dried over calcium chloride, followed by fractional distillation on a short column. The fraction of b.p. 80–81°C was used. Acetone (puriss) was boiled for several hours on a reflux condenser over sodium carbonate and then subjected to repeated distillation. The fraction of b.p. 56–57°C was used as a dye solvent. Light petroleum (purum) was subjected to fractional distillation and the fraction of b.p. 64–66°C was used. Chloroform (puriss) was washed with 10% sodium hydrogen carbonate solution and water, then dried over calcium chloride and subjected to fractional distillation. The fraction of b.p. 57–58°C was used. Glacial acetic acid was boiled for 4 h on a reflux condenser over 3% CrO₃ and then subjected to distillation on a short column. The fraction of b.p. 115–116°C was used. The remaining solvents were purified after distillation of the analytical-reagent grade products.

The specimens investigated were applied on the starting line as a 0.1% solution in acetone according to Rettie and Haynes². The chromatography was carried out to the edges of the sheet, taking about 3 min.

The best solvent systems proved to be the following: (S1) benzene–light petroleum–methanol–glacial acetic acid (3:9.5:1:0.1); (S2) light petroleum–chloroform–methanol–glacial acetic acid (6:1:0.3:0.2); (S3) chloroform–*n*-hexane–methanol–glacial acetic acid (5:30:2:0.1); and (S4) light petroleum–benzene–methanol (5:11:2).

TABLE I

TLC OF DISPERSE DYES USING SOLVENT SYSTEMS S1–S4 ON POLYAMIDE SHEETS

No.	Dye*	Colour of spots	<i>R_F</i> value**			
			S1	S2	S3	S4
1	Terasil brillant yellow	Lemon yellow 6G	0.35	0.24	0.22	0.32
2	Terasilmarineblau BGL	Yellow-brown	—	—	0.00	
		Blue	0.42	0.34	0.30	
		Blue	0.68	0.48	0.48	
		Blue	0.90	0.68	0.68	
3	Terasilrot 3BL	Red	0.05	0.00	0.00	0.02
		Purple	0.18	0.08	0.08	0.11
		Red	0.54	0.37	0.32	0.46
4	Terasilbraun 3R	Brown	0.19	0.08	0.08	
5	Terasilbrillantviolet BL	Blue	0.30t	0.12t	0.12	
		Violet	0.58	0.36	0.30	
6	Terasilschwarz BL	Grey	0.00	0.00	0.00	
		Brown	0.20	0.09	0.08	
		Light brown	0.22	0.12	0.11	
		Light brown	0.30	0.20	0.18	
		Blue	0.43	0.35	0.29	
		Grey	0.68	0.48	0.46	
		Blue	0.91	0.69	0.67	

(Continued on p. 450)

No.	Dye*	Colour of spots	R_f value**			
			S1	S2	S3	S4
7	Dispersol blue D-2R	Blue	0.00	0.00	0.00	0.00
		Blue	—	—	—	0.21t
		Blue	0.16t	0.10t	0.06t	0.75t
8	Dispersol red C-3B	Pink	0.00	0.00	0.00	
		Pink	0.13	0.08	0.07	0.11
		Red	0.56	0.42	0.36	0.46
9	Dispersol yellow C-42	Orange-yellow	0.00	0.00	0.00	0.22t
10	Resolinmarineblau GLS 200%	Blue	0.69	0.52	0.47	
11	Resolinrot BBL 200%	Pink	0.00	0.00	0.00	—
		Pink	0.12	0.08	0.07	0.10
		Red	0.56	0.42	0.36	0.46
12	Resolinorange 3GL	Yellow	0.00	0.00	0.00	0.24d
13	Syntengelb P-5G	Yellow	0.48	0.24t	0.26t	0.38t
14	Syntenblau P-BGI	Blue	0.04t	0.00	0.00	0.00
		Blue	0.28t	0.12	0.14	0.75
15	Sytenrubin P-3B	Ruby	0.16	0.05	0.08	
16	Syntenblau GRL	Grey	0.00			
		Blue	0.10	0.05dt	0.05dt	0-0.45 dt
		Pink	0.84	0.24	0.24	
17	Syntenbraun P-RBL	Grey	0.02dt		0.02	
		Pink	0.12	0.04	0.05	
		Light brown	0.16		0.09	
		Blue	0.32	0.16	0.17	
		Orange	0.53	0.28	0.27	
		Yellow-brown	0.68	0.37	0.36	
		Blue	0.84	0.51	0.53	
18	Sytenschwarz P-2BL	Grey	0.02dt		0.02	
		Pink	0.12	0.04	0.05	
		Light brown	0.16		0.09	
		Blue	0.32	0.16	0.17	
		Orange	0.53	0.28	0.27	
		Yellow-brown	0.68	0.37	0.36	
		Blue	0.84	0.51	0.53	

* Producers of dyes: Terasil, Ciba-Geigy; Dispersol, ICI; Resolin, Bayer; Synten, Ciech.

** d = Diffuse spot; t = tailing.

The dye specimens were selected so as to contain individual synthetic dyes from four manufacturers; some of them could be the same chemical products as well as dyes representing a complex composition of several components, say black and brown. The names of these dyes and manufacturers are given in Table I.

RESULTS AND DISCUSSION

The heterogeneity of the investigated dyes obtained by TLC on micropolyamide sheets is given in Table I. Figs. 1-4 indicate the quality of the separation process achieved with the use of the above four solvent systems.

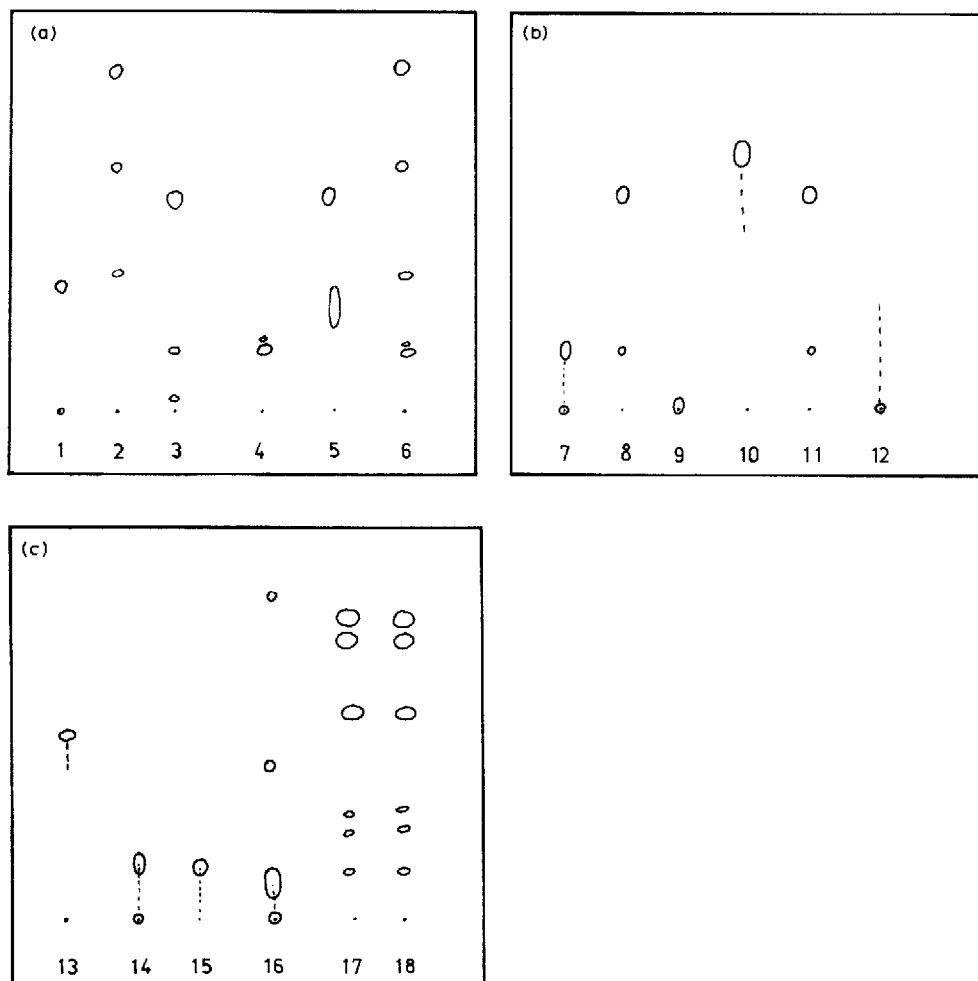


Fig. 1. TLC of dyes in benzene-light petroleum-methanol-glacial acetic acid (3:9.5:1:0.1) (system S1).

Solvent system S4 allows the migration of the dyes that showed complete immobility in the other systems. In this system the other dyes move very fast and therefore the information obtained refers to the heterogeneity only of the dyes which in the other two systems remain at the start.

As can be seen from the results, although the R_F values of the dyes were higher in S1, the separation effect was equal for S1, S2 and S3. The separation of the dyes investigated in this work showed considerably comparable heterogeneity to that obtained by TLC on silica gel. The particularly high sensitivity of the present method is apparent in the separation of the complex mixture Syntenschwarz P-2BL, where six components were separated, whereas Dousheva *et al.*¹ found only four components. The compactness of the chromatographic spots obtained on polyamide is an advantage. On the basis of the results, we conclude that Terasilmarineblau BGL is included in the combination of Terasilschwarz BL, and that Syntenbraun P-RBL

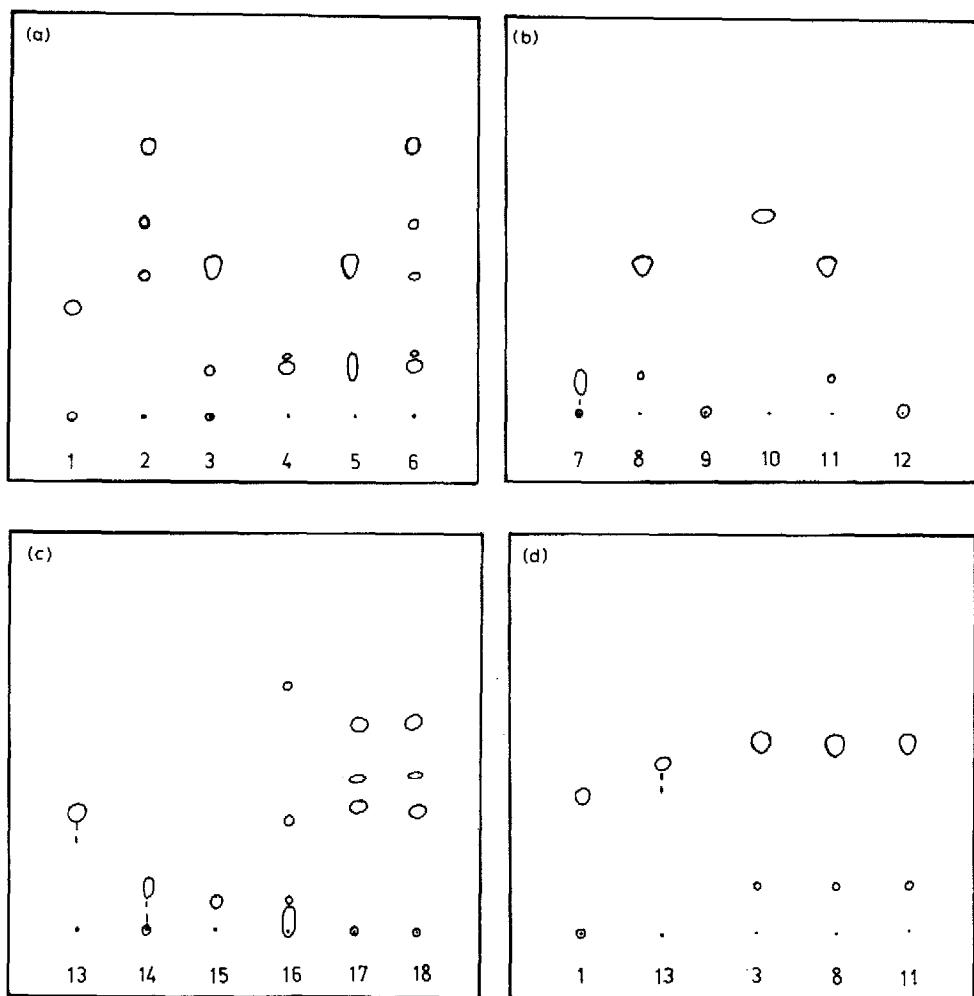


Fig. 2. TLC of dyes in light petroleum-chloroform-methanol-glacial acetic acid (6:1:0.3:0.2) (system S2).

and Syntenschwarz P-2BL are also mixtures of the same components in different proportions.

The proposed method can rapidly solve the question of the interchangeability of the dyes from different producers. Thus, from Fig. 4 it can be seen that Dispersol blue D-2R and Syntenblau P-BGL are similar chemical products. From Fig. 2d and from the other figures it is clear that Terasilrot 3BL, Dispersol red C-3B and Resolinrot BBL 200% are identical products. It can be assumed that the presence of the two admixed red components with low mobility in the three dyes explains their technological origin. In fact, the difference between these three products proved to be the different amounts of the admixed components. Although composed of only one component with similar chromatographic behaviour (Fig. 1b), the identity of Dispersol yellow C-4R (No. 9) and Resolinorange 3GL (No. 12) is apparent in Fig. 4. Although system S4 leads to considerable tailing for some dyes, it proved useful in solving the

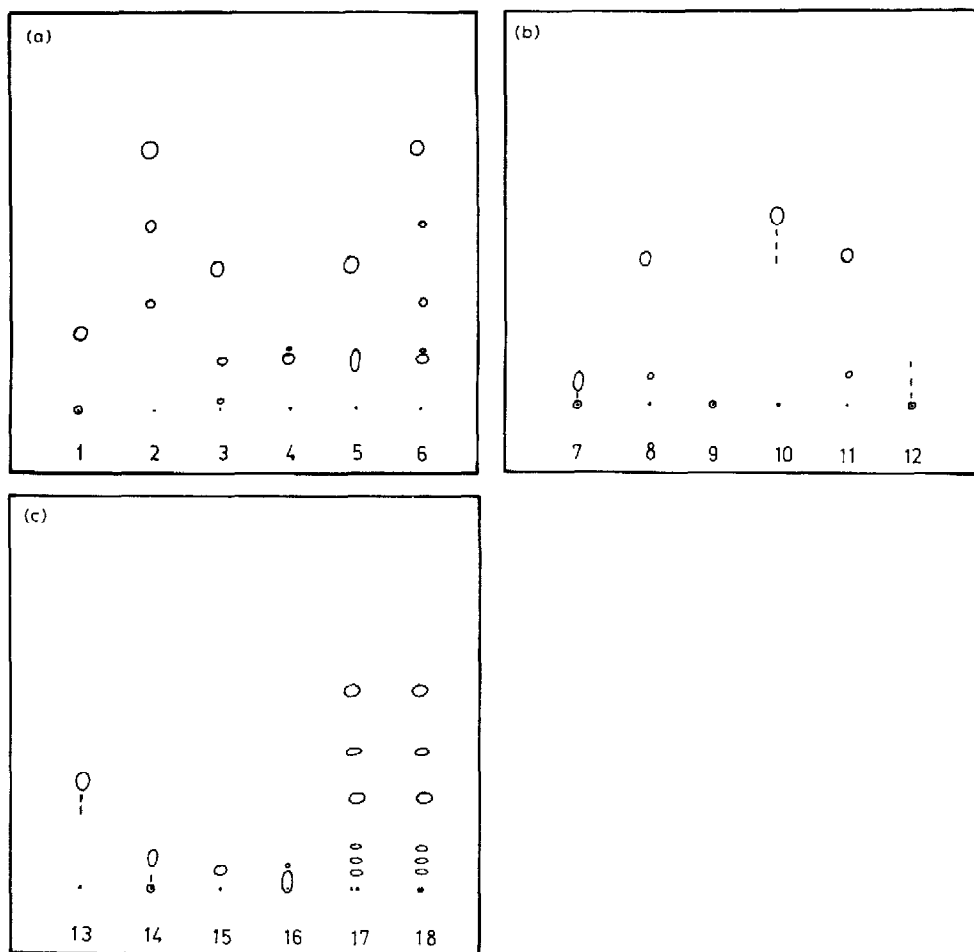


Fig. 3. TLC of dyes in chloroform-*n*-hexane-methanol-glacial acetic acid (5:30:2:0.1) (system S3).

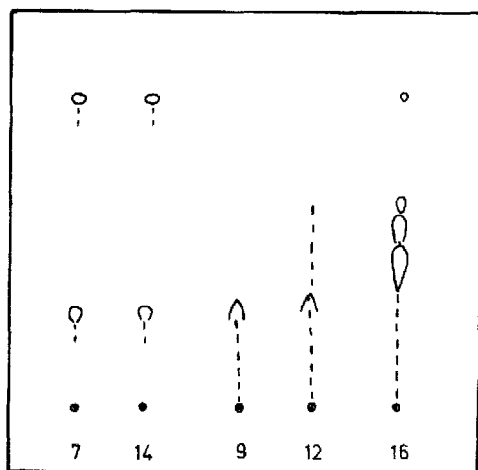


Fig. 4. TLC of dyes in light petroleum-benzene-methanol (5:11:2) (system S4).

problems of homogeneity and chromatographic comparability. The individuality of the two yellow dyes, Nos. 1 and 13 (Fig. 2d), is proved in the same manner.

These results show the advantage of having more than one solvent system and the possibility of solving some difficult questions without applying other methods. They also show that the proposed chromatographic systems make it possible to investigate disperse dyes rapidly and with sufficient reliability as regards their heterogeneity and identification. Naturally, in the latter instance it is necessary to extract the different fractions from the thin-layer plate with a solvent (acetone) and to compare the absorption spectra of the dyes in the visible and UV regions. Because of its rapid application and high sensitivity, the proposed method is very useful for the industrial control of the synthesis of disperse dyes and for toning finished commercial products.

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