

Joanna Paluszkiewicz,  
Edyta Matyjas\*,  
Kazimierz Blus

Technical University of Łódź, Institute of Dyes

\*Technical University of Łódź, Institute of  
Chemical Treatment of Textiles

ul. Żeromskiego 116, 90-543 Łódź

# Di- and Tetrafunctional Reactive Red Dyes

## Abstract

Several reactive red dyes have been prepared which derive from 1-amine-8-hydroxynaphthalene-3,6-disulphonic acid, and contain in a molecule two systems of monochloro-1,3,5-triazine or two systems of monochloro-1,3,5-triazine as well as two vinylsulphonyl systems. The spectrophotometric properties and fastness of the prepared dyes were measured, and the effect of the diamine bridge joining two chromophore systems on the degrees of dye exhaustion from dyebath and dye bonding with the cellulose fibre were examined. Owing to the presence of many salt-forming groups and their symmetric arrangement in dye molecules, the prepared dyes are characterised by high water solubility. This makes it possible to carry out dyeing processes with a low liquor ratio such as 1:5, which decreases the salt content in dyeing effluents. The type of the diamine used as a bridge which joins two chromophore systems exerts a significant influence on the dye affinity to cellulose fibres. Apart from the derivatives of ethylene-1,2-diamine, the remaining dyes are characterised by a very high degree of dye exhaustion from the dyebath. The dyes applied to cellulose fibres are practically combined with them in a quantitative manner. The bridge which increases the dye affinity to cellulose fibres consequently increases the degree of the dye's bonding with the fibre. The prepared dyes can be successfully used for dyeing cellulose fibres by the exhaustion process.

**Key words:** reactive dyes, reactive red dyes, tetrafunctional reactive dyes.

## Introduction

Cellulose fibres are of principal importance in the textile industry, owing to the very good quality of fabrics made of them, as well as their low price. More and more attention is paid to enriching the finishing of fabrics to prolong their working life. Cellulose fibres can be dyed with reactive, direct, vat, and sulphur dyes, as well as with insoluble azoic dyes formed on fibres. The requirements of today's customers are fully met by the reactive dyes which form covalent bonds with cellulose [1,2].

Reactive dyes include dyes for printing and dyes for dyeing by exhaustion. The users of the latter are interested in dyes which can be quantitatively exhausted from the dyebath, show a high degree of combination with fibre, and require no salt in application processes [3-13].

One can obtain such dye properties by an appropriate modification of the dye's molecular structure. In dyeing cellulose fibres by the exhaustion method, great industrial importance is attached to the reactive dye of Procion H-E type. They possess two or four reactive systems and molecular weights of over 1000.

The aim of the present study was to examine a new group of reactive reds of Procion H-E type, the derivatives of

1-amine-8-hydroxynaphthalene-3,6-disulphonic acid. The structure of the obtained dyes is shown by the general formula (Figure 1), where:

- A - the active component,
- A1 - anthranilic acid,
- A2 - 4-(β-ethylsulphate)sulphonylaniline,
- A3 - orthanilic acid,
- Dw - diamines:
  - Dw-1 - phenylene-1,4-diamine,
  - Dw-2 - phenylene-1,3-diamine,
  - Dw-3 - phenylene-1,2-diamine,
  - Dw-4 - diaminestilbene-2,2'-disulphonic acid,
  - Dw-5 - 4,4'-diaminebenzoanilide,
  - Dw-6 - ethylene-1,2-diamine.

These studies concerned the number and type of reactive systems, and the effect of the diamine bridge on the degree of dye exhaustion and dye bonding with cellulose fibres. The application and fastness tests carried out made it possible to assess the

usability of the compounds obtained for dyeing cellulose fibres by the exhaustion process.

## Experimental

### Dye synthesis

The dyes shown by the general formula (Figure 1) can be prepared by several methods.

### Method 1 (Figure 2)

The reaction parameters were determined by experiment. The synthesis was controlled by the TLC method, using Silufol UV<sub>254</sub> plates and the eluent ethyl acetate-propanol-water in the volumetric proportions of 1:6:3. Chromatographic measurements have shown that the coupling reaction of diazotised anthranilic acid with N-cyanur(1-amine-8-hydroxynaphthalene-3,6-disulphonic acid proceeds slowly, which is associated with the low reactivity of the diazo compound. A prolonged reaction time or increased pH

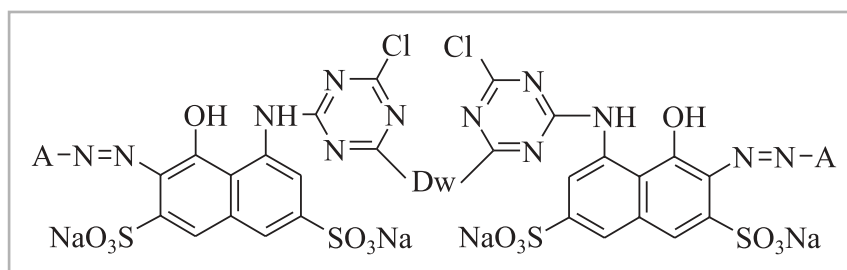


Figure 1. The general formula of the structure of the dyes obtained.

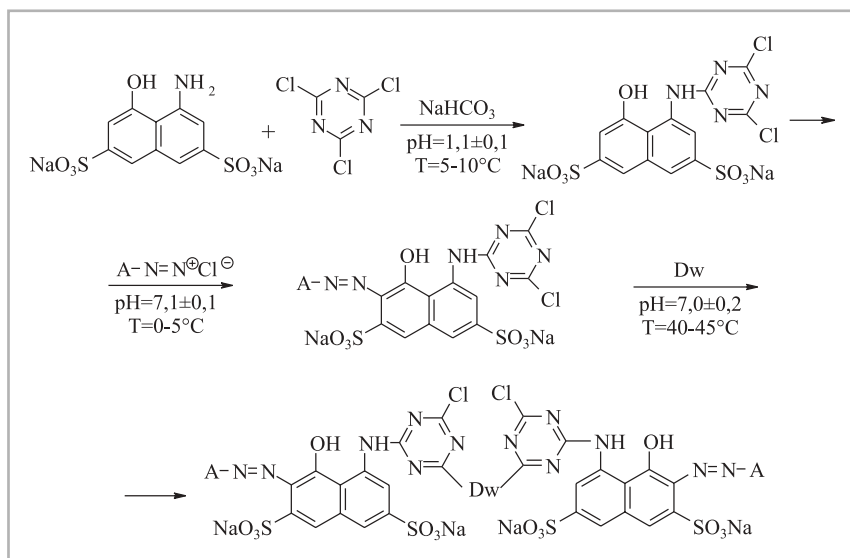


Figure 2. Method I of dye preparation.

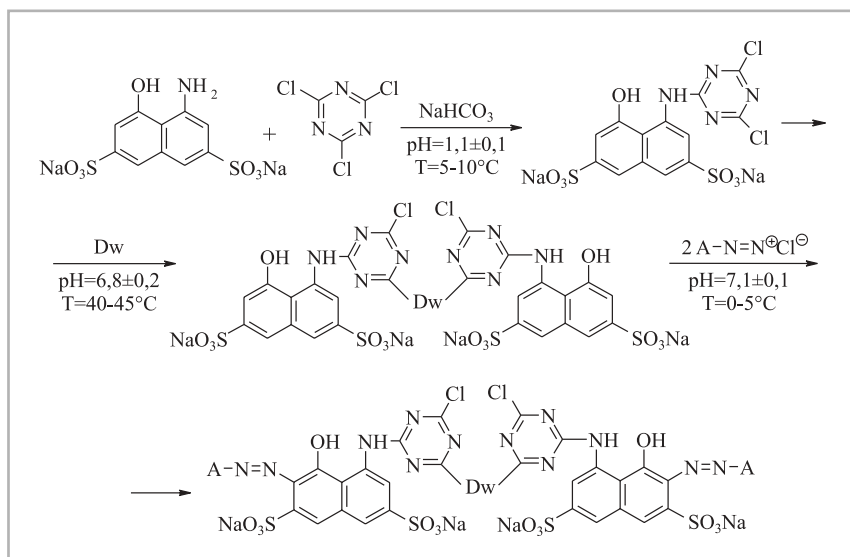


Figure 3. Method II of dye preparation

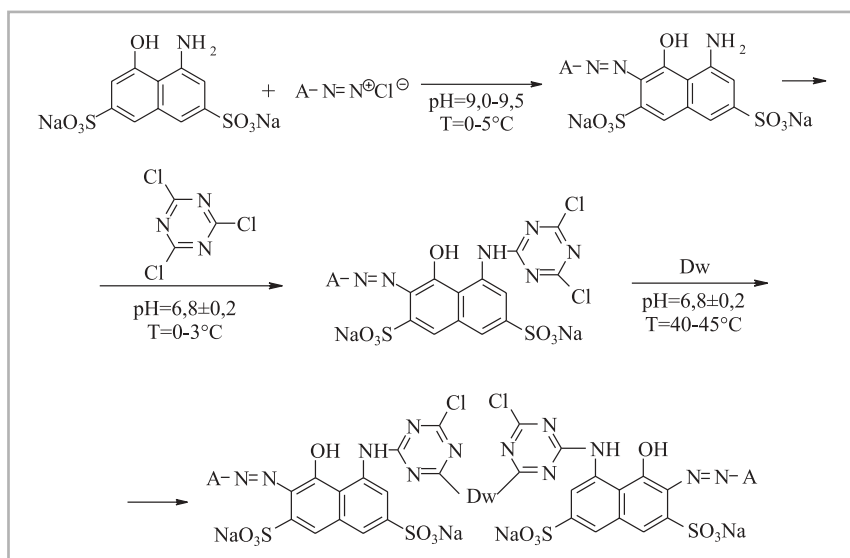


Figure 4. Method III of dye preparation.

value brings about an increase in the reactive system hydrolysis.

#### Method II (Figure 3)

In the first stage, the synthesis of the dicoupling components was carried out. The coupling of diazotised anthranilic acid and 4-(β-ethylsulphate)sulphonylaniline with the dicoupling components was carried out at a temperature of 0-5°C and a pH of 7.2±0.2, maintaining the conditions under control for 8 h. 4% sodium hydroxide, 10% sodium carbonate and 10% trisodium orthophosphate solutions were used as neutralising and buffering agents. The use of trisodium orthophosphate made it possible to obtain reactive dyes with high purity, and consequently with a high colouring yield. This also applies to the reactive dyes derived from anthranilic acid. Disodium orthophosphate is an agent which buffers the reaction medium and stabilises the diazonium compound. The mixture of phosphates are used for the stabilisation of pH in commercial products. The use of phosphates in the coupling reaction was justified.

#### Method III (Figure 4)

During the coupling reaction, by-products are formed such as a product of coupling in ortho position to amine group and a product of double coupling with 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid. The resultant dyes were purified by fractional separation with sodium chloride. The dyes were isolated from the reaction medium by salting out with sodium or potassium chloride. The dyes with the highest purity were selected for further examinations. The structures of selected dyes are listed in Table 1.

#### Spectrophotometric properties

The dyes were subjected to spectrophotometric analysis, i.e. performing  $\lambda_{\max}$  measurements in water and 50% acetone with a Specord M-40 spectrophotometer. The dye concentrations in water were  $2 \cdot 10^{-5}$  mol/dm<sup>3</sup>. The results obtained are listed in Table 2.

#### Dye application

Fabric samples were dyed in a laboratory Roaches dyeing machine using 1% of dye in relation to fibres. Dyeings with a strength lower than 1/1 of reference standard were obtained. The temperature course of dyeing is shown in Figure 5. It was established that the salt content in the application processes should be 80 g/dm<sup>3</sup> to ensure an exhaustion level of over 90%. The dyeing liquor ratio was established by measuring the degree of dye exhaus-

tion from dyebaths which was calculated from the following formula:

$$W = \frac{c_1 - c_2}{c_1} \cdot 100\% \approx \frac{A_1 - A_2}{A_1} \cdot 100\%$$

where:

W - the degree of exhaustion,  
 $c_1, c_2$  - dye concentrations before and after dyeing, respectively,  
 $A_1, A_2$  - solution absorbance before and after dyeing, respectively.

The results presented in Table 3 were obtained for dye B-13.

Trisodium orthophosphate in a quantity of 5 g/dm<sup>3</sup> was used as an alkalising agent, since it allowed a higher degree of dye bonding with fibre to be obtained. The degrees of dye exhaustion from dyebaths are listed in Table 4.

The dyed fabric was boiled off twice for 30 min in a mixture of pyridine and water (70:30), which allowed the degree of dye bonding with fibre to be determined. The dye concentration in fibre was determined by three methods:

1. The determination of dye which passed to the pyridine solution was carried out by the method of solution absorbance measurement using a reference curve. The difference between the quantity of dye in fibre and that passed to the pyridine solution was used to determine the degree of dye bonding with fibre.
2. Reflection spectra of the dyed fabric before and after boiling off. The dyeing

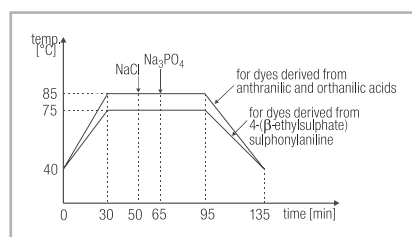


Figure 5. Temperature course of the dyeing process.

Table 3. Dependence of the liquor ratio on the degree of exhaustion for dye B-13.

| Liquor ratio | Type of alkalis                 | Degree of exhaustion, % |
|--------------|---------------------------------|-------------------------|
| 1 : 5        | Na <sub>2</sub> CO <sub>3</sub> | 95.0                    |
| 1 : 5        | Na <sub>3</sub> PO <sub>4</sub> | 95.0                    |
| 1 : 10       | Na <sub>2</sub> CO <sub>3</sub> | 93.0                    |
| 1 : 10       | Na <sub>3</sub> PO <sub>4</sub> | 93.3                    |
| 1 : 20       | Na <sub>2</sub> CO <sub>3</sub> | 90.4                    |
| 1 : 20       | Na <sub>3</sub> PO <sub>4</sub> | 90.4                    |

Table 1. Dye structures and salt content in dyes; \*C.I. Reactive Red 120 (model dye).

| Dye symbol | Dye structure   |         | Synthesis method | Salt content, % |      |                                  |
|------------|-----------------|---------|------------------|-----------------|------|----------------------------------|
|            | Diazo component | Diamine |                  | NaCl            | KCl  | Na <sub>2</sub> HPO <sub>4</sub> |
| B - 1      | A - 1           | Dw - 1  | II               | 27.7            | -    | 11.2                             |
| B - 2      | A - 1           | Dw - 2  | II               | 29.1            | -    | 27.7                             |
| B - 3      | A - 1           | Dw - 3  | II               | 25.6            | -    | 11.3                             |
| B - 4      | A - 1           | Dw - 4  | II               | -               | 28.7 | 15.6                             |
| B - 5      | A - 1           | Dw - 5  | II               | 27.3            | -    | 10.7                             |
| B - 6      | A - 1           | Dw - 6  | II               | 27.2            | -    | 24.2                             |
| B - 7      | A - 2           | Dw - 1  | II               | -               | 25.0 | 10.2                             |
| B - 8      | A - 2           | Dw - 2  | II               | 24.1            | -    | 24.6                             |
| B - 9      | A - 2           | Dw - 3  | II               | 22.3            | -    | 20.2                             |
| B - 10     | A - 2           | Dw - 4  | II               | 20.1            | -    | 20.5                             |
| B - 11     | A - 2           | Dw - 5  | II               | 24.6            | -    | 20.7                             |
| B - 12     | A - 2           | Dw - 6  | II               | -               | 24.2 | 30.9                             |
| B - 13*    | A - 3           | Dw - 1  | I                | 26.3            | -    | 11.2                             |

Table 2. Spectrophotometric properties of dyes and their fastness to light.

| Dye symbol | Water                 |   | 50% acetone           |   | Fastness to light Xenotest 1/1 |
|------------|-----------------------|---|-----------------------|---|--------------------------------|
|            | $\lambda_{\max}$ , nm | $\epsilon_{\max}$ , dm <sup>3</sup> /mol × cm | $\lambda_{\max}$ , nm | $\epsilon_{\max}$ , dm <sup>3</sup> /mol × cm |                                |
| B - 1      | 517.6                 | 3.47 × 10 <sup>4</sup>                        | 517.6                 | 4.14 × 10 <sup>4</sup>                        | 4                              |
|            | 544.7                 | 3.43 × 10 <sup>4</sup>                        | 549.5                 | 4.44 × 10 <sup>4</sup>                        |                                |
| B - 2      | 517.6                 | 5.30 × 10 <sup>4</sup>                        | 515.5                 | 6.54 × 10 <sup>4</sup>                        | 4                              |
|            | 547.0                 | 5.18 × 10 <sup>4</sup>                        | 551.9                 | 7.40 × 10 <sup>4</sup>                        |                                |
| B - 3      | 515.5                 | 5.37 × 10 <sup>4</sup>                        | 517.6                 | 6.04 × 10 <sup>4</sup>                        | 4                              |
|            | 544.7                 | 5.12 × 10 <sup>4</sup>                        | 549.5                 | 6.32 × 10 <sup>4</sup>                        |                                |
| B - 4      | 515.5                 | 4.29 × 10 <sup>4</sup>                        | 519.8                 | 4.59 × 10 <sup>4</sup>                        | 4                              |
|            | 547.0                 | 4.32 × 10 <sup>4</sup>                        | 551.8                 | 5.06 × 10 <sup>4</sup>                        |                                |
| B - 5      | 519.8                 | 3.74 × 10 <sup>4</sup>                        | 517.6                 | 4.15 × 10 <sup>4</sup>                        | 4                              |
|            | 547.0                 | 3.64 × 10 <sup>4</sup>                        | 549.5                 | 4.42 × 10 <sup>4</sup>                        |                                |
| B - 6      | 517.6                 | 4.94 × 10 <sup>4</sup>                        | 517.6                 | 5.31 × 10 <sup>4</sup>                        | 4                              |
|            | 544.7                 | 4.88 × 10 <sup>4</sup>                        | 549.5                 | 5.57 × 10 <sup>4</sup>                        |                                |
| B - 7      | 515.5                 | 5.43 × 10 <sup>4</sup>                        | 526.3                 | 7.44 × 10 <sup>4</sup>                        | 3 - 4                          |
| B - 8      | 507.1                 | 5.81 × 10 <sup>4</sup>                        | 524.1                 | 6.97 × 10 <sup>4</sup>                        | 3 - 4                          |
| B - 9      | 517.6                 | 6.21 × 10 <sup>4</sup>                        | 519.8                 | 7.00 × 10 <sup>4</sup>                        | 3 - 4                          |
| B - 10     | 519.8                 | 5.49 × 10 <sup>4</sup>                        | 524.1                 | 5.74 × 10 <sup>4</sup>                        | 3 - 4                          |
| B - 11     | 519.8                 | 4.95 × 10 <sup>4</sup>                        | 524.0                 | 5.67 × 10 <sup>4</sup>                        | 3 - 4                          |
| B - 12     | 515.5                 | 6.32 × 10 <sup>4</sup>                        | 517.6                 | 7.32 × 10 <sup>4</sup>                        | 3 - 4                          |
| B - 13     | 513.3                 | 4.67 × 10 <sup>4</sup>                        | 515.5                 | 5.22 × 10 <sup>4</sup>                        | 4                              |
|            | 535.3                 | 4.63 × 10 <sup>4</sup>                        | 542.3                 | 5.45 × 10 <sup>4</sup>                        |                                |

intensity ratio in percent is a degree of dye bonding with fibre.

3. The dyed fabrics were dissolved in 96% sulphuric acid. The resultant solution after dilution with water were used to measure their absorbance. The concentrations of dyes in solutions were read from the reference curves. The ratio of dye concentrations before and after boiling-off in percent is a degree of dye bonding with fibre.

The results obtained are listed in Table 4.

## Results and Discussion

A group of reactive reds, derivatives of 1-amine-8-hydroxynaphthalene-3,6-disulphonic acid which contain two or four reactive systems, were synthesised. The dyes obtained show various contents of impurities depending on the synthesis method used. The best

results regarding dye purity and colour yield were obtained by method II, i.e., by coupling diazo compounds with doubled N-cyanur(1-amine-8-hydroxynaphthalene-3,6-disulphonic) acid. This procedure could well be used especially in the synthesis of anthranilic acid derivatives. The coupling reaction is best carried out in the presence of orthophosphates which both buffer the reaction medium and stabilise the diazonium compound.

The derivatives of 4-(β-ethylsulphate)sulphonylaniline are red dyes, while those of anthranilic acid are reds of crimson type. All the dyes obtained were characterised by high coefficients of molar absorption. Despite their high molecular weights (1349 - 1991), these dyes show only a slight tendency to aggregation in aqueous solutions. This is connected with a high number of salt-forming groups (from 6 to 8) in the

**Table 4.** Degrees of dye exhaustion from dyebath and dye bonding with fibre (1\* - in relation to the dye in dyebath; 2\* - in relation to the dye in fibre).

| Dye symbol | Degree of exhaustion, % | Degree of dye bonding, % |      |           |      |            |      |
|------------|-------------------------|--------------------------|------|-----------|------|------------|------|
|            |                         | Method I                 |      | Method II |      | Method III |      |
|            |                         | 1*                       | 2*   | 1*        | 2*   | 1*         | 2*   |
| B - 1      | 94.8                    | 91.6                     | 96.6 | 92.6      | 97.7 | 93.5       | 98.6 |
| B - 2      | 88.8                    | 84.2                     | 94.8 | 83.4      | 93.9 | 81.6       | 91.9 |
| B - 3      | 87.2                    | 83.7                     | 96.0 | 84.1      | 96.5 | 81.5       | 93.5 |
| B - 4      | 87.8                    | 83.8                     | 95.5 | 82.7      | 94.2 | 82.2       | 93.6 |
| B - 5      | 92.5                    | 86.9                     | 93.9 | 83.5      | 90.3 | 82.0       | 88.6 |
| B - 6      | 68.9                    | 65.4                     | 94.9 | 62.4      | 90.6 | 48.1       | 73.6 |
| B - 7      | 95.9                    | 95.4                     | 99.5 | 95.1      | 99.2 | 95.5       | 99.6 |
| B - 8      | 93.7                    | 93.1                     | 99.4 | 92.2      | 99.0 | 92.5       | 98.7 |
| B - 9      | 86.2                    | 85.5                     | 99.2 | 85.0      | 98.6 | 84.5       | 98.0 |
| B - 10     | 89.6                    | 88.9                     | 99.2 | 88.7      | 99.0 | 88.8       | 99.1 |
| B - 11     | 95.4                    | 94.4                     | 98.9 | 90.7      | 95.1 | 91.9       | 96.3 |
| B - 12     | 64.8                    | 64.0                     | 98.8 | 62.5      | 96.4 | 63.1       | 97.3 |
| B - 13     | 95.0                    | 89.3                     | 94.0 | 90.3      | 95.0 | 86.4       | 90.9 |

dye molecule. As expected, the dyes possess high water solubility due to the presence of many sulphonic groups and their symmetric arrangement in the dye molecule. Their good solubility in dyebaths make it possible to carry out application processes with a liquor ratio of 1:5, using 80 g of NaCl per 1 dm<sup>3</sup> of dyebath. The low liquor ratio decreases the salinity of dye house effluents. At the same time, the relatively large molecule size of the dyes causes their high affinity to cellulose fibres. Apart from the derivatives of ethylene-1,2-diamine, the obtained dyes show degrees of exhaustion from the dyebath of over 86%. The type of the diamine used exerts a considerable influence on the degree of dye exhaustion from the dyebath. Among the phenylenediamine derivatives, the highest degree of dye exhaustion are shown by the derivatives of phenylene-1,4-diamine, which is probably associated with the possibility of assuming the coplanar structure of the dye molecules. The non-coplanar derivatives of ethylene-

1,2-diamine possess degrees of exhaustion of 68.9% for B-6 dyes and 64.8% for B-12 dyes. As confirmed by tests, the dyes applied to cellulose fibres are practically combined quantitatively with the fibres. In dyeing processes, it is beneficial to use trisodium orthophosphate as an alkalisng agent. As expected, higher degrees of dye bonding are shown by the tetrafunctional dyes (B-7 - B-12) as compared with the difunctional dyes (B-1 - B-6). The obtained difunctional dyes derivatives of anthranilic acid are characterised by comparable degrees of dye bonding with the fibre in relation with the model dye B-13 (C.I. Reactive red 120). The higher degree of sample B-13 (also B-1 - B-12) dye bonding with respect to market products is caused by both lower concentration on the fibre and the absence of any hydrolysis of the reactive system in the dyes tested. However, the results obtained confirm the thesis that the dye structure, and especially the type of diamine bridge linking two chromophore systems, exert a considerable

effect on the degree of dye exhaustion from the dyebath, and consequently the degree of dye bonding with fibre. The light fastness of the dyes derivatives of anthranilic acid are the same in comparison with the model dye B-13. The light fastness of the dye derivatives of 4-( $\beta$ -ethylsulphate)sulphonylaniline is lower, and results from the different position of deactivating substituent with respect to the azo group (absence of intermolecular interactions). Despite the same restriction concerning light fastness, some of the dyes obtained can be successfully used for dyeing cellulose by the exhaustion process.

□

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□ Received 28.11.2001 Reviewed: 11.10.2002

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