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Note

Thin-layer chromatography of disperse dyes

M. DOUSHEVA, A. ARSOV, V. KOSTOVA and B. MESROB
Institute of Chemical Technology, Sofia 56 (Bulgaria)
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Disperse dyes are being increasingly used in the man-made fibre industry, in particular with polyester fibres. As with other types of dyes, disperse dyes are blends of several components. These blends may differ owing, on the one hand, to the production process, in which side reactions occur, and, on the other, to a shaded blending which is often used in order to obtain a particular type of dye. A knowledge of the character of these blends and of the number of components in mixed dyes is indispensable for the proper control of dye synthesis as well as for characterizing different commercial products. The successful thin-layer chromatography (TLC) of dye mixtures is also of great importance in studies of the structures of the different components, which must first be isolated in a pure state.

In the investigation of disperse dyes, however, TLC has been used only to a limited extent. Wollenweber[1] used TLC to separate disperse dyes on a thin layer of acetylated cellulose with ethyl acetate–tetrahydrofuran–water (6:35:47) as solvent. Subsequently, Rettie and Haynes[2] separated these dyes on silica gel plates with tetrahydrofuran–water–4 *N* acetic acid (80:54:0.05) and chloroform–acetone (90:10) as solvents. More recent work[3] recommends the TLC of disperse dyes with cyclohexane–nitrobenzene–methyl ethyl ketone (8:7:3) and chloroform–*n*-hexane–acetone (3:1:1) as solvents. Another solvent system, proposed by Schweppe[4] for TLC on silica gel plates, is chloroform–methanol (95:5). Gemzova and Gasparič[5] succeeded in separating disperse dyes on Silufol plates in chloroform and chloroform–acetone (5:1).

The main purpose of this work was to make more extensive use of TLC in the study of disperse dyes during their production and application. Tests were made on 27 dyes produced by four companies. The TLC of many of these dyes was not successful when using the previously recommended conditions.

MATERIALS AND METHODS

TLC was performed according to Stahl[6] on 10 × 14-cm glass plates with kieselgel G nach Stahl (Type 60) as carrier and on 20 × 20-cm Merck Fertigplatten with the same carrier.

The solvent systems used were prepared with the following components. Ethyl acetate (puriss) was washed with a 10% sodium hydrogen carbonate solution to a neutral reaction and then with a portion (20% of the solvent's volume) of 50% calcium chloride solution. After drying over sodium sulphate and distillation, the

54–56° b.p. fraction was used. Benzene (purum) was shaken twice with concentrated sulphuric acid (10:1, v/v) for 30 min. After washing with water, 2 *M* sodium carbonate solution and water, it was dried over calcium chloride, followed by fractional distillation on a short column. The distillate of b.p. 80–81° 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° was used. Light petroleum (purum) was subjected to fractional distillation and the fraction of b.p. 64–66° was used. Chloroform (puriss) was washed with a 10% sodium hydrogen carbonate solution and water, then dried over calcium chloride and subjected to fractional distillation. The distillate of b.p. 57–58° was used. The remaining solvents were used after a single distillation of the analytical-reagent grade products.

The specimens investigated were applied on the starting line as a 0.2% solution in acetone according to Rettie and Haynes[2]. The chromatograms were run until the solvent front had travelled 120–140 mm.

The dyes investigated were selected so as to contain individual synthetic dyes, dyes subsequently corrected by blending them with others, counter-dyes produced by different firms, and dyes representing a complex composition of several components, say black or brown. The names and trademarks of these dyes are given in Table I.

RESULTS AND DISCUSSION

When the solvent systems cited in the literature were applied to the dyes tested here, the results were unsatisfactory as many of them had high mobilities without the successful separation of the components.

In the course of developing optimal solvent systems, the components tested included *n*-heptane, *n*-propanol, isopropanol, *n*-butanol, methyl ethyl ketone, acetic acid, chloroform and dimethylformamide, but only those systems which gave a satisfactory separation of all dyes are mentioned here. The best chromatographic systems proved to be the following: S_1, *n*-hexane–ethyl acetate–acetone (5:4:1); S_2, light petroleum–tetrahydrofuran–acetone (6:2:1); S_3, benzene–methanol–acetone (20:2:1); and S_4, benzene–ethyl acetate (5:5).

The TLC results with these systems on a silica gel thin-layer plate are shown in Table I, which indicates the C.I. number, colour and R_F values of the components into which the tested dyes separated. The separations with solvent systems S_1, S_2 and S_3 are shown in Figs. 1, 2 and 3.

The chromatograms revealed that the dyes tested are separated best with system S_1. The mobility of the dyes in system S_2 is more compact, while in S_3 dyes Nos. 10 to 27 are distributed along the whole length of the plate. Also in systems S_3 the dyes of the Synten type (Ciech) (except Syntenrot P-G-RL and Syntenblau P-3B) move very fast and are not separated satisfactorily. System S_4 gave a similar unsatisfactory separation of the Synten dyes, but the other dyes were very well separated, with as a good distribution along the plate as in system S_1. S_4 is the only system to give diffuse spots for two Foron dyes. The general shapes of the spots in all of the proposed systems are good, being compact even for high R_F values. The sensitivity of the method increases with continuing use of these chromatographic systems, owing to the weak diffusion during movement along the plate. As can be seen from Table I,

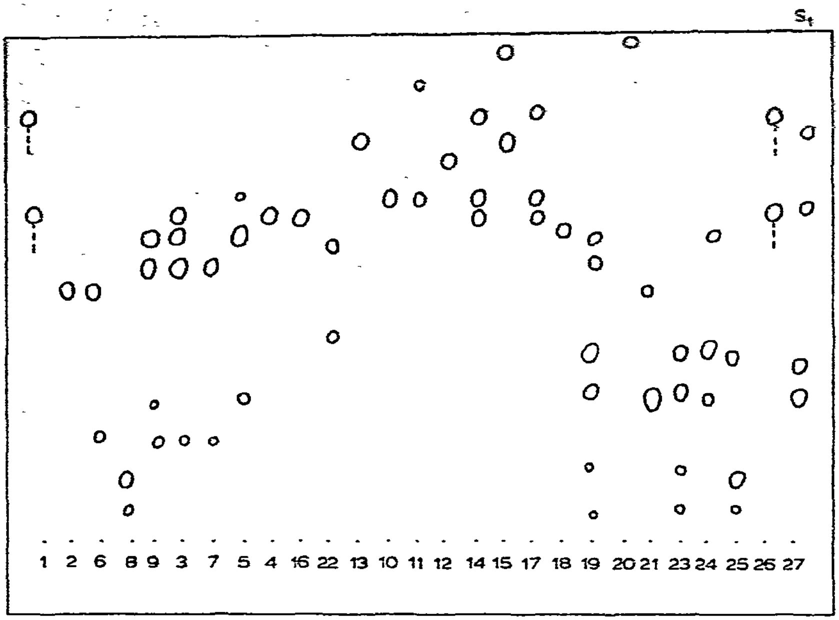

Fig. 1. TLC of dyes investigated in the *n*-hexane–ethyl acetate–acetone (5:4:1) system (S_1).

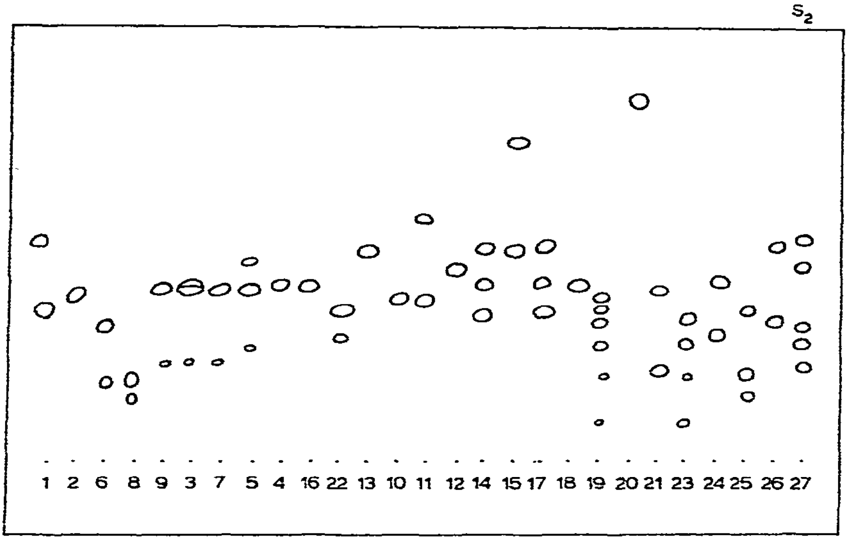

Fig. 2. TLC of dyes investigated in the light petroleum–tetrahydrofuran–acetone (6:2:1) system (S_2).

each system has particular advantages in the dye separations. The rate of development of the chromatograms is fairly good (Table II).

The quality of some of the dyes investigated can be deduced from Fig. 1. It can be seen, for instance, that Syntenblau P-BGL is a counter-dye of Terasilblau R, and this was also confirmed by the chromatograms in the other systems. There is probably much in common in the synthesis of these dyes, for in both instances two

TABLE I

TLC OF DISPERSE DYES USING SOLVENT SYSTEMS S_1–S_4

No.	Dye	Producer	Colour Index No.	Colour of spots	R_F value*,**			
					S_1	S_2	S_3	S_4
1	Syntenblau P-BGL	Ciech	C.I. Disperse blue 73	Blue	0.83t	0.52	0.87	0.79t
				Blue	0.65t	0.33	0.48	0.68t
2	Syntengelb P-5G		C.I. Disperse yellow 5.12790	Lemon yellow	0.49	0.75	0.37	0.50
3	Syntenschwarz P-2BL		—	Orange-yellow	0.64			0.63
				Scarlet	0.61	0.39	0.74	0.60
				Marine blue	0.54		0.71	0.57
				Orange	0.27	0.27	0.35	0.27
				Blue	0.19	0.23	0.35	0.20
4	Syntengelbbrown P-2RL		C.I. Disperse orange 30	Orange-yellow	0.64	0.39	0.75	0.63
5	Syntenrot P-3GL		C.I. Disperse red 54	Scarlet	0.61	0.39	0.74	0.60
				Pink	0.68	0.47		
				Orange	0.27	0.27	0.35	0.27
6	Syntenrot P-GRL		—	Red	0.49	0.34	0.69	0.57
				Pink-red	0.21	0.19	0.33	0.25
7	Synten marine blau P-BL		C.I. Disperse blue 79	Marine blue	0.54	0.39	0.71	0.57
				Blue	0.19	0.23	0.37	0.19
8	Synten rubin P-3B		C.I. Disperse red 5.11215	Ruby	0.12	0.20	0.23	0.10
				Pink-red	0.06	0.09	0.10	0.06
9	Synten goldgelb P-2BL		—	Scarlet	0.61	0.39	0.73	0.60
					0.54		0.71	0.57
10	Resolin rot BRL	Bayer	C.I. Disperse red 134	Red	0.66	0.37	0.85	0.74
11	Resolin orange 3GL		C.I. Disperse orange 60	Orange	0.67	0.37	0.40	0.82
				Yellow	0.90	0.54		0.67
				Yellow				
12	Forongelb SE-6GFL	Sandoz	—	Lemon yellow	0.74	0.43	0.62	0.75
13	Resolingelbbraun G-LS	Bayer	C.I. Disperse orange 67	Orange-yellow	0.80	0.48	0.92	0.81
14	Foronbraun S-2BL	Sandoz	—	Orange	0.67	0.41	0.73	0.63d
				Blue-violet	0.63		0.80	0.70
				Blue	0.83	0.52	0.87	0.79d
				Blue	0.65	0.33	0.48	0.68
15	Foronrot S-2GL		—	Blue-violet	0.96	0.73	0.98	0.90
				Orange-red	0.79	0.49	0.87	0.76

16	Forongelbbraun S-2RFL		C.I. Disperse orange 30	Orange-yellow	0.64	0.39	0.75	0.63
17	Forongrau S-GL		—	Orange	0.67	0.41	0.73	0.63d
				Blue-violet	0.63		0.80	0.70
				Blue	0.83	0.52	0.87	0.79d
				Blue	0.65	0.33	0.48	0.68
18	Foronscharlach S-3GFL		C.I. Disperse red 54	Scarlet	0.61	0.39	0.74	0.60
19	Terasilschwarz S-RL	Ciba-Geigy	—	Orange	0.59	0.34	0.63	0.52
				Red	0.53	0.37		0.50
				Marine blue	0.36	0.32	0.66	0.39
				Blue	0.28	0.25	0.58	0.32
				Blue	0.13	0.19	0.35	0.21
				Blue	0.09	0.09	0.31	0.14
20	Terasilgelb 3RL		C.I. Disperse yellow 84	Lemon yellow	0.98	0.82	0.99	0.96
21	Terasilorange 3RL		C.I. Disperse orange 38	Orange	0.26	0.38	0.57	0.49
				Yellow-orange	0.50	0.20	0.23	0.35
				Orange				0.67
22	Terasilgelbbraun 2R		C.I. Disperse orange 68	Yellow	0.58	0.34	0.68	0.61
				Yellow-orange	0.40	0.28	0.56	0.41
23	Terasilmarineblau S-GL		—	Marine blue	0.36	0.32	0.66	0.39
				Blue	0.28	0.25	0.58	0.32
				Blue	0.13	0.19	0.35	0.21
				Blue	0.09	0.09	0.31	0.14
24	Terasilorange R		C.I. Disperse orange 80	Orange	0 38	0.27	0.70	0.58
				Yellow	0.61	0.39	0.60	0.46
				Yellow	0.26	0.08	0.32	0.09
25	Terasilbraun 3R		C.I. Disperse brown	Brown	0.12	0.20	0.18	0.09
				Orange	0.37	0.35	0.32	0.28
				Orange	0.06	0.14	0.14	0.05
26	Terasilblau R		C.I. Disperse blue 73	Blue	0.83t	0.52	0.87	0.79t
				Blue	0.65t	0.33	0.48	0.68t
27	Terasilschwarz SL		—	Blue	0.79	0.49	0.60	0.67t
				Blue	0.67	0.43	0.50	0.53t
				Pink-red		0.27	0.31	0.25
				Yellow-brown	0.28	0.21	0.22	0.33
				Blue	0.35	0.30	0.32	0.27

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[*] d = diffuse spot.

[**] t = tailing.

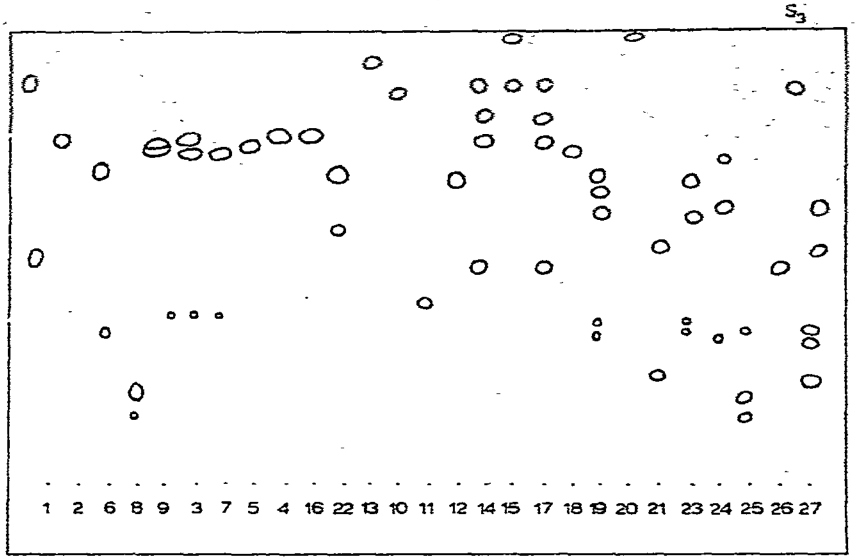

Fig. 3. TLC of dyes investigated in the benzene–methanol–acetone (20:2:1) system (S_3).

TABLE II

LENGTH AND TIME OF DEVELOPMENT WITH THE FOUR SOLVENT SYSTEMS

Solvent system	*Total run (mm)*	*Time (min)*
S_1	140	70
S_2	117	60
S_3	120	40
S_4	140	45

monochrome dyes (probably isomers) are obtained in almost the same ratios. Their identity is also suggested by the similar chromatographic behaviour of the spots: in S_1 they give identical although very weak tailing. The view that these dyes are chemically identical was also confirmed by previous studies of their visible and IR spectra[7].

Another interesting fact is that the dyes Foronbraun S-2RFL and Forongrau S-GL contain the same bluec omponents as Terasilblau R. This is more pronounced in S_3 (Fig. 3). All chromatograms suggest that Syntengelbbraun P-2RL and Forongelbbraun S-2RFL are identical. Likewise, Forongelbbraun S-2RFL forms part of the dyes Foronbraun S-2BL and Forongrau S-GL, which makes it clear that these dyes are colour combinations in different ratios.

The possibility of using more than one system permits greater reliability to be achieved in TLC identifications. For instance, in system S_3 the dyes Syntengelb P-5G and Syntengelbbraun P-2RL have the same R_F values although they obviously differ in colour. System S_1, however, reveals that these dyes also differ substantially in their R_F values (0.48 and 0.62, respectively).

The results show that the proposed solvent systems make it possible to investigate disperse dyes quickly and with sufficient reliability as regards homogeneity, components and identity. Of course, a definite conclusion about identities should be drawn only after extracting the spots from the plate with acetone and comparing their absorption spectra in the visible and UV regions. The systems also permit the industrial and laboratory syntheses of these dyes to be controlled and, in the course of synthesis, changes to be made in the proportions of the reaction products in the blend. The relatively compact character of the spots of the different dye components renders the proposed solvent systems most convenient for preparative TLC purification of the dye components in order to study their structure and colour behaviour.

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