

PAPER CHROMATOGRAPHY OF DYES

I. PAPER CHROMATOGRAPHY OF DISPERSE DYES*

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The establishment of a suitable chromatographic method for the determination of the purity and identity of disperse dyes, has aroused interest because of the importance of these dyes for the treatment of synthetic fibres.

INTRODUCTION

Paper chromatography of disperse dyes was described by a number of authors¹⁻¹⁴. We have studied these methods and found that they are generally not sufficiently sensitive for the separation of more complex mixtures of disperse dyes, and, furthermore, that with the majority of methods there is a lack of relation between the chemical constitution of the dyes and their chromatographic behaviour, this being an indispensable requirement for exact analysis. Very satisfactory results were obtained by the method of GASPARIČ AND TÁBORSKÁ^{12, 13}. The only drawbacks are the necessity of impregnating the chromatography paper with 1-bromonaphthalene, a rather time-consuming procedure, and the unpleasant odour of this substance.

While developing our method we found very effective chromatographic separation of disperse dyes could be obtained on unmodified chromatography paper by employing aqueous pyridine solvent systems. Of thirty brands of chromatography papers, Schleicher & Schüll 589³ (blue ribbon) quantitative filter paper proved the only one suitable^{11, 14}.

CHROMATOGRAPHIC TECHNIQUE

In the developing of chromatograms, the ascending technique was employed. The distance from the start of the chromatogram to the edge of the paper was 30 mm and the separation track was 400 mm long. Solutions of dyes were applied as spots of 1% acetone solution by means of a micro pipette in 0.05 mg quantities. Chromatograms were developed for 12 hours at 20-22°.

For disperse azo dyes, the solvent system pyridine-water (1:3), and for anthraquinone disperse dyes the solution pyridine-water (1:5) were found suitable.

The R_F values of disperse dyes in pyridine eluent systems depend on the chemical structure of the dyes and on the functional groups and substituents.

Figs. 1 and 2 show the chromatographic separation of a mixture of disperse azo dyes and Fig. 3 shows that of a mixture of anthraquinone disperse dyes.

* This topic was briefly dealt with in the report entitled "Systematic method of paper chromatography of water-soluble and insoluble dyes" presented at the Conference and Symposium on Paper Chromatography (Prague, 1961).

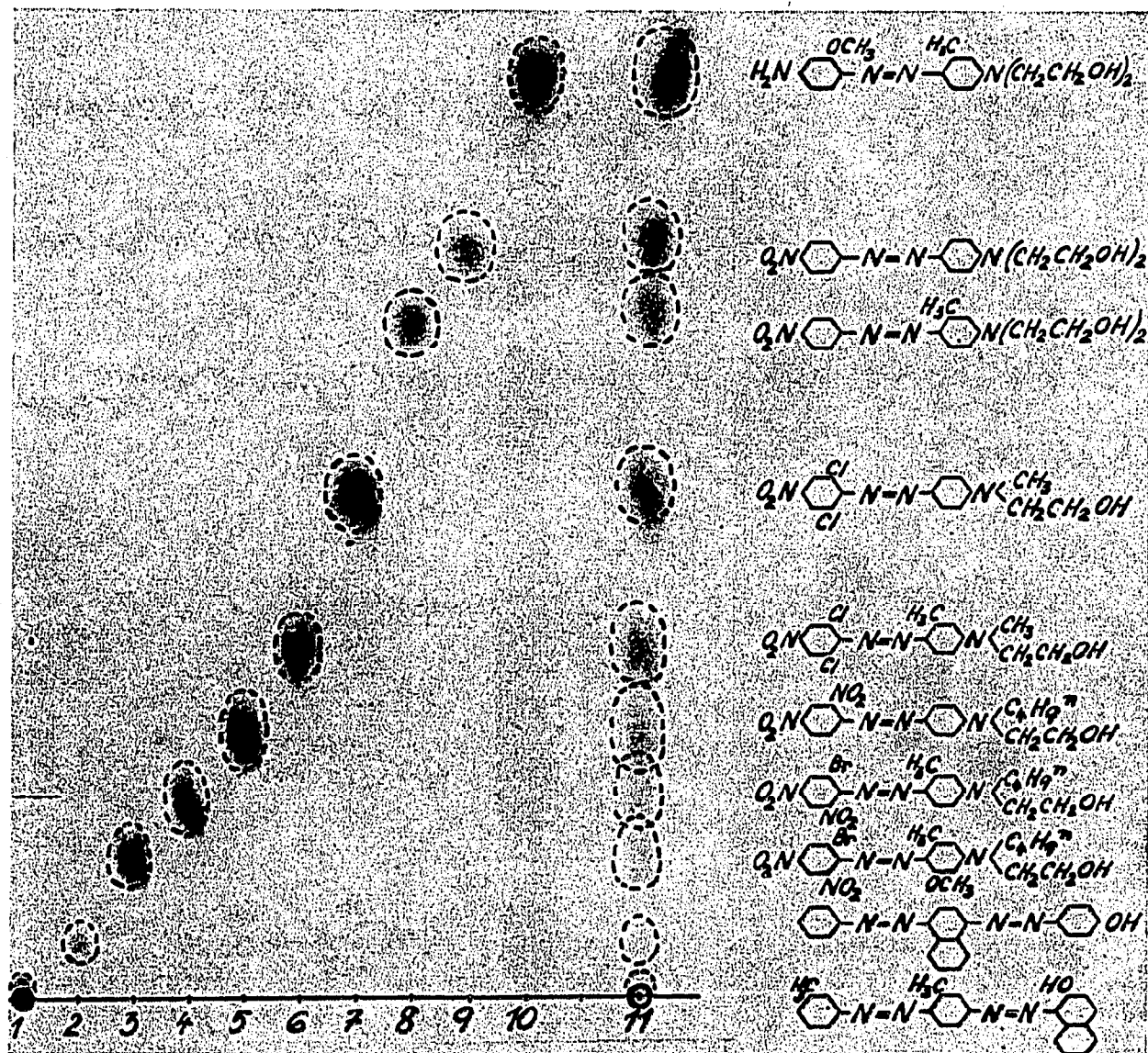


Fig. 1. Example of chromatographic separation of a mixture of disperse azo dyes.

RESULTS

We have analysed by the method described some six hundred disperse dyes of various commercial names. The results obtained have enabled us to complete some data given in the Colour Index¹⁵ on analogous disperse dyes of varying trade names. In Table I a compilation is made of the results of separation of the more important disperse dyes of known constitution. In this compilation, the system used in the Colour Index was followed.

From the results shown in Table I, it is evident that in many cases the dyes contain secondary components (often isomers) originating in the reaction by which

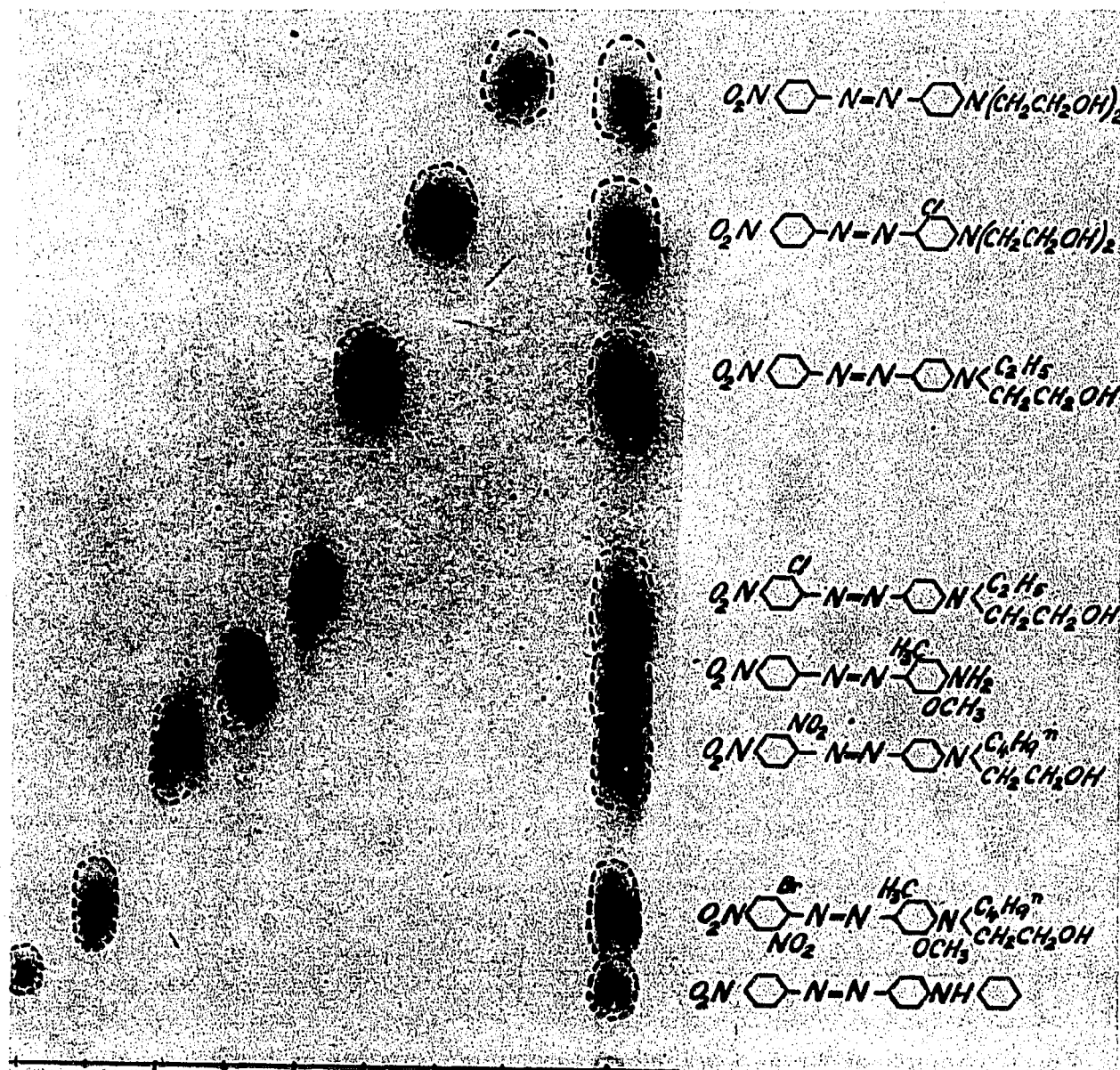


Fig. 2. Example of chromatographic separation of a mixture of disperse azo dyes.

they are produced. Anthraquinone blue dyes of more complex chemical constitution (more complex substitution) contain the most secondary components.

The number and character of the secondary components (by-products) in analogous dyes is not always the same. This may be explained by the varying degree of purity of intermediate products and the perfection of the method of manufacture.

CONCLUSIONS

From the chromatographic behaviour of these dyes the following conclusions may be made:

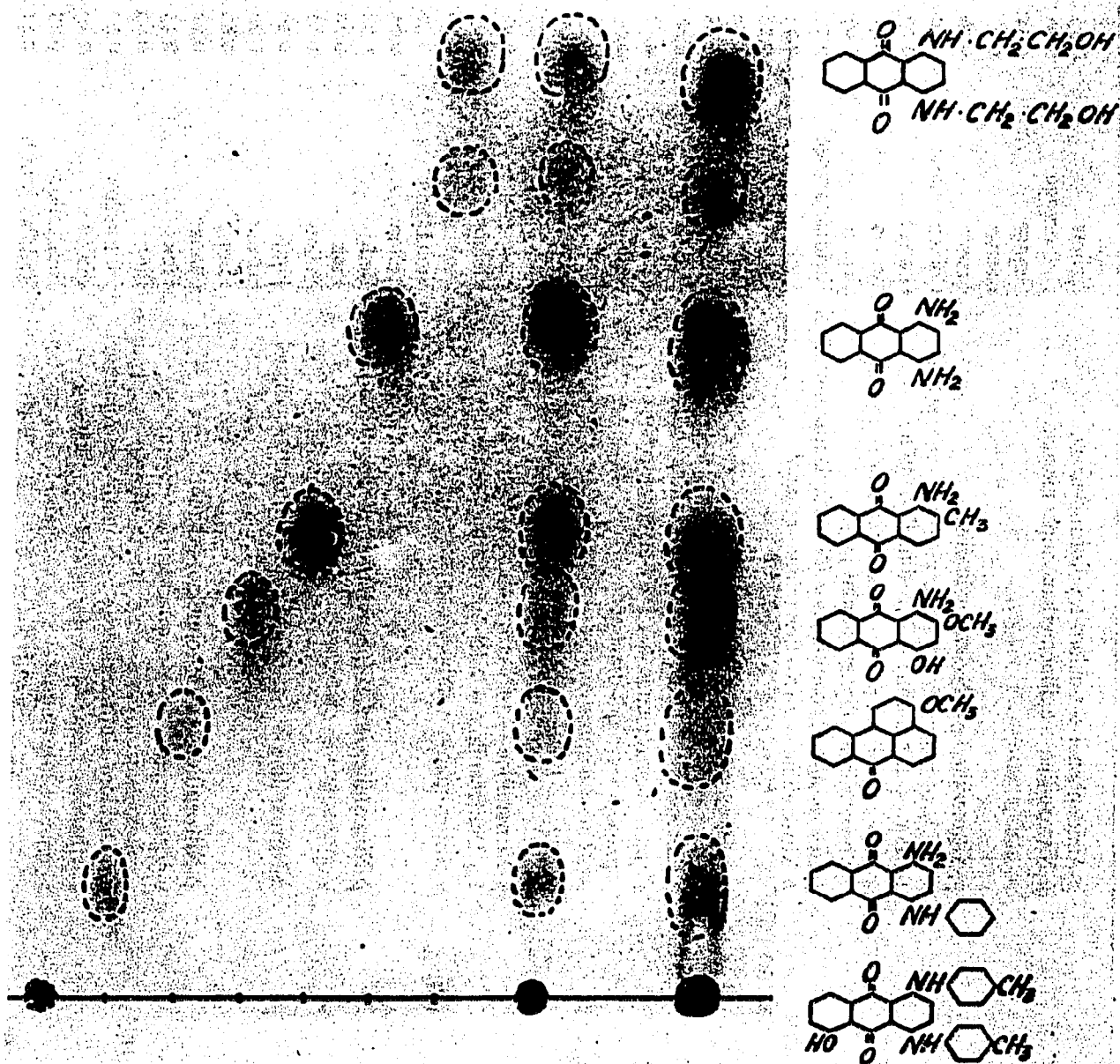


Fig. 3. Example of chromatographic separation of a mixture of anthraquinone disperse dyes.

- (a) Disazo dyes possess a lower R_F value than monoazo dyes.
- (b) Substitution of azo- and anthraquinone derivatives entailing a substantial influence on molecular weight tends to lower the R_F value.
- (c) Anthraquinone dyes are adsorbed to a lesser degree, therefore possess a higher R_F value than azo dyes, nitro dyes, methine derivatives and dyes of the arylaminoquinone and aminonaphthalimide group.
- (d) The presence of $-\text{OCH}_3$ and $-\text{CH}_3$ groups and of halogens decreases the R_F value of azo dyes as their number increases.
- (e) With anthraquinone dyes, considerable decrease of R_F value is caused by alkylation and arylation of the amino group in the nucleus. With aminoanthraquinones

TABLE 1
RESULTS OF CHROMATOGRAPHIC SEPARATION OF DISPERSE DYES

Colour index	Commercial name	Chemical constitution	Colour of band	R _F
10350	Celliton Fast Yellow RR	<i>p</i> -Amidophenol → 1-chloro-2,4-dinitrobenzene	Yellow	0.55
11005	Celliton Fast Orange GR	<i>p</i> -Nitroaniline → aminomethanesulphonic acid	Dull orange	0.00
			Orange	0.51
			Orange*	0.87
11025	Diazo Nero Microsetile G	<i>p</i> -Nitroaniline → <i>N,N</i> -dimethylaniline	Brown	0.00
11035	Cellitazol AZN	2-Chloro-4-nitroaniline → <i>N,N</i> -dimethylaniline	Golden yellow	0.72
			Orange	0.00
			Brown	0.46
11080	Dispersol Fast Orange A	<i>p</i> -Nitroaniline → diphenylamine	Orange	0.07
11100	Celliton Fast Brown 3R	2,6-Dichloro-4-nitroaniline → 2-(<i>N</i> -methylanilino)-ethanol	Reddish orange	0.56
11110	Dispersol Fast Scarlet B	<i>p</i> -Nitroaniline → 2-(<i>N</i> -ethylanilino)-ethanol	Pink	0.23
			Pink*	0.28
			Red	0.59
			Pink*	0.68
11115	Celliton Fast Rubine B	2-Chloro-4-nitroaniline → 2-(<i>N</i> -ethylanilino)-ethanol	Yellow*	0.00
			Pink*	0.12
			Yellow*	0.15
			Pink*	0.21
			Bordeaux	0.40
			Pink*	0.53
11118	Artisil Fast Scarlet GP	<i>p</i> -Nitroaniline → 3-(<i>N</i> -ethylanilino)-1,2-propanediol	Pink	0.65
11120	Celliton Red Violet RR	2,4-Dinitroaniline → 2-(<i>N</i> -butylanilino)-ethanol	Violet	0.03
			Pink*	0.16
			Violet	0.30
			Yellow	0.81
			Red	0.68
			Pink	0.80
			Yellow	0.82
11130	Dispersol Fast Red R	<i>p</i> -Nitroaniline → 2,2'-(phenylimino)-diethanol	Pink*	0.56
			Scarlet	0.76
			Pink	0.82
11150	Celliton Fast Scarlet R	2-Nitroaniline → 2,2'-(<i>m</i> -chlorophenylimino)-diethanol	Orange*	0.02
			Pink	0.45
11180	Celliton Red R	<i>p</i> -Nitroaniline → 2-(<i>m</i> -toluidino)-ethanol	Pink	0.69
11190	Celliton Fast Brown 5R	2,6-Dichloro-4-nitroaniline → 2-(<i>N</i> -methyl- <i>m</i> -toluidino)-ethanol	Dull yellow	0.00
			Pink	0.16
			Dull yellow	0.23
			Reddish brown	0.41
11195	Celliton Violet R	2,4-Dinitroaniline → 2-(<i>N</i> -butyl- <i>m</i> -toluidino)-ethanol	Pink	0.53
11200	Celliton Discharge Violet B	2-Bromo-4,6-dinitroaniline → 2-(<i>N</i> -butyl- <i>m</i> -toluidino)-ethanol	Violet	0.24
			Violet*	0.11

11205	Celliton Discharge Blue 3R	2-Bromo-4,6-dinitroaniline → 2-(N-butyl-5-methyl- <i>o</i> -anisidino)-ethanol	Blue	0.07
11210	Celliton Fast Red GG	<i>p</i> -Nitroaniline → 2,2'-(<i>m</i> -tolylimino)-diethanol	Pink	0.58
11215	Celliton Fast Rubine 3B	2-Chloro-4-nitroaniline → 2,2'-(<i>m</i> -tolylimino)-diethanol	Red	0.75
11220	Cellitazol GG	4-Nitro- <i>o</i> -anisidine → 2,2'-(<i>m</i> -tolylimino)-diethanol	Orange	0.86
11225	Celliton Discharge Rubine BBF	2-Amino-5-nitrophenol → 2,2'-(<i>m</i> -tolylimino)-diethanol	Crimson	0.62
11230	Celliton Fast Scarlet RN	<i>p</i> -Nitroaniline → (N-2-hydroxyethyl- <i>m</i> -toluidino)-propionitrile	Brown	0.78
11250	Cibacet Scarlet G	<i>p</i> -Nitroaniline → cresidine	Brown	0.85
11255	Cibacet Diazo Black B	Reduce the nitro group of C.I. 11250	Pink	0.63
11365	Cibacet Diazo Black GN	<i>p</i> -Nitroaniline → 1-naphthylamine	Pink	0.07
11410	Celliton Discharge Blue RRF	2-Bromo-4,6-dinitroaniline → 1- <i>sec</i> -.butyl-1,2,3,4-tetrahydro-7-methyl-3-quinolinol	Scarlet	0.37
11430	Celliton Discharge Blue 3G	2-Chloro-4-nitroaniline → 1,2,3,4-tetrahydrobenzo(<i>h</i>)quinoline-3,7-diol	Scarlet	0.50
11435	Celliton Discharge Blue 5G	2-Amino-6-methoxybenzothiazole → 1,2,3,4-tetrahydrobenzo(<i>h</i>)quinoline-3,7-diol	Pink	0.70
11835	Celliton Fast Yellow G	<i>p</i> -Aminoacetamide → <i>p</i> -cresol	Scarlet	0.75
12700	Sudan Yellow 3G	Aniline → 3-methyl-1-phenyl-5-pyrazolone	Pink	0.86
12790	Celliton Yellow 5G	<i>m</i> -Nitroaniline → 4-hydroxy-1-methylcarbostyryl	Pink	0.31
12795	Celliton Yellow 3GN	<i>o</i> - and <i>p</i> -Nitroaniline → 4-hydroxy-1-methylcarbostyryl	Brown	0.00
26080	Dispersol Fast Orange B	Aniline → 1-naphthylamine → phenol	Brown	0.67
26090	Celliton Fast Yellow 5R	<i>p</i> -Phenylazoaniline → <i>o</i> -cresol	Brown	0.79
37235	Cellitazol BN	<i>o</i> -Dianisidine	Reddish brown	0.00
48000	Celliton Fast Yellow 7G "F"	Condense ethyl cyanoacetate with <i>p</i> -(N-butyl-2-chloroethyl-amino)-benzaldehyde	Reddish brown	0.52
			Brown	0.77
			Dull brown*	0.88
			Bluish green	0.94
			Blue	0.20
			Blue	0.25
			Blue*	0.46
			Blue	0.78
			Blue	0.80
			Yellow	0.62
			Yellow	0.20
			Yellow	0.63
			Dull yellow*	0.86
			Yellow	0.82
			Orange	0.00
			Orange	0.09
			Yellow	0.09
			Brown	0.00
			Brown*	0.18
			Brown	0.82
			Yellow	0.26

(continued on p. 482)

TABLE 1 (continued)

Colour index	Commercial name	Chemical constitution	Colour of band	R _F
48005	Celliton Fast Yellow 3G "F"	Condense ethyl cyanoacetate with <i>p</i> -(N-methyl- <i>p</i> -phenetidine)-benzaldehyde	Yellow	0.38
56060	Celliton Fast Green 3B	Condense the leuco form of 8-amino-5-hydroxy-1,4-naphthoquinone imine with <i>p</i> -benzoyloxy-aniline, then oxidise with air	Yellow Bluish green Green	0.95 0.69 0.87
56200	Celliton Brilliant Yellow FFA-CF	Condense 4-aminonaphthalic anhydride with 2,4-xylydine	Yellow	0.86
58900	Duranol Brilliant Yellow 6 G	Benzanthrone, 3-methoxy-	Yellow	0.25
60505	Celliton Pink R	Anthraquinone, 1-methylamino-	Pink	0.68
60700	Celliton Orange R	Anthraquinone, 1-amino-2-methyl-	Orange	0.42
60710	Duranol Red 2B	Anthraquinone, 1-amino-4-hydroxy-	Red	0.72
60755	Celliton Fast Pink RF	Anthraquinone, 1-amino-2-methoxy-4-hydroxy-	Pink	0.33
61100	Cibacet Violet 2R	Anthraquinone, 1,4-diamino-	Pink Violet	0.75 0.00
61105	Celliton Fast Violet 6B	Anthraquinone, 1-amino-4-methylamino-	Violet Violet	0.73 0.81
61110	Artisil Direct Blue 2RP	Anthraquinone, 1-amino-4-anilino-	Pink Violet	0.74 0.79
61115	Celliton Fast Blue FR	Anthraquinone, 1-amino-4-aminomethoxy-	Blue Blue Blue Blue*	0.82 0.00 0.18 0.86
61500	Celliton Fast Blue B	Anthraquinone, 1,4-dimethylamino-	Grey Blue	0.00 0.27
61505	Celliton Fast Blue FFR	Anthraquinone, 1-methylamino-4-(2-aminoethanol)	Violet Bluish violet Violet	0.61 0.68 0.78
61510	Celliton Fast Blue FW	Anthraquinone, 1-methylamino-4-[2-(2-aminoethoxy)-ethanol]	Blue Blue Blue Blue Blue Blue	0.85 0.50 0.66 0.68 0.76 0.81
61540	Celliton Fast Green 5	Anthraquinone, 1-methylamino-4-(1- <i>p</i> -aminoanilino-2-hydroxyethyl)-	Blue Bluish green Bluish green	0.34 0.54 0.64
61545	Celliton Fast Blue BF	Anthraquinone, 1,4-di-(2-aminoethanol)	Blue Violet	0.80 0.71
62015	Duranol Red X3B	Anthraquinone, 1,4-diamino-2-methoxy-	Blue	0.82
62030	Celliton Fast Violet B	Anthraquinone, 1,4-diamino-5-nitro-	Blue Red Bluish violet	0.47 0.59 0.66 0.77 0.82

62035	Celliton Fast Blue FFB	Anthraquinone, 1-amino-2-carbamyl-4-methylamino-	Blue	0.61
			Blue	0.70
62050	Celliton Fast Blue FFG	Anthraquinone, 1-amino-2-carbamyl-4-cyclohexylamino-	Dull violet	0.83
			Blue	0.08
			Blue	0.46
			Dull blue*	0.58
			Dull blue	0.65
62500	Artisil Blue Green GP	Anthraquinone, 1,4-di-(2-hydroxyethyl)-2-amino-5,8-dihydroxy-	Dull violet	0.82
			Blue	0.40
			Blue	0.51
			Blue	0.62
63305	Duranol Blue G	Anthraquinone, 1,5-bis-methylamino-4,8-dihydroxy-	Dull blue	0.83
			Blue	0.25
			Blue	0.71
64500	Celliton Blue ex.	Anthraquinone, 1,4,5,8-tetraamino-	Blue	0.81
			Grey	0.00
			Blue	0.29
			Violet	0.58
64505	Celliton Blue 3G	Anthraquinone, 1,4,5,8-tetraamino-, methylated	Blue	0.83
			Bluish violet	0.00
			Blue	0.07

* Spot hardly visible.

the R_F value is dependent on the number of amino groups in the nucleus and decreases proportionally with their number. Hydroxyethanolamino derivatives possess a higher R_F value than the amino derivatives.

(f) Methine derivatives possess a lower R_F value than nitro dyes and dyes of the arylaminoquinone and aminonaphthalimide groups.

(g) The position and character of the substituents in aromatic nuclei considerably influence the R_F value. With compounds of the same fundamental skeleton and of a different character of substituents, dyes with smaller dipole moments show a higher R_F value.

SUMMARY

Disperse dyes have been separated, using two aqueous pyridine eluents. The relation between dye constitution and chromatographic behaviour has been examined.

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