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Reactive Dyes for Single-Bath and Single-Stage Dyeing of Polyester-Cellulose Blends

Abstract
Cellulose fibres were dyed with selected dyes containing 3'-carboxypirydyno-triazine reactive systems. The dyeing processes were carried out at a temperature of 130 °C in phosphate buffers within a pH range of 6-8. It was found that the degree of dye exhaustion and degree of dye fixation with cellulose fibre are high, which confirms the usefulness of these dyes for dyeing cellulose fibres in a neutral medium at the specific temperature while dyeing polyester fibres (130 °C). The results indicate the possibility of using dyes of this type in mixtures with disperse dyes for the single-bath and single-stage dyeing of polyester-cellulose blends.

Key words: *Reactive dyes, 3'-carboxypirydyno-triazine reactive dyes, exhaust dyeing of cotton, dyeing cotton-polyester blends.*

In recent years, the production of polyester fibres has been dynamically increased, accompanied by the common use of polyester-cellulose blends. Textiles made from blends of polyester and cellulose fibres constitute about 10% of the total consumption of textile materials. Polyester and cellulose fibre blends show the advantages of both components of the textile fabric. Due to significant differences in the chemical structure of both types of fibres, the problems of effectively dyeing such blends have been extensively studied.

Polyester fibres show a definitive hydrophobic character and a high degree of crystallinity, being difficult to penetrate with dyes. Besides mass-colouration of polyester fibres, they can be dyed by the conventional dyeing method, but only with the use of disperse dyes. These dyes, as non-ionic compounds, are usually applied at elevated temperatures (130-135 °C) under pressure in a weakly acidic medium (pH 5-7) [1,2]. During the dyeing process, disperse dyes penetrate to the amorphous region of polyester fibres. The cellulose component can be dyed with direct, reactive, vat, sulphur or azoic dyes, while polyester-cotton blends are mostly dyed with disperse and reactive dyes [3].

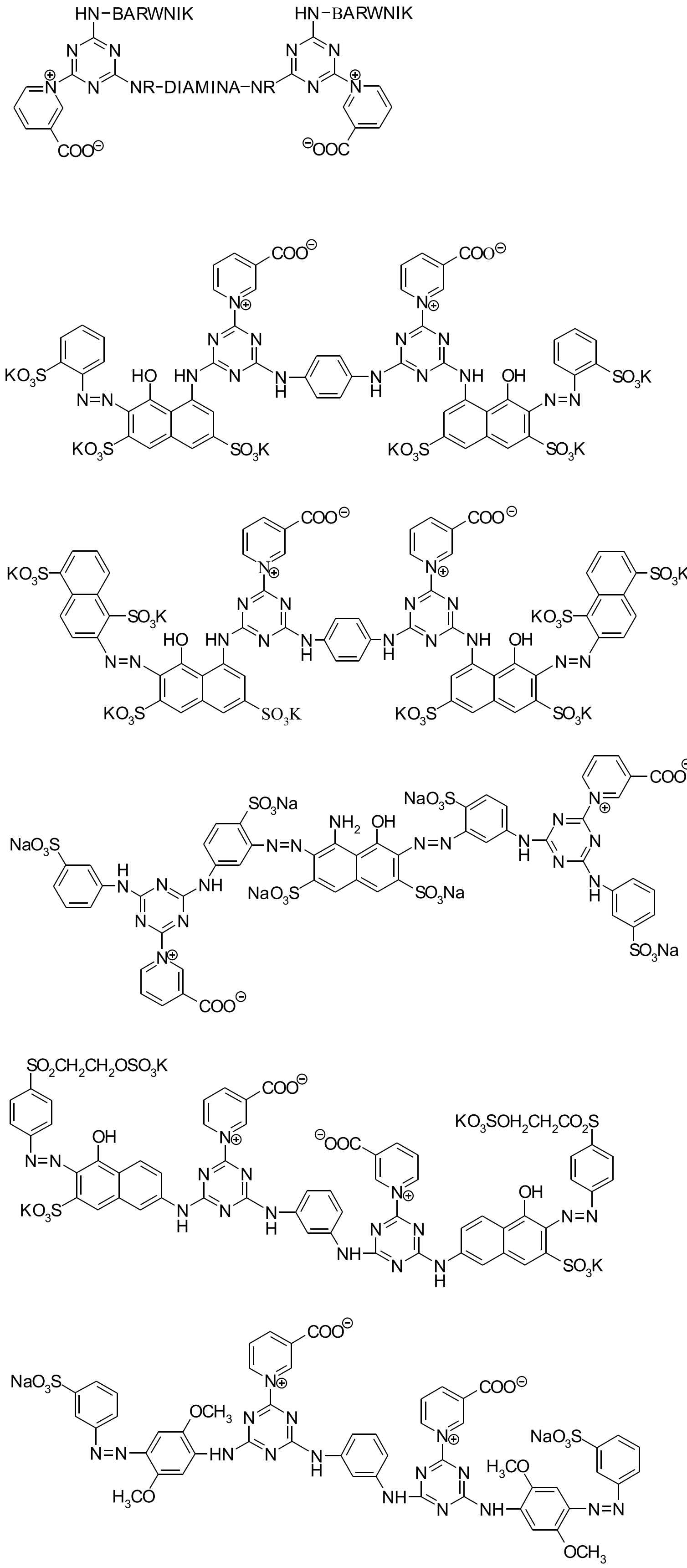
The polyester-cellulose blends are mostly dyed during a two-stage process: first, the polyester component is dyed with a disperse dye at 130-135 °C under pressure, after which the cellulose component is dyed in the second bath with a reactive dye. An alternative method is the single-bath process carried out in two stages.

During the dyeing process, reactive dyes form covalent bonds with the cellulose fibre. In practice, the most popular types of reactive dyes are derivatives of monochlorotriazine and 4-(β-ethylsulphate)sulphonyloaniline. Both reactive systems require a strong alkaline bath (pH 10-11). This results from the need to provide an adequately high concentration of Cellulose-O^{-} ions, which is indispensable for the proper course of the process, and also from the mechanism of the dye-fibre reaction.

The alkaline medium adversely affects disperse dyes, causing the hydrolysis of some functional groups present in them (ester, nitrile and acetylamide groups); the degree of dye dispersion is deteriorated and the crystalline structure of dyes may be changed, which can finally lead to the deterioration of the colour effects from the dyeing [2,4].

One attempt to cope with the problem mentioned above has been the development of special reactive disperse dyes. These products (Dybln, Procilen, Celestren) are capable of dyeing both types of fibres at the same time, but they have not gained noticeable popularity, due to the necessity of using elevated temperatures of fixation and special auxiliary agents; they also lacked bright shades and showed deteriorated dyeing fastness [5,6].

A research problem to be solved is the development of a group of reactive dyes which would enable the adequate dyeing of the cellulose component under the optimal dyeing conditions required for the polyester component (preferably in a neutral or weakly acidic medium).



G - 1

B - 1

B - 2

B - 3

B - 4

B - 5

__Figure 1.__ Chemical formulae G-1 and B-1, ..., B-5.

This would allow the dyeing process to ne radically simplified, and considerably save time and energy.

As follows from literature reports [7-9,14] and the studies carried out at our Institute [10,11] in the field of environmentally friendly reactive dyes, some of the more frequently mentioned dyes which can react with cellulose fibres in a neutral medium are derivatives of 3'-carboxypirydinium-triazine (Kayacelon React, Nippon Kayaku). The general structure of these dyes with the general formula G - 1 is presented in Figure 1.

At the present moment, the structures of the commercially accessible Kayacelon React dyes are unknown besides a few examples.

The aim of the present study was to investigate the dyeing of cellulose fibres with selected reactive dyes containing a 3'-carboxypirydinium triazine reactive system under conditions typical while applying disperse dyes to polyester fibres (at a temperature of 130 ºC). Our investigations concerned the influence of the pH of the dye bath (ranging from 6 to 8) on the degree of dye-fibre combination, and the effect of electrolyte quantity on the degree of dye exhaustion from the dye bath. The investigations performed were part of more extensive studies concerned with the search for reactive and disperse dye compositions for the single-stage and single-bath dyeing of polyester-cotton blends.

Experimental

The following group of model 3'-carboxypirydino-triazine reactive dyes represented by formulae B-1÷B-5 (slown in Figure 1) was used in the present study.

The synthesis of dyes B-1, B-2, B-3 and B-5 consisted in condensing their di(monochlorotriazine) precursors [11,12] with nicotinic acid in an aqueous medium at a pH of 6.5 ± 0.2 and a temperature of 85 ± 2 ºC for 5-6 h. Dye B-4 was prepared in a coupling process of diazotized 4-(β-ethylsulphate)sulphonyloaniline with an appropriate bi-functional coupling component derived from 6-amino-1-hydroxy-naphthalene-3-sulphonic acid. All reactions were monitored by chromatography. The final dyes were precipitated by salting out with sodium or potassium chloride. The salt content (sodium or potassium chlorides) in the obtained dyes was esti-

Table 1. *Spectrophotometric properties of dyes, salt content and molecular weights.*

Dye symbol	Molecular weight, g/mol	Salt content, %	Spectroscopic properties		Colour
			λ_{max}, nm	Approximated ε_{max}, dm^3/mol cm	
B – 1	1740	31,3	507,8	25,6	red
B – 2	2074	28,8	520,5 543,2	25,6 24,6	red with a blue hue
B – 3	1571	36,5	609,3	23,8	navy blue
B – 4	1718	44,8	489,9	25,3	orange
B – 5	1222	44,2	420,7	25,9	yellow

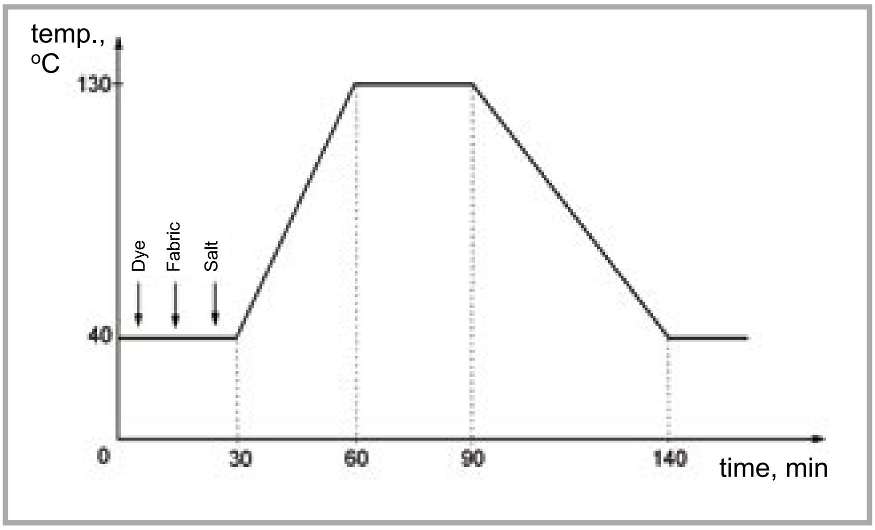


Figure 2. *Temperature dyeing schedule.*

mated by the potentiometric method, and the properties of aqueous dye solutions were measured by spectrophotometry. The results are listed in Table 1.

As can be seen from the presented data, dyes of comparable salt content and comparable colouristic strength were obtained.

The dyeing experiments were carried out with Noris 1/150 STB bleached cotton fabric, (previously washed in a solution of a non-ionic surface-active agent), using a laboratory dyeing machine from Roaches-Rotec (England). The temperature schedule of the dyeing process is shown in Figure 2.

1% dyeings were carried out within the 6-8 pH range in a phosphate buffer prepared from a 1/15M solution of KH_2PO_4 and Na_2HPO_4 [13]. The quantity of phosphates in the bath was about 10 g/dm^3. The content of sodium chloride in the dyeing processes varied from 0 to 60 g/dm^3. The dyeings were performed at the temperature of 130 °C, with a fabric to liquor ratio of 1:10. The dyeings were also carried out in distilled water at a pH of 7.5 (from sodium carbonate), at the temperature of 130 °C, with a liquor ratio of 1:10.

The degree of dye exhaustion from the dye bath (E) was determined by spectrophotometric measurements of the absorption of the dye bath, before (A_1) and after dyeing (A_2).

$$E(\%) = (1 - A_2/A_1) \times 100\% \qquad (1)$$

The degree of dye fixation on the fibre (F) was estimated by spectrophotometric comparison of the dye concentration in the dyed fabric before (C_1) and after extraction with pyridine-water azeotrope (C_2). In the first method, we used Kubelka-Munk's equation, in which the relative dyeing strength (K/S) is proportional to the concentration of dye in the fibre C_W [3].

$$(K/S)_1 = (1-R)^2/(2\,R) = k\,C_1 \qquad (2)$$

where:
R – the reemission coefficient,
K – the absorption coefficient,
S – the reflection coefficient.

The relative degree of dye fixation was assessed by the comparison of the relative strength of dyeings.

$$F_1(\%) = C_2/C_1 \times 100\% = = (K/S)_2/(K/S)_1 \times 100(\%) \qquad (3)$$

The measurements were carried out by the use of a Data Colour reflexive spectrophotometer.

In the second method, both fabric samples, after disintegration into single filaments, were dissolved in 96% sulphuric acid at 0-5 °C. After dilution with ice water to a strictly specified, constant volume, the absorbances of both solutions were measured. The relative degree of dye fixation to the cellulose fibre was calculated from the following formula:

$$F_2(\%) = C_2/C_1 \times 100\% = \cong (B)_2/(B)_1 \times 100(\%) \qquad (4)$$

where:

B_1 – the absorbance of the solution obtained from the fabric sample without extraction,
B_2 – the absorbance of the solution obtained from the fabric sample extracted with the pyridine-water azeotrope.

The total efficiency of dyeing (T) was calculated from the following formula:

$$T_1(\%) = E(\%) \times F_1(\%) / 100(\%) \qquad (5)$$

The values of the degree of dye exhaustion and the degree of dye fixation with the fibre are listed in Table 2 (see page 78).

Discussion

From the dyeing experiments we performed, it can be seen that the reactive dyes containing 3'-carboxypirydyno-triazine reactive systems are suitable for dyeing cellulose fibres in an aqueous medium at the temperature of 130 °C, within the pH range of 6-8 (phosphate buffer).

The degrees of dye exhaustion depend on the concentration of electrolyte in the dye bath and the chemical structure of the dye molecules. In the case of the dyeings carried out in the phosphate buffer containing about 10 g of phosphates per 1 dm^3 of dye bath, the degrees of exhaustion are in the range from 70% to 80%. An additional amount of sodium chloride added to the dye bath increases dye absorption on the fibre. Some effect on the degree of exhaustion is exerted by the structure of dye molecules; for example, dye B-3 shows higher degrees of exhaustion than dye B-2.

The degrees of dye fixation with cellulose fibre in the phosphate buffer are

*Table 2. Dye exhaustion degree (E), dye fixation with cotton fibre (F), and the total efficiency of dyeing (T) of the examined dyes; * – dyeing in distilled water (pH corrected with a solution of sodium carbonate).*

Dye symbol	pH of dyebath	NaCl content g/dm^3 in dyebath	E	F_1	F_2	T_1
B – 1	7,47	60	95.7	94.0	93.7	90.0
	7,47	40	92.5	94.5	94.1	87.4
	7,47	20	89.5	93.2	93.0	83.4
	7,47	0	77.2	89.5	88.9	69.1
	7,50*	0	14.6	60.8	60.2	8.9
	8,04	20	90.5	95.1	95.2	86.1
	6,98	20	90.0	91.0	92.1	81.9
	6,04	20	87.1	86.3	86.9	75.2
B – 2	7,47	60	91.3	94.8	94.1	86.6
	7,47	40	88.9	91.9	92.0	81.7
	7,47	20	82.7	89.1	90.1	73.7
	7,47	0	67.2	79.7	78.9	53.7
	7,50*	0	10.8	47.8	48.0	5.2
	8,04	20	83.8	95.1	94.9	79.7
	6,98	20	82.5	87.8	88.1	72.4
	6,04	20	82.6	80.6	80.4	66.6
B – 3	7,47	60	98.1	97.5	97.0	95.6
	7,47	40	96.9	96.8	96.9	93.8
	7,47	20	94.1	96.8	96.8	91.1
	7,47	0	83.4	85.9	86.0	71.6
	7,50*	0	32.4	75.4	75.6	25.6
	8,04	20	94.4	94.5	94.0	89.2
	6,98	20	93.8	90.8	90.0	85.2
	6,04	20	93.3	88.7	87.9	82.8
B – 4	7,47	60	98.6	98.3	97.0	96.9
	7,47	40	98.4	98.3	97.0	96.7
	7,47	20	92.1	96.0	95.0	88.4
	7,47	0	83.3	95.3	95.6	79.4
	7,50*	0	57.5	80.4	82.3	46.2
	8,04	20	93.4	98.6	98.0	92.1
	6,98	20	92.0	96.0	96.3	88.3
	6,04	20	92.3	82.9	83.0	76.5
B – 5	7,47	60	90.8	70.9	71.3	64.4
	7,47	40	89.0	67.4	66.9	60.0
	7,47	20	84.7	66.1	64.7	56.0
	7,47	0	63.6	62.0	64.0	39.4
	7,50*	0	42.4	48.1	48.4	20.4
	8,04	20	86.4	70.9	70.3	61.3
	6,98	20	80.1	64.8	62.9	51.9
	6,04	20	79.4	53.0	52.5	42.1

very high and dependent on the pH. The higher pH of the dye bath yields in the higher degree of dye fixation with the fibre, which is probably due to the increase in the ionisation of hydroxylic groups in cellulose. The differences observed in the degrees of dye fixation with the fibre between dyeings in a buffer of pH 6.04 and that with a pH of 8.04 varies from several percent (B-1, B-3) to a dozen or so percent (B-2, B-4, B-5). Very high degrees of dye fixation were obtained while dyeing cellulose fibres in phosphate buffer close to a pH of 7.0, which is very important in terms of dyeing polyester-cellulose blends.

The decrease in dye exhaustion from the dye bath is accompanied by a decrease in the dye fixation with fibre. This fact may be caused by the higher affinity of hydrolysed reactive dyes to the cellulose fibre in comparison with unhydrolysed dyes.

Conclusion

All reactive dyes containing two 3'-carboxypirydinotriazine reactive systems which were the object of this work are characterised by a high affinity to cellulose fibre in an almost neutral (7.0-7.5) pH of the dyeing bath. Very good exhaustion degrees at relatively low concentration of electrolytes (30 g/dm^3) were in most cases accompanied by very high (over 90%) fixation values on the dyed fibre, with a total dyeing efficiency exceeding 80%. The latter value is specific to the best traditional reactive dyes present nowadays on the market, although they require an alkaline environment. The results obtained during this work confirm the usefulness of this type of reactive dyes in mixtures with disperse dyes for a single-bath and single-stage dyeing of polyester-cellulose blends. However, it would be necessary to develop suitably environment-friendly, phosphate-free buffers to perform dyeing processes.

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