

PAPER CHROMATOGRAPHY OF DYES

III. PAPER CHROMATOGRAPHY OF SOLUBILIZED VAT DYES

JIŘÍ ŠRÁMEK

*Research Institute of Textile Finishing,
Dvůr Králové n.L. (Czechoslovakia)*

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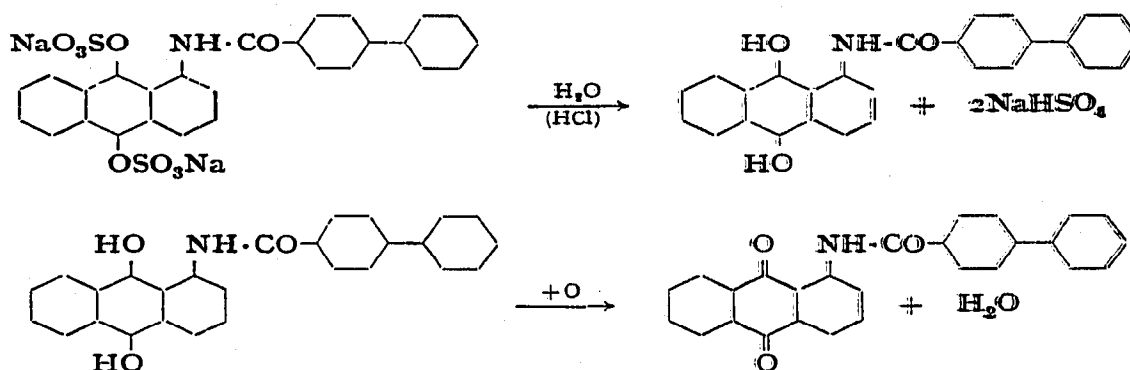
INTRODUCTION

Chemically solubilized vat dyes, "Indigosols", are soluble derivatives of vat dyes. These solubilized dyes are sodium salts of sulphuric esters of the leuco form ($\geq C-OSO_3Na$) of the vat dye. The reaction:



for the preparation of these sulphuric ester salts of the leuco compounds may, in principle, be applied to all anthraquinoid and indigoid vat dyes.

Indigosols are very readily soluble in water. They are transformed to an insoluble form by oxidation in acid medium. During the process of oxidation the sulphuric esters of the leuco vat dyes are first hydrolysed, and then oxidized to the original parent dye. For example in the case of Indigosol Yellow V:



Up till now little information has been published on the chromatography of indigosols. RUGGLI AND STÄUBLE¹ chromatographed these dyes on a column of Al_2O_3 or $CaCO_3$. In our previous work^{2,3} indigosols were chromatographed on paper by means of the ascending technique employing Whatman No. 1 paper and an aqueous pyridine solution as solvent. MATRKA, NAVRÁTIL AND FILIPÍ⁴ employed paper chromatography to identify the dispersing and stabilizing agents present in indigosols (4-dimethylaminobenzenesulphonic acid, glucose, molasses, urea). Recently the paper chromatography of indigosols has been described by KOLŠEK, MLAKAR AND PERPAR⁵

who applied the ascending technique on SS 2043b paper with the following solvent systems: butan-1-ol-acetic acid-water (4:1:5) and butan-1-ol-pyridine-water (4:1:1).

In our institute paper chromatography of indigosols is performed by means of the descending technique, using as solvent system either methanolic ammonia solution, or a mixture of pyridine, isoamyl alcohol and ammonia, or a mixture of methanol and acetic acid. These solvent systems have also been used in centrifugal chromatography⁶.

EXPERIMENTAL

(a) *Descending technique*

Whatman No. 1 paper was used, the size of the chromatograms being 160 × 470 mm with a running length of 400 mm. Spots of freshly prepared 1 % aqueous solutions of the dyes were applied on the start in 0.05 mg quantities by means of a micropipette. The chromatograms were developed at a temperature of 20–22°.

The following solvent systems were used:

S_1 = ammonia (25 %)-methanol-water (1:2:3),

S_2 = pyridine-isoamyl alcohol-ammonia (25 %) (1.3:1:1),

S_3 = methanol-acetic acid-water (4:1:1).

The R_F values with the S_1 system are dependent on the chemical structure of the dyes and on their functional groups and substituents. The S_2 system gives excellent separations suitable for estimating the purity and identity of the indigosols. The relation between the R_F value and the chemical structure of the dyes is, however, not as obvious as with the S_1 system. S_3 is suitable for some dyes only.

Acid solvent systems, although they find application for indigosols⁵, are not suitable on account of the fact that during development of the chromatograms with acid systems a gradual hydrolysis of the sulphuric ester of the leuco dye takes place under formation of the monoester, which is in itself an inhibitor of oxidation.

The partially hydrolysed dye is exceedingly prone to autooxidation. In the course of the development of the chromatogram, autooxidation of the dye by atmospheric oxygen occurs under formation of semiquinone derivatives.

Alkaline systems preclude the possibility of autooxidation.

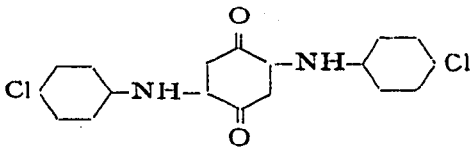
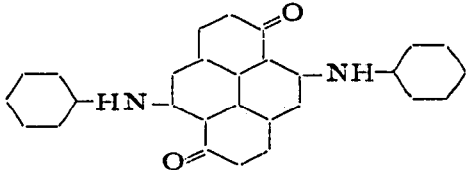
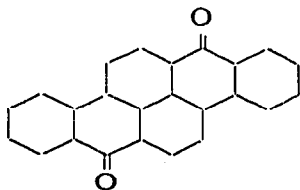
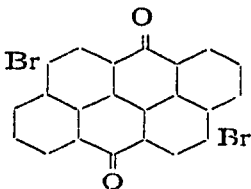
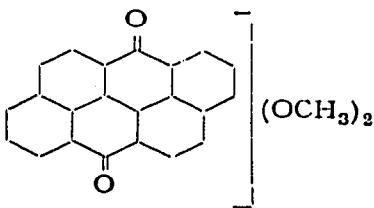
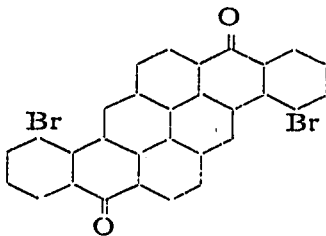
(b) *Centrifugal chromatography*

This was carried out with the pressureless apparatus with central spot development described previously by PAVLÍČEK, ROSMUS AND DEYL^{7,8}.

The chromatograms were cut from Whatman No. 3 paper and the separation was performed during 45 min at 600 r.p.m. The chromatograms were always developed with the same solvent system that was used for the descending technique.

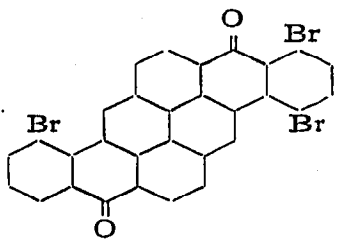
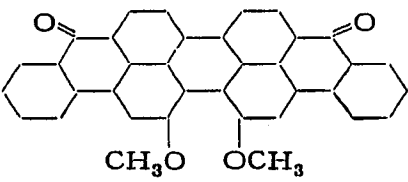
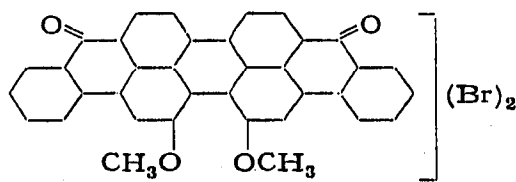
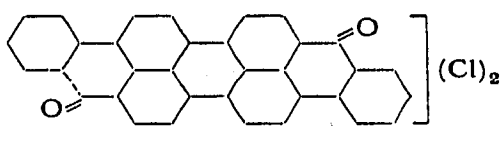
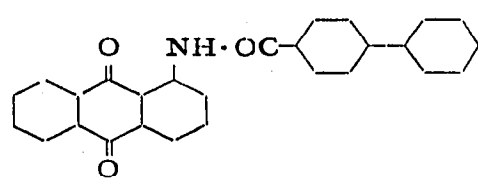
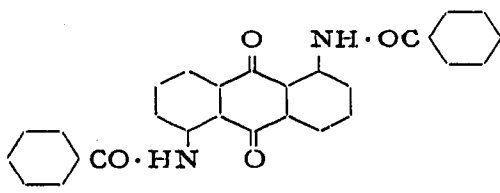
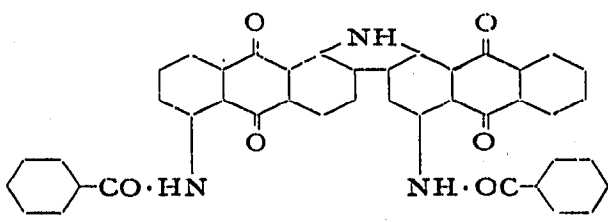
With a few exceptions, the colour of indigosols is very faint, thus making detection of the chromatograms necessary. This can be performed by spraying the chromatogram with a warm (40°) solution of NaNO_2 (2 %) in 2 % hydrochloric acid. On spraying, immediate coloration of the dyes occurs, due to the oxidizing action of the reagent. It is also possible to utilize the high sensitivity of indigosols to autooxidation for detection purposes. The dried chromatograms are exposed to ultra-violet radiation and coloration of the dye will follow immediately.

TABLE I
CHROMATOGRAPHIC SEPARATION OF SOLUBILIZED VAT DYES

| Colour index No. | Commercial name* | Solubilized form of the parent dye | <i>R_F</i> values and colour** | | |
|------------------|----------------------------------|---|--|-----------------------|-----------------------|
| | | | <i>S</i> ₁ | <i>S</i> ₂ | <i>S</i> ₃ |
| 56006 | Anthrasol Yellow HCG |  | 0.70 Y | 0.43 Y | 0.82 Y |
| | | | 0.76 Y | 0.58 Y | 0.86 GY |
| | | | 0.82 Y | 0.65 GY | — |
| | | | 0.90 Y | 0.85 Y ⁺ | — |
| 59051 | Anthrasol Green I 3G |  | 0.00 G | 0.00 G | 0.00 G |
| | | | 0.55 G | 0.60 G | 0.55 G |
| | | | 0.87 G ⁺ | 0.65 G | 0.62 G 0.72 G |
| 59101 | Anthrasol Yellow IGK |  | 0.00 Y | 0.47 Y | 0.52 Y |
| | | | 0.16 Y | 0.53 Y | — |
| | | | 0.32 Y | 0.58 Y | — |
| | | | — | 0.80 Y ⁺ | — |
| 59106 | Tinosol Golden Yellow RK | Brominated CI 59101 | 0.00 Y | 0.57 Y | 0.00 Y |
| | | | 0.31 Y | 0.80 Y ⁺ | 0.26 Y |
| | | | 0.87 Y ⁺ | — | 0.46 Y |
| 59301 | Cibantine Brilliant Orange RK |  | 0.42 O | 0.52 O | 0.57 O |
| | | | | | |
| 95316 | Indigosol Red Violet IRRL |  | 0.35 V | 0.41 V | 0.57 V |
| | | | | | |
| 59706 | Indigosol Golden Orange 12 R |  | 0.26 O | 0.50 O | 0.00 O |
| | | | — | 0.60 O | 0.07 O |
| | | | — | 0.65 O | 0.32 O |
| | | | — | — | 0.40 O |

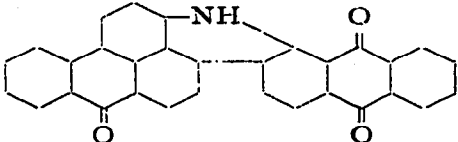
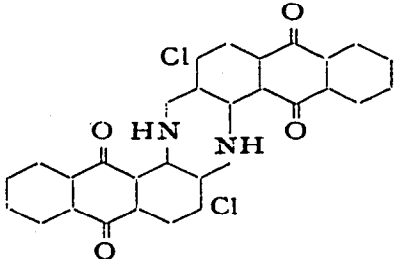
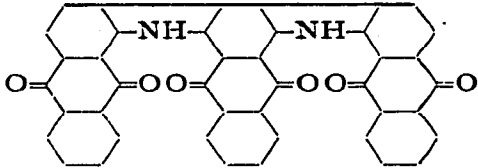
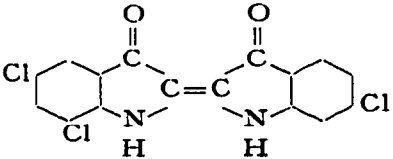
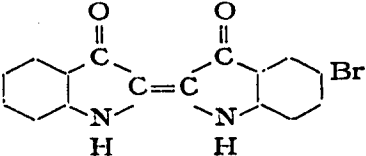
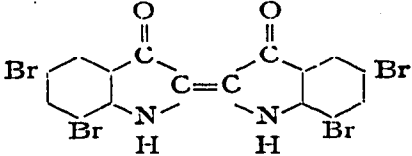
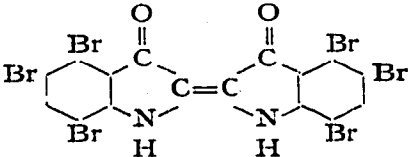
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TABLE I (continued)

| Colour index No. | Commercial name* | Solubilized form of the parent dye | <i>R_F</i> values and colour** | | |
|------------------|---------------------------------|--|---|---|--|
| | | | <i>S</i> ₁ | <i>S</i> ₂ | <i>S</i> ₃ |
| 59711 | Indigosol Orange 18 R |  | 0.21 O — — | 0.51 O 0.63 O — | 0.00 O 0.26 O 0.35 O |
| 59826 | Cibantine Brilliant Green BF |  | 0.00 G 0.03 G 0.10 G ⁺ — | 0.00 G 0.37 G 0.53 G 0.65 G ⁺ 0.75 G ⁺ | 0.00 G 0.11 G 0.27 G — — |
| 59831 | Anthrasol Green IGG |  | 0.00 G 0.02 G 0.05 G 0.38 B ⁺ 0.50 B ⁺ 0.60 B ⁺ | 0.00 G 0.10 B 0.17 B 0.27 B ⁺ 0.36 G ⁺ 0.58 G | 0.00 G 0.02 G 0.07 G 0.35 B — — |
| 60011 | Indigosol Brilliant Violet 14 R |  | 0.07 V — — — | 0.00 V 0.38 V ⁺ 0.41 O ⁺ 0.46 V ⁺ 0.57 V | 0.00 V 0.06 V 0.18 V 0.28 V — |
| 60531 | Tinosol Yellow V |  | 0.00 Y 0.62 Y | 0.55 Y 0.85 Y | 0.00 Y 0.80 Y |
| 61726 | Indigosol Yellow 2 GB |  | 0.00 Y 0.85 Y — | 0.00 Y ⁺ 0.56 Y 0.78 Y ⁺ 0.86 Y ⁺ | 0.00 Y 0.72 Y ⁺ 0.85 Y — |
| 69016 | Soledon Brown R |  | 0.00 Br 0.17 Br ⁺ 0.62 Br ⁺ 0.85 Br | 0.00 Br ⁺ 0.33 Br 0.40 Br ⁺ 0.63 Br ⁺ | 0.00 Br 0.73 Br — — |

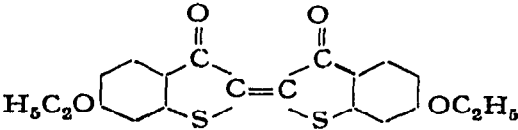
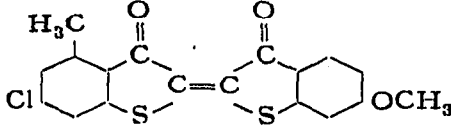
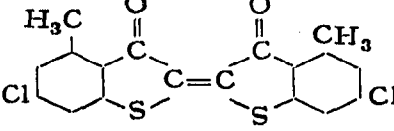
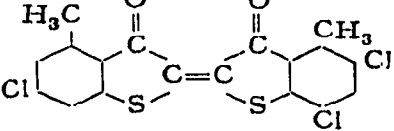
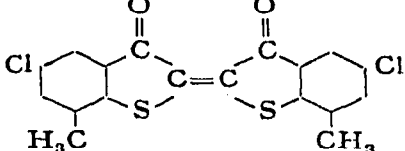
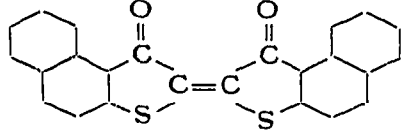
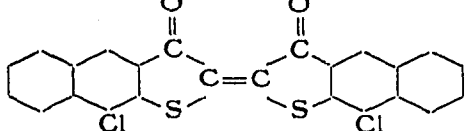
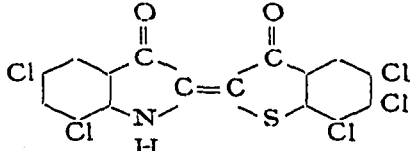
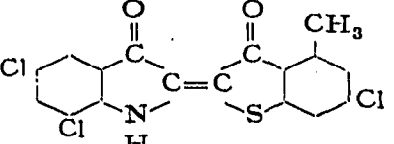
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TABLE I (continued)

| Colour index No. | Commercial name* | Solubilized form of the parent dye | <i>R_F</i> values and colour** | | |
|------------------|--------------------------|---|---|---|---|
| | | | <i>S</i> ₁ | <i>S</i> ₂ | <i>S</i> ₃ |
| 69501 | Indigosol Olive Green IB |  | 0.00 OG 0.30 OG — — — | 0.00 Gr ⁺ 0.02 OG ⁺ 0.41 OG 0.46 OG 0.50 OG | 0.00 OG 0.08 OG — — — |
| 69826 | Cibantin Blue CF |  | 0.67 B — — | 0.07 B 0.13 B 0.26 B | 0.03 B 0.10 B 0.18 B ⁺ |
| 70801 | Cibantin Brown BR |  | 0.00 Br 0.07 Br 0.16 Br 0.25 Br — | 0.02 Br 0.06 Br 0.10 Br 0.20 Br 0.31 Br | 0.00 Br 0.03 Br 0.51 Y ⁺ — — |
| 73031 | Indigosol Violet AZB |  | 0.33 V — | 0.37 Y ⁺ 0.53 V | 0.70 V — |
| 73056 | Indigosol OR |  | 0.27 B 0.32 B ⁺ 0.42 B 0.58 B | 0.40 Y ⁺ 0.47 B 0.52 B 0.58 B | 0.61 B 0.71 B 0.78 Y ⁺ — |
| 73066 | Indigosol O4B |  | 0.27 B 0.55 V ⁺ | 0.41 Y 0.58 B | 0.72 B 0.78 Y ⁺ |
| 73076 | Indigosol O6B |  | 0.22 B — — | 0.43 B ⁺ 0.60 B 0.78 Y ⁺ | 0.65 B 0.71 B — |

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TABLE I (continued)

| Colour index No. | Commercial name* | Solubilized form of the parent dye | R _F values and colour** | | |
|------------------|-------------------------------|---|--|--|---|
| | | | S ₁ | S ₂ | S ₃ |
| 73336 | Indigosol Orange HR |  | 0.00 O ⁺ 0.55 O — | 0.43 Y ⁺ 0.52 O — | 0.00 O 0.46 O 0.58 O 0.75 O |
| 73356 | Indigosol Scarlet IB |  | 0.45 S ⁺ 0.56 S 0.65 S 0.87 Y ⁺ | 0.00 S ⁺ 0.37 Y ⁺ 0.52 S 0.61 S | 0.00 S 0.76 S — |
| 73361 | Anthrasol Pink IR |  | 0.00 P ⁺ 0.70 P | 0.00 P 0.61 P | 0.00 P 0.72 P |
| 73366 | Indigosol Brilliant Pink 13B |  | 0.00 P ⁺ 0.70 P — | 0.00 P 0.41 Y ⁺ 0.62 P | 0.00 P 0.82 P — |
| 73386 | Anthrasol Red Violet IRH |  | 0.36 V 0.55 V — | 0.57 V — — | 0.27 V 0.38 V 0.66 V 0.75 V |
| 73411 | Anthrasol Brown IRRD |  | 0.00 Br ⁺ 0.48 Br — | 0.00 Br ⁺ 0.41 Br ⁺ 0.56 Br | 0.00 Br ⁺ 0.71 Br — |
| 73421 | Indigosol HB |  | 0.00 B ⁺ 0.22 B — | 0.00 B ⁺ 0.38 Y ⁺ 0.46 V 0.56 B | 0.00 B ⁺ 0.57 B — |
| 73596 | Anthrasol Printing Violet BBF |  | 0.00 V ⁺ 0.41 V — | 0.41 Y ⁺ 0.61 V — | 0.00 V 0.70 V 0.80 Y ⁺ |
| 73601 | Anthrasol Printing Violet IRR |  | 0.00 V ⁺ 0.48 V 0.56 V ⁺ | 0.58 V — — | 0.00 V 0.75 V — |

(continued on p. 45)

TABLE I (continued)

| Colour index No. | Commercial name* | Solubilized form of the parent dye | <i>R_F</i> values and colour** | | |
|------------------|-----------------------------|------------------------------------|--|----------------------------------|---|
| | | | S ₁ | S ₂ | S ₃ |
| 73671 | Cibantine Grey BL | | 0.00 Gr 0.27 Gr 0.30 T | 0.56 Gr — — | 0.00 Gr 0.61 Gr 0.77 Y ⁺ |
| 73801 | Anthrasol Blue AGG | | 0.67 B | 0.57 B | 0.80 B |
| 73821 | Indigosol AZG | | 0.00 B ⁺ 0.45 B — | 0.43 Y ⁺ 0.58 — | 0.00 B 0.70 B 0.72 B |
| 73831 | Anthrasol Printing Black IB | | 0.00 Bl ⁺ 0.28 Bl — | 0.55 Bl — — | 0.00 Bl 0.42 Bl 0.51 Bl |

* Dye manufacturers names: Anthrasol: Farbwerke Hoechst A.G., Frankfurt/Main—Hoechst, Germany; Cibantine: Ciba Ltd., Basle, Switzerland; Indigosol: Durand & Huguenin S.A., Basle, Switzerland; Soledon: Imperial Chemical Industries Ltd., Dyestuffs Division, Manchester, England; Tinosol: J. R. Geigy S.A., Basle, Switzerland.

** Solvents: S₁ = 25 % ammonia-methanol-water (1:2:3); S₂ = Pyridine-isoamyl alcohol-25 % ammonia (1.3:1:1); S₃ = Methanol-acetic acid-water (4:1:1).

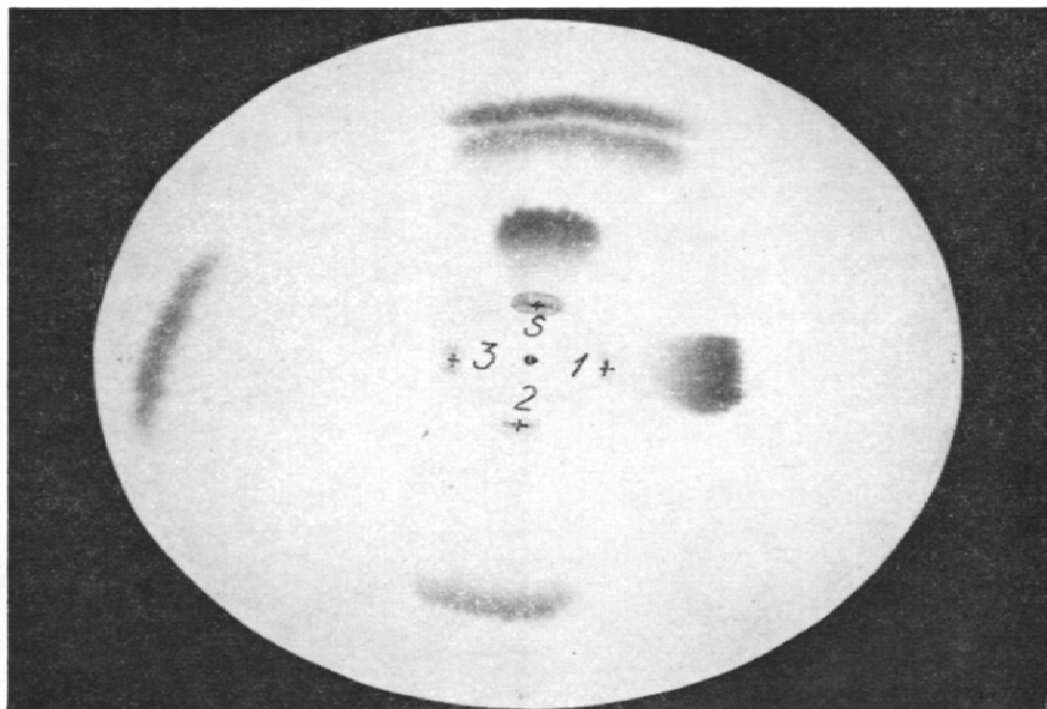
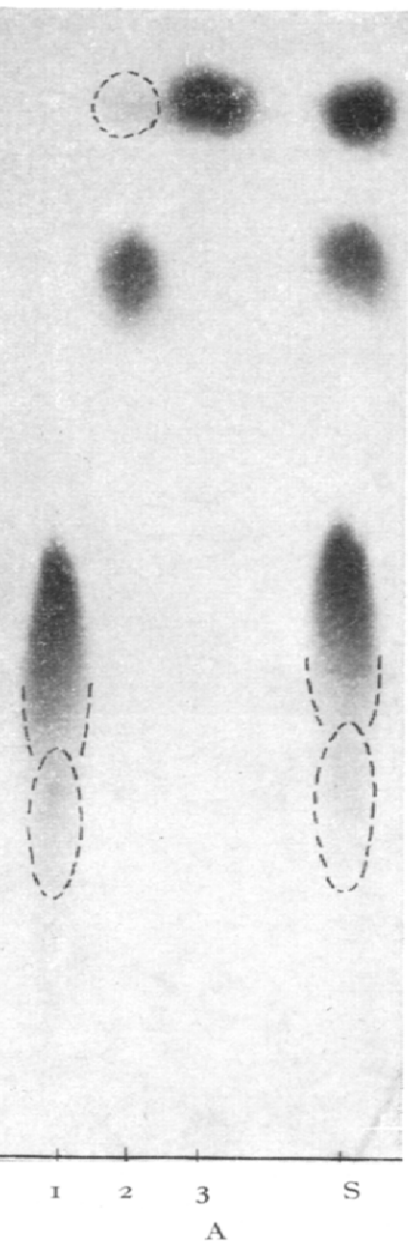
Abbreviations: B = blue; Bl = black; Br = brown; G = green; Gr = grey; O = orange; OG = olive; P = pink; S = scarlet; T = turquoise; V = violet; Y = yellow; + = spot hardly visible

RESULTS AND DISCUSSION

Some 160 commercial brands of indigosols were analysed by means of the descending chromatographic technique described above. Chromatographically interesting dyes were also chromatographed centrifugally in order to compare the separations achieved with the two techniques. The results of the descending chromatographic technique are shown in Table I. This table contains most of the important dyes of known constitution.

Figs. 1, 2 and 3 illustrate the chromatographic separation of artificially prepared mixtures of indigosols.

A comparison of the descending and centrifugal chromatograms shows that there is good agreement in the separating power of the two techniques. The sequence of the dyes is identical in the two cases. The chromatograms were developed with the solvent system S₁.



B

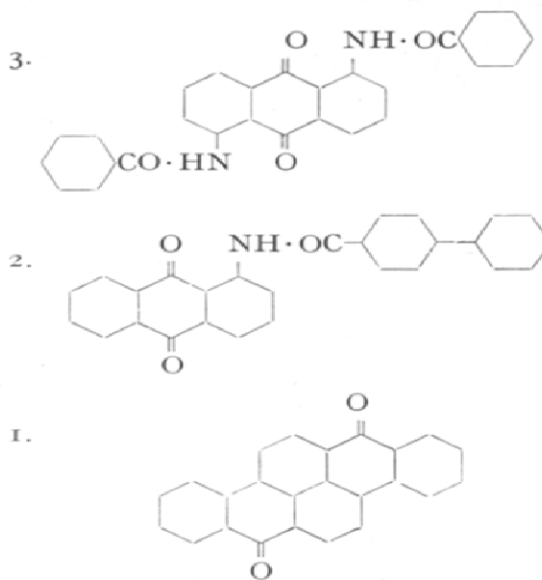
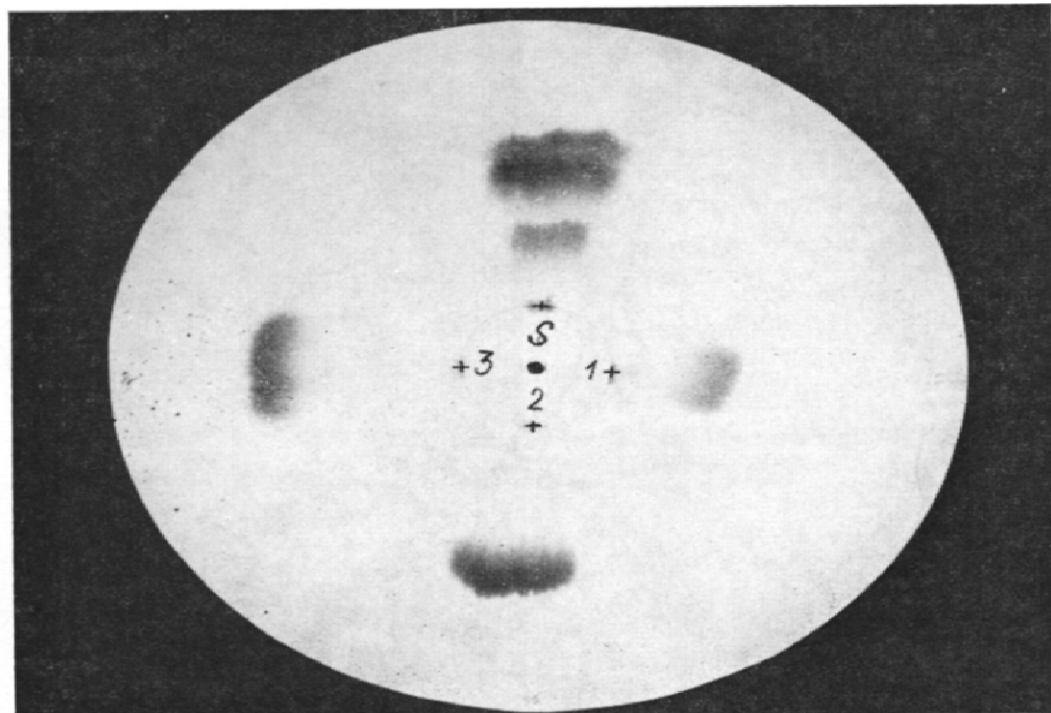


Fig. 2. Example of a chromatographic separation of a mixture of solubilized vat dyes. A. Descending technique. B. Centrifugal technique. 1 = Indigosol Golden Yellow IGK; 2 = Tinosol Yellow V; 3 = Indigosol Yellow 2 GB; S = mixture of 1, 2 and 3.



B

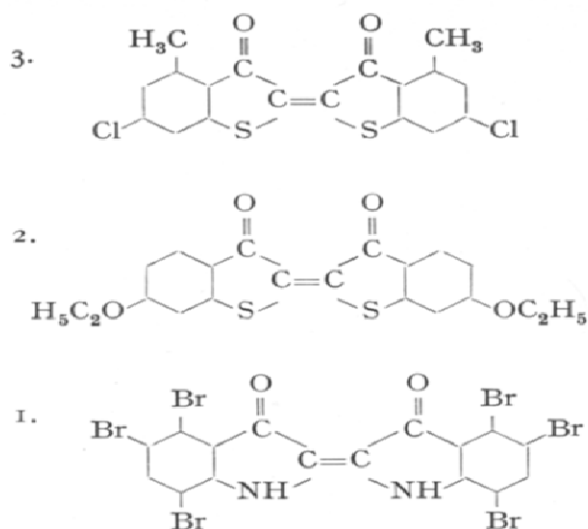


Fig. 3. Example of a chromatographic separation of a mixture of solubilized vat dyes. A. Descending technique. B. Centrifugal technique. 1 = Indigosol O6B; 2 = Indigosol Orange HR; 3 = Anthrasol Pink IR; S = mixture of 1, 2 and 3.

With solvent system S_1 , the following relationships were established between the chromatographic behaviour of the solubilized vat dyes and their chemical structure:

(1) In all instances it is obvious that the chromatographic behaviour of the vat dyes (parent dyes) is analogous, the size of the dye molecule being of decisive influence. Dyes with a simple structure possess the highest R_F value, and this decreases with increasing size of the molecule as a result of increasing dye adsorption.

(2) Simpler indigoid, thioindigoid and arylaminoquinone dyes have a higher R_F than the more complex anthraquinone dyes.

(3) Thioindigoid dyes have a higher R_F than indolethionaphthene dyes and miscellaneous dyes.

(4) Symmetrical indigoid dyes usually have a higher R_F than asymmetrical dyes.

(5) Dibenzanthrones have a higher R_F value than isodibenzanthrones.

(6) In the case of dyes with the same carbon skeleton, an increase in the number of substituents, e.g. —Cl, —Br, —CH₃, —OCH₃, causes the R_F value to decrease.

ACKNOWLEDGEMENTS

The authors are grateful to Messrs. Ing. Z. DEYL, CSc and Ing. J. ROSMUS of the Central Research Institute of Food Industry, Prague, for kindly allowing them to carry out centrifugal chromatography on their apparatus and for their valuable assistance in the field of centrifugal chromatography.

SUMMARY

Solubilized vat dyes were separated by paper chromatography, using a methanolic solution of ammonia as solvent system. A system containing pyridine, isoamyl alcohol and ammonia, as well as a mixture of methanol and acetic acid were also used. Both descending and centrifugal chromatography were employed. The relation between dye constitution and chromatographic behaviour has been examined.

REFERENCES

- ¹ P. RUGGLI AND M. STÄUBLE, *Helv. Chim. Acta*, 23 (1940) 689.
- ² J. ŠRÁMEK, *Textil*, 13 (1958) 346.
- ³ J. ŠRÁMEK, *Paper presented at the 1st Conference V T S* (Czechoslov. Scientific Technical Organization), Brno, Nov. 1958.
- ⁴ M. MATRKA, F. NAVRÁTIL AND J. FILIPI, *Chem. Průmysl*, 7 (1957) 343.
- ⁵ J. KOLŠEK, F. MLAKAR AND M. PERPAR, *Z. Anal. Chem.*, 188 (1962) 345.
- ⁶ J. ŠRÁMEK, *Textil*, 17 (1962) 147.
- ⁷ J. ŠRÁMEK, *Paper presented at the Symposium on Chromatography in the Centrifugal Field*, Prague, Feb. 1962.
- ⁸ M. PAVLÍČEK, J. ROSMUS AND Z. DEYL, *J. Chromatog.*, 7 (1962) 19.
- ⁹ M. PAVLÍČEK, J. ROSMUS AND Z. DEYL, *J. Chromatog.*, 9 (1962) 92.