

PAPER CHROMATOGRAPHY OF DYES

II. PAPER CHROMATOGRAPHY OF VAT AND SULPHUR DYES

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INTRODUCTION

Dyes insoluble in water, particularly the fast vat dyes and sulphur dyes occupy an outstanding place in the technology of dyeing and printing.

Vat dyes consist of any organic colouring matter (with the exception of basic and sulphur dyes) that is capable of undergoing a reversible reduction-oxidation cycle without serious colour loss or change of shade. Such dyes are the polycyclic and indigoid vat dyes (chemical derivatives of anthraquinone and polycyclic quinones with a larger number of condensed isocyclic and heterocyclic rings and derivatives of Indigo and Thioindigo). No general formula can be given for a vat dye. It is almost always a coloured organic compound containing two or more keto groups ($>C=O$) which are capable of being reduced by sodium hydrosulphite and alkali to give a leuco compound ($\geq C-ONa$) which has affinity for cellulosic fibre.

The sulphur dyes are a class of highly coloured water-insoluble products reducible by dilute aqueous sodium sulphide to water-soluble derivatives which are substantive to cellulosic fibres; they are principally complicated thionated aromatic compounds of a rather high molecular weight, containing thiazole or thiazine or azine rings in the molecule.

The paper chromatography of these dyes is considerably more complicated than that of water-soluble dyes. Its success depends in the first place on the discovery of suitable solvents for the dye and secondly on the chromatographic technique itself. Despite these difficulties we were successful in elaborating a chromatographic method that would give reproducible and practical results¹⁻⁵.

Chromatography of vat and sulphur dyes is generally performed by the classical column method, while paper chromatography rarely finds application. The methods used are based on separating the dyes in their leuco forms by means of reducing solvents based on sodium hydrosulphite made alkaline with tetraethylenepentamine^{6,7} or containing Cellosolve⁸. TAJIRI⁹ has described the paper electrophoresis of vat and sulphur dyes in the presence of reducing agents; he concludes that normal paper chromatography is unsatisfactory; JUNGBECK¹⁰ has stated that there is no reliable overall method of paper chromatography of these dyes, although JANICKA AND KAPRZAK¹¹ have described the separation of vat dyes on columns of cotton fibre. KOLŠEK, MLAKAR AND PERPAR¹² have described the paper chromatography of vat dyes in unreduced form. The vat dyes are dissolved in organic solvents.

Sulphur dyes present a complex problem, for usually they are not chemical individuals but a mixture of products of various sulphuration and condensation reactions. Thus, after fusion reactions with sulphur or polysulphides the final product contains various starting materials and intermediates, e.g. azines and carbazole. The literature contains few references to paper chromatography¹⁻⁵ and electrophoresis⁶ of these dyes. Here again, reduction to the leuco form is essential.

EXPERIMENTAL

Vat dyes

Several methods were tried and it was found that the most consistent results were obtained by means of ascending chromatography at 80°, using an alkaline aqueous reducing solution of pyridine as eluent. The leuco compound was separated on the chromatogram after eluting for 2 h; Schleicher & Schüll 589³ (blue ribbon) and Whatman No. 1 papers were found to be the most suitable.

Materials

The leuco compound of the dye, prepared according to normal commercial methods, is used in the form of a 1% solution.

The reducing eluent has the composition:

Distilled water	32 ml
Turkey Red oil (tech.)-sodium alkylsulphonate, 1% soln.	48 ml
Sodium hydroxide, 35% soln.	4 ml
Sodium hydrosulphite	4 g
Pyridine	16 ml

When the solution is prepared, the components must be added in the order given above. For chromatograms 13 cm long, 10 ml of this solution are required, and for those 22 cm long, 15 ml. The solution should be freshly prepared for each determination.

Apparatus

The chromatographic test tubes have an inside diameter of 1.8 cm and are 20 cm long, and sufficient solvent is added to reach just below the starting point of the chromatogram. Four to eight test tubes are placed at the same time in a vertical position in a 3-l thermostat heated to 80° (Fig. 1).

The chromatogram is suspended from a hook in the rubber stopper of the test tube and small glass weights attached to its base keep it taut. During the separations the tubes must be completely immersed in the thermostat to prevent condensation of solvent vapours in the upper part of the test tubes and it is therefore essential that the rubber stopper fits tightly. If necessary it can be covered by a heavier rubber plug.

Method

The chromatograms generally used were 1 cm × 16 cm strips, the starting line being 2 cm from the lower edge and the distance from the starting line to the solvent front being 13 cm. For the separation of complex, artificial mixtures it is advisable to use 25 cm strips with a start-solvent front distance of 22 cm.

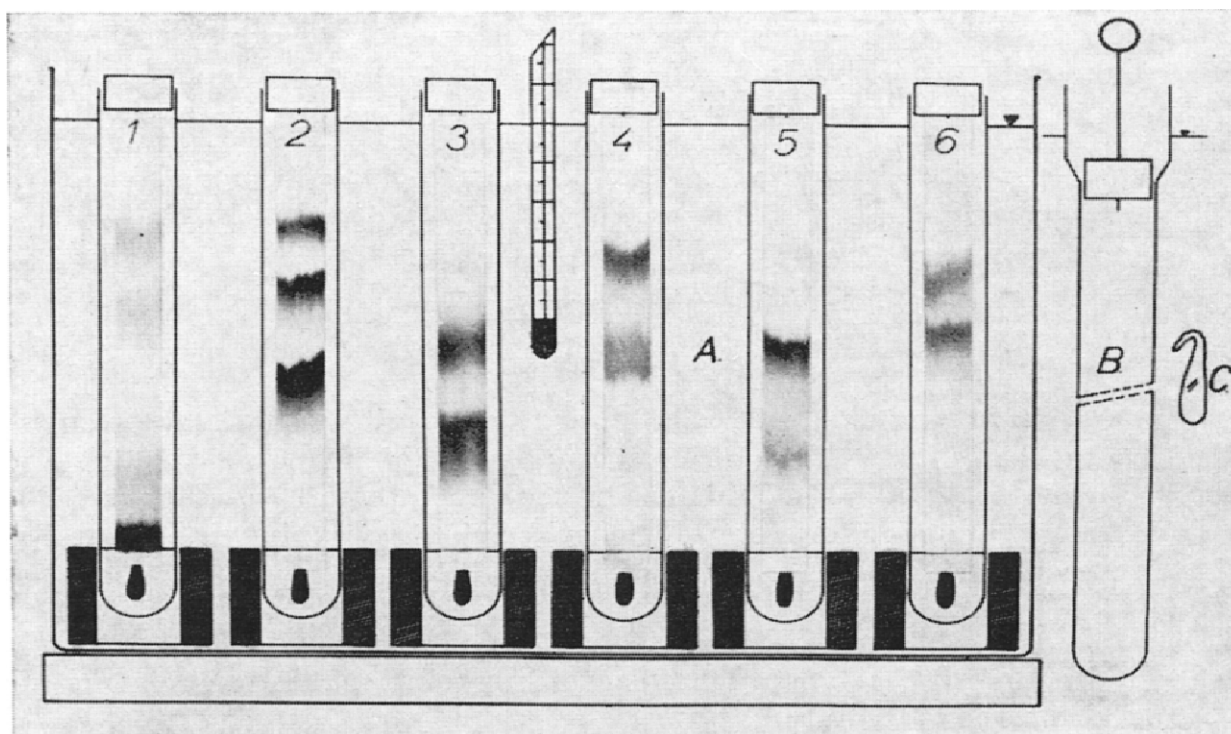


Fig. 1. Apparatus for chromatography of vat dyes with typical examples of the separation of their mixtures. A = thermostat; B = test tube for separation of complex mixtures; C = glass weight.

Chroma- logram No.	Commercial name	C.I. No.
1.	Mixture of: Indanthrene Khaki GG Indanthrene Yellow 4GF Indanthrene Brilliant Green B Brilliant Indigo 4B	71050 68420 59825 73065
2.	Mixture of: Indanthrene Scarlet R Indanthrene Red GG Algol Scarlet B	71140 71130 71135
3.	Mixture of: Indanthrene Orange RRT Indanthrene Red Brown RR	59705 59500
4.	Mixture of: Helindon Yellow CG Indanthrene Yellow 6GD	56005 56080
5.	Mixture of: Indanthrene Blue GCD Indanthrene Orange F3R	69815 69540
6.	Mixture of: Indanthrene Cyanine B Indanthrene Brilliant Green B	60015 59825

The leuco vat dye (5–10 μl of 1% solution) is applied by means of a micropipette to the starting line on the chromatogram, which is quickly placed (without being dried) in a test tube containing the solvent (10 ml for a 13 cm chromatogram, 15 ml for a 22 cm chromatogram) at 80°, so that the reducing solvent quickly begins to ascend the paper. Although some oxidation of the leuco compound occurs, the re-

ducing solvent quickly reduces the vat dye back to the leuco compound and separation then begins. The separation is complete after 2 h with the shorter chromatogram and after 4 h with the longer one. After the separation the chromatogram is exposed to the air and rinsed in water to remove residual solvent.

Sulphur dyes

Sulphur dyes are chromatographed under conditions identical to those used for vat dyes, the leuco compounds in this instance being obtained by dissolving the dye in sodium hydroxide and sodium hydrosulphite.

RESULTS AND DISCUSSION

Vat dyes

By means of the technique described above, all the important dyes of known constitution listed in the *Colour Index*¹³, as well as some mixtures, have been examined. The results are reproducible and the method is sufficiently sensitive to permit separation of structurally similar compounds.

The rate of movement of the dye depends on the size of the molecule and its chemical structure. Large molecules travel slowly, owing to increased substantivity for the paper and decreased solubility in the mobile phase; the chemical groups present will affect the solubility of the dye, smaller molecules being most affected.

Such separations are particularly useful for testing the purity of dyes during manufacture and they also indicate the probable dyeing characteristics on cellulosic materials¹⁴.

Vat dyes can be divided into five groups on the basis of their rate of movement on the chromatogram, *viz.*

- (1) The main spot does not move, but forms a slight forward tail.
- (2) The main spot moves slightly, but tails back to the origin.
- (3) The dye moves up to half-way along the chromatogram.
- (4) The dye moves up to two-thirds of the length of the chromatogram.
- (5) The dye moves with the solvent front.

Fig. 2. is a representation of this classification.

The individual groups of vat dyes behave as shown in Table I.

From the results the following general conclusions concerning the chemical structure can be drawn.

(1) Substitution by $-\text{CH}_3$, $-\text{OCH}_3$ or benzoylamino reduces the rate of movement; substitution by halogens increases it.

(2) Dyes containing a thiazole, oxazole, acridone, cyanuric or N,N'-dihydropyrazine ring travel more slowly than dyes without such a ring, the thiazole ring having the greatest effect.

(3) Increasing the number of keto groups in the dye progressively reduces the rate of movement.

(4) Dibenzanthrones travel faster than isodibenzanthrones.

(5) Thioindigoid dyes travel faster than indigoid dyes.

(6) Of naphthoylenebenzimidazoles having *cis*- and *trans*-isomers, the *cis*-isomers travel most rapidly.

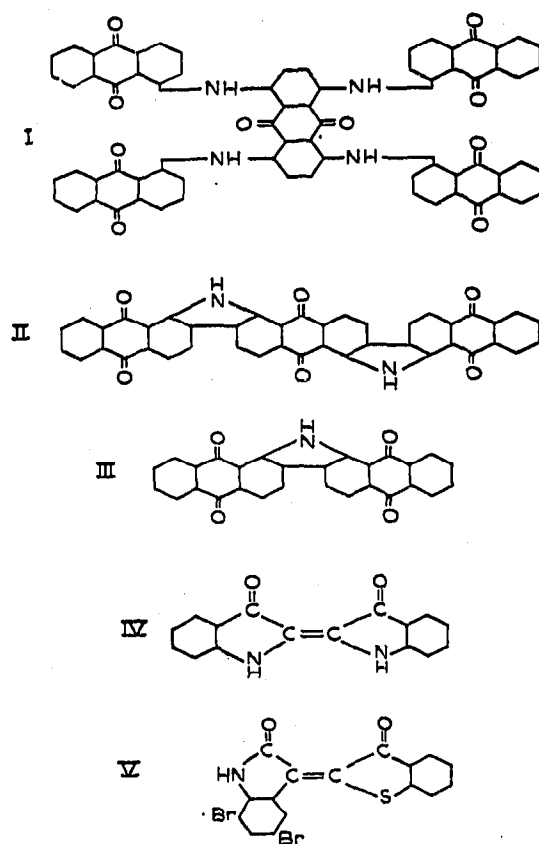
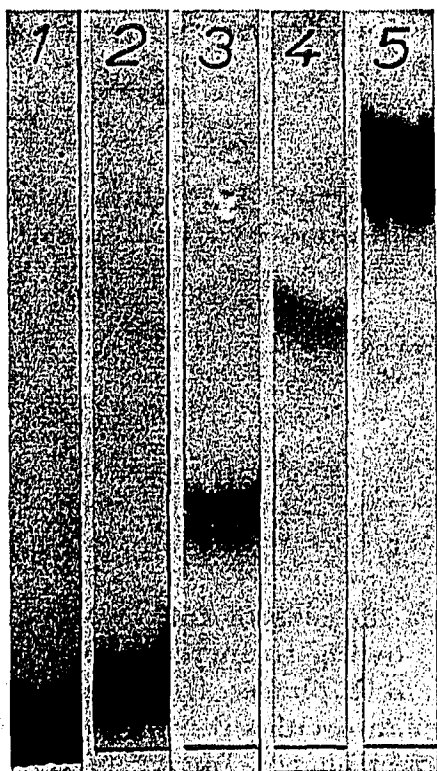


Fig. 2. Influence of molecular complexity on chromatographic behaviour of vat dyes.

Chromatogram No.	Commercial name	Separation group	Structural formula
1.	Indanthrene Khaki GG	1.	I.
2.	Indanthrene Yellow 3R	2.	II.
3.	Indanthrene Yellow FFRK	3.	III.
4.	Indigo	4.	IV.
5.	Ciba Red G	5.	V.

TABLE I

	Chemical type	Separation group
1.	Thiazine	4
2.	Sulphur	4
3.	Arylaminoquinones	4 (3)
4.	Acylaminoanthraquinones	2, 3, 4
5.	Anthraquinonylaminothiazines	2, 3, 4
6.	Anthraquinonylamines (Anthrimides)	2, 3
7.	Anthraflavones	3
8.	Anthraquinonecarbazoles (Diphthaloylcarbazoles)	2, 3 (5)
9.	Benzanthranylaminanthraquinone Benzanthrone "Acridone"	1, 2
10.	Anthraquinonethiazoles	1, 2
11.	Anthraquinoneiminazoles	1, 2

(continued on p. 529)

TABLE I (continued)

	Chemical type	Separation group
12.	Anthraquinoneoxazoles	1, 2
13.	Anthraquinoneacridones	1
	Anthraquinoneacridones (unmodified)	3
14.	Anthraquinonethioxanthenes	3
	Pyrazinoanthraquinones	
15.	N,N'-Dihydro-anthraquinone-azines (Indanthrones)	3
16.	Flavanthrones	3
17.	Pyranthrones	2, 3
18.	Anthrones, Dibenzopyrenequinones, Acedianthrones	1, 2, 3, 4
19.	Anthrapyrimidines	3,4
	Pyridoanthrones	
20.	Bispyrazoleanthrones	3
	Thiabenzanthrones	
21.	Dibenzanthrones, Violanthrones	(1) 2, 3, 4
22.	Isodibenzanthrones, Isoviolanthrones	2, 3, 4
23.	Benzanthranylpyrazoleanthrones	1, 2
24.	Perylenetetracarboxylic acid	2, 3, 4
25.	Naphthoylenebenzimidazoles	2, 3
26.	Phthalocyanines	3
27.	Indigoid, Thioindigoid	4, 5
	Indole-thianaphthene	

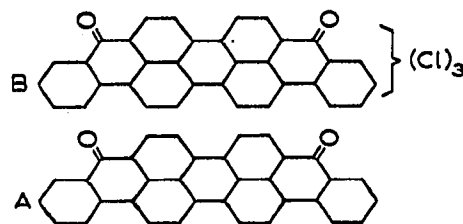
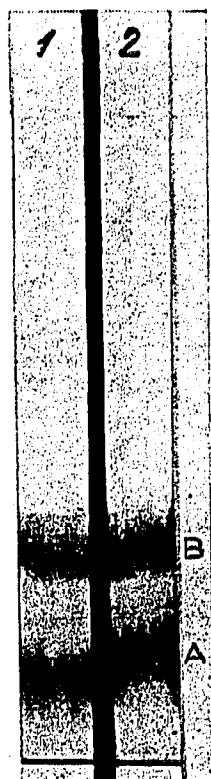


Fig. 3. Separation of a mixture of dyes of the dibenzanthrone type (Violanthrones). Chromatogram Nos. 1 and 2: Mixture of A and B.

	Commercial name	C.I. number
A.	Indanthrene Dark Blue BOA	59800
B.	Cibanone Navy Blue RA	59815

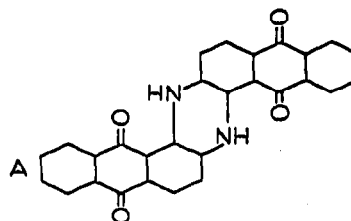
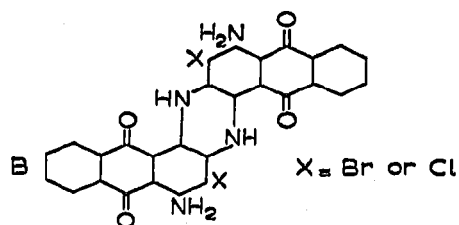
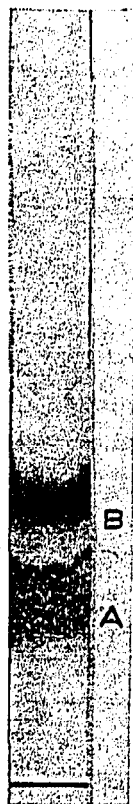


Fig. 4. Separation of a mixture of dyes of the indanthrone type (*N,N'*-dihydro-anthraquinone-azines).

	Commercial name	C.I. number
A.	Indanthrene Blue RSN	69800
B.	Indanthrene Green BB	69850

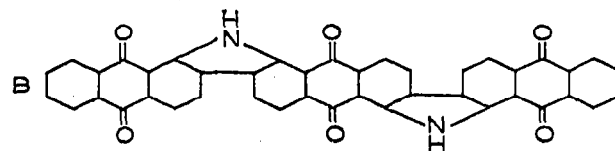
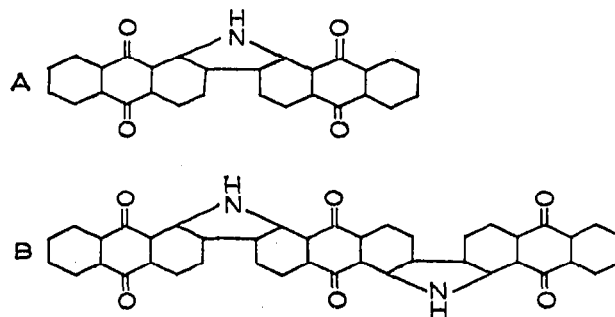
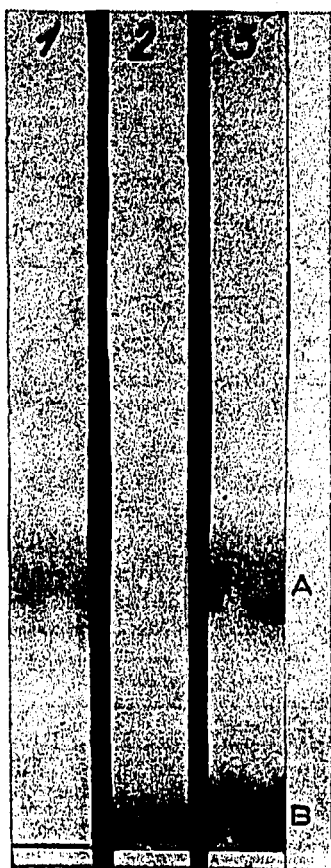


Fig. 5. Separation of a mixture of dyes of the anthraquinonecarbazole type.

Chromatogram No.	Commercial name	C.I. number
1.	A. Indanthrene Yellow FRK	69000
2.	B. Indanthrene Yellow 3R	70805
3.	Mixture of A and B	

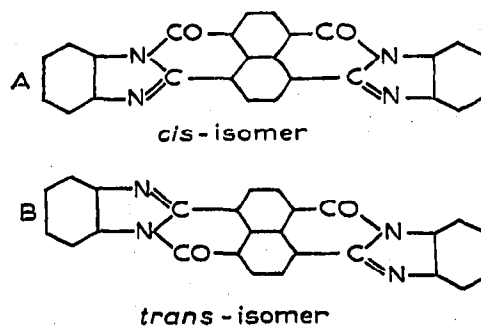
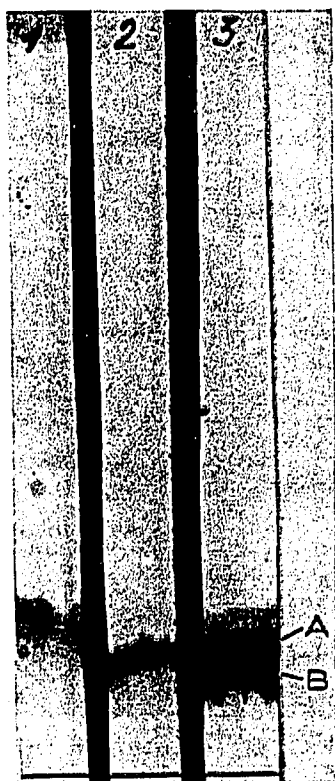


Fig. 6. Separation of *cis*- and *trans*-isomers (naphthylene-benzimidazole).

Chromatogram No.	Commercial name	C.I. number
1.	A. Indanthrene Bordeaux HRR (<i>cis</i> -isomer)	71100
2.	B. Indanthrene Brilliant Orange GR (<i>trans</i> -isomer)	71105
3.	Indanthrene Scarlet GG (an isomeric mixture of A and B)	71110

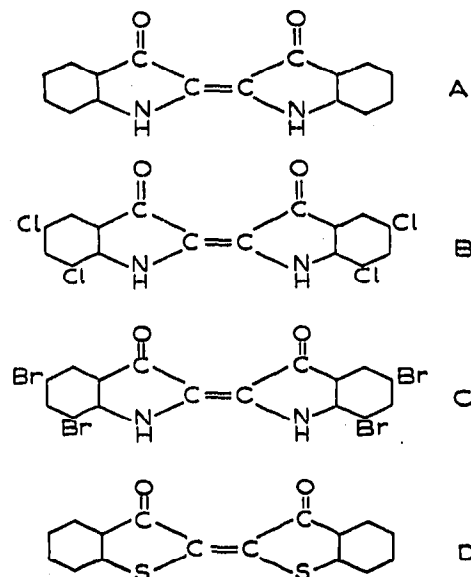
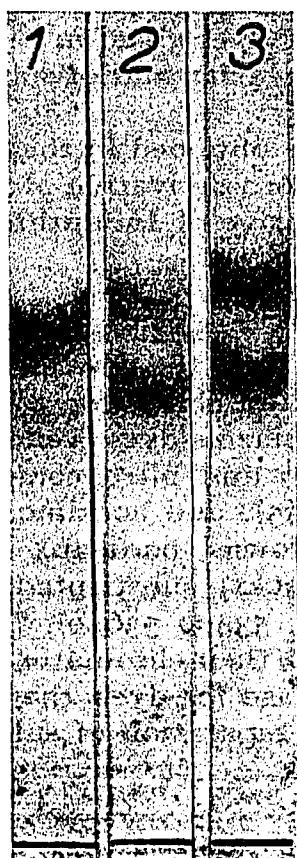


Fig. 7. Separation of a mixture of dyes of the indigoid and thioindigoid type.

Structural formula	Commercial name	C.I. number
A.	Indigo (synthetic)	73000
B.	Brilliant Indigo B	73040
C.	Brilliant Indigo 4 B	73065
D.	Thioindigo Red B	73300

Chromatogram No. 1 = mixture of A and B;
No. 2 = mixture of A and C; No. 3 = mixture of A and D.

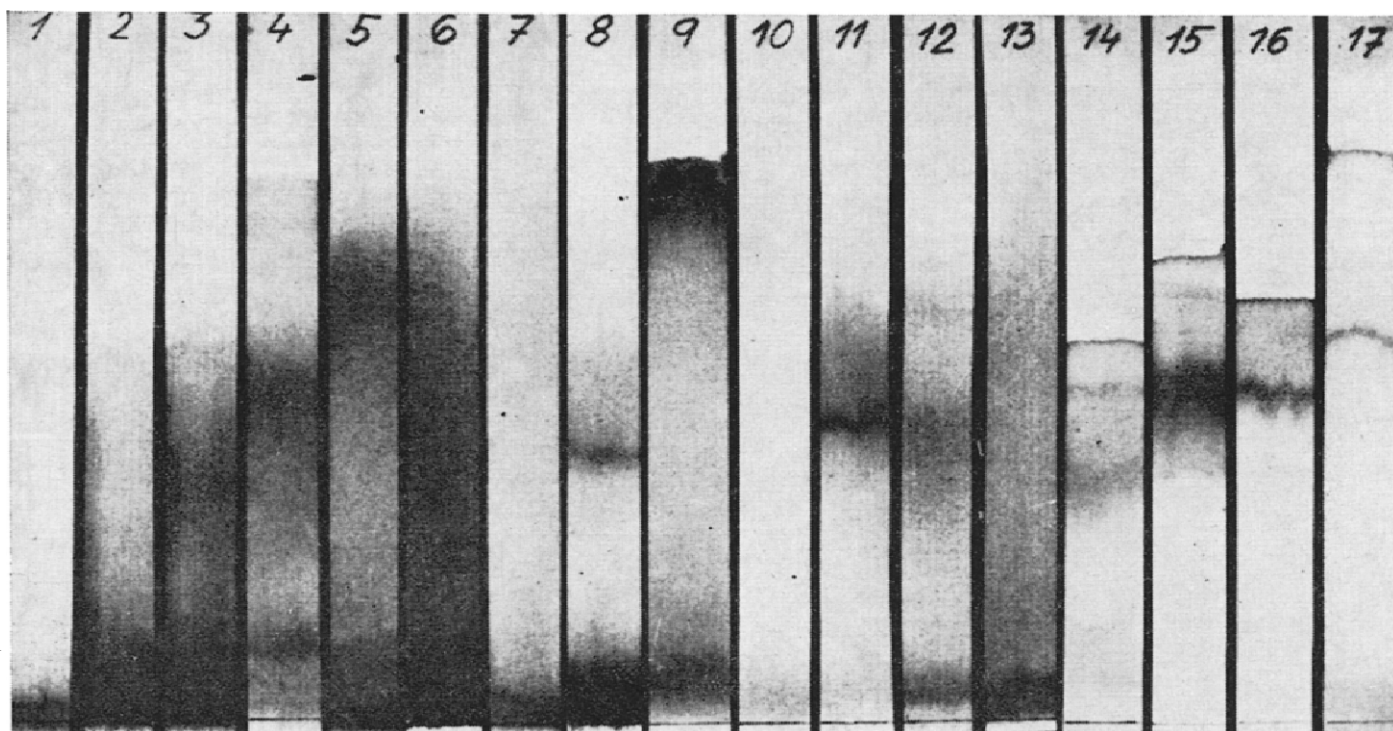


Fig. 8. Chromatograms of sulphur dyes. 1 = Sulfogen Yellow G; 2 = Sulfogen Orange G; 3 = Sulfogen Yellow R; 4 = Sulfogen Yellow Olive G; 5 = Immedial Yellow Brown GL (C.I. 53325); 6 = Immedial Catechu 4 RL'F" (C.I. 53320); 7 = Immedial Brown GGL (C.I. 53327); 8 = Sulfogen Red Brown 4 R; 9 = Sulfogen Brilliant Black B 4 R; 10 = Sulfogen Dark Blue 6 BZ; 11 = Immedial Fast Blue 6 GL (C.I. 53460); 12 = Sulfogen Green 2 G; 13 = Sulfogen Dark Green B; 14 = Sulfogen Green Blue CV ex; 15 = Sulfogen Green 3 G; 16 = Sulfogen Green MK; 17 = Sulfogen Green G.

The examples of the separation of mixtures of vat dyes given in Figs. 3, 4, 5, 6 and 7 demonstrate the influence of the molecular complexity and of substituents on the chromatographic behaviour of the vat dyes.

Evidence of configuration isomers can further be obtained in the case of analogues of Indanthrene Scarlet G G, that is with the chloro-derivative of Indanthrene Printing Brown 5R (C.I. 71115) and the ethoxy-derivative of Indanthrene Printing Brown B (C.I. 71120).

Sulphur dyes

Sulphur dyes are either (a) eluted only with difficulty from the starting point or (b) move a considerable distance. Dyes in group (a) must be eluted for 30–60 min and those in group (b) for 10–15 min. Group (a) includes thiazole dyes (yellows, oranges, and browns), mono- and binuclear-substituted amino and nitro compounds (C.I. 53005–53160), polycyclic compounds (C.I. 53320–53335), and acridine, azine, oxazone, and thiazone derivatives (C.I. 53680–53830) (browns, bordeaux and violets). Group (b) includes thiazine dyes (blues, greens, and blacks), substituted phenols and naphthalenes (C.I. 53165–53300), and indophenols (C.I. 53400–53640).

Because of the complex nature of the sulphur dyes, their chromatograms usually consist of a series of bands. This is particularly the case for dyes that fall within group (b). In Fig. 8 a chromatogram illustrating the separation of sulphur dyes is given.

SUMMARY

The paper chromatography of vat and sulphur dyes, using reducing solvents at 80°, has been carried out, the dyes being separated as their leuco compounds. In both cases ascending paper chromatography was applied. The relation between dye constitution and chromatographic behaviour has been examined.

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