INVESTIGATIONS ON THE DYEING ABILITY OF SOME REACTIVE TRIAZINE AZO DYES CONTAINING TETRAMETHYLPIPERIDINE FRAGMENT

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ABSTRACT

Three monofunctional reactive triazine dyes, containing tetramethylpiperidine fragment and an identical chromophore, but different reactive group (chlorotriazine or allylamine/allyloxy), were used for dyeing cotton and wool with the application of different methods of dyeing: exhaust, pad-batch and printing. The degree of exhaustion and fixation, as well as the fastness properties of the dyed samples in respect to washing, acidic and alkaline perspiration, dry and wet rubbing and light fastness were assessed. The influence of the dye bath temperature on the percentage of exhaustion and color intensity was determined. It was found that the monochlorotriazine reactive dye may be used for dyeing cellulosic textile materials, while the most suitable were the methods of exhaust at 80°C, pad-dry, pad-dry-steam, cold pad-batch and printing. The dyes containing an allylic group were found applicable to wool dyeing with the application of the method of exhaust at 80°C. The investigated dyed samples showed good light fastness properties.

Keywords: reactive triazine azodyes, tetramethylpiperidine fragment, dyeing ability fastness properties.

INTRODUCTION

The textile industry exploits diverse types of dyes and pigments. Textile azo/reactive dyes present a significant group of synthetic organic dyes utilized in the textile business and therefore are widespread industrial contaminants. These pollutants are formed in massive quantities and can go into the environment all the way through production [1, 2]. With rising attractiveness of reactive dyes in respect to cellulosic fabric dyeing, the environmentally related problems connected with their utilization have acknowledged consideration.

Reactive dyes are anionic compounds soluble in water due to the existence of a sulfonic group in the molecule. Due to the presence of a reactive group, they are able to fix covalently to the textile fibers macromolecules forming etheric, thioetheric, aminic or amidic bonds. Upon dyeing, the dye molecules and the textile fibers macromolecules form unique colored molecules of very good resistance to wet treatment [3]. These dyes are generally used on higher value clothes, which are normally mercerized [4]. Reactive dyes, as a group, provide achieving a wide variety of fast, bright shades in dyeing and printing [5-7]. The class of reactive dyes with a triazine ring is an important class of dyes [8-30].

The reactive triazine dyes have numerous advantages. But they have a significant disadvantage as well. The latter refers to the relatively low light stability of the orange, scarlet and red colors.

Increasing attention has been lately paid to the textiles protective properties against UV radiation originating from sunlight. Different additives are applied to the ma-
materials in order to prevent or decrease their photodegradation. A large number of different types of compounds are described in the literature as photostabilizers. The most important and efficient stabilizers are the organic ones, containing 2,4-hydroxybezophenones, s-triazines, hydroxyphenylbenzothiazoles and especially 2,2,6,6-tetramethylpiperidine (HALS) derivatives [31].

We have previously reported the synthesis of some polymerizable reactive triazine dyes containing a stabilizer in their molecule. They are suitable for “one-step” materials coloration and stabilization [32-34]. We have synthesized [33] dyes described by formula I. The present study is focused on these dyes application in case of cotton and wool materials and the determination of the fastness properties of the samples dyed. As the dyes pointed above show high photostability in an aqueous and polymer solution [33], it is also of interest to study the photostability of the samples prepared.

![Formula I](image)

where R stands for: -Cl (dye 1); -NHCH₂CH=CH₂ (dye 2) and -OCH₂CH=CH₂ (dye 3).

**EXPERIMENTAL**

**Materials and methods**

The dyes used were previously synthesized by us [33]. The absorbance of each dye in an aqueous solution was measured using 1 cm quartz cells housed in a visible scanning spectrophotometer.

The application and fastness tests for the pretreated and dyed cotton fabrics were conceded on tasting machine. The dyeing procedure was performed on 100 % cotton and wool fabric (15 cm x 25 cm). The application of monochlorotriazine dye 1 was accomplished in correspondence with the methods for dyeing with monochlorotriazine dyes described in various company catalogs. In absence of any methods, described in the literature, for dyeing with reactive dyes containing allyl group, the dyeing of wool was carried out following the procedure used in case of dyeing with vinyl sulfone fiber reactive dyes. The methods used for dyeing cotton were:

1. **Exhaust at 40°C, 60°C and 80°C.**

The dyeing was performed according to Schemes 1-3.

![Scheme 1. Exhaustion at 40°C.](image)

![Scheme 2. Exhaustion at 60°C.](image)

![Scheme 3. Exhaustion at 80°C.](image)

A. Glauber’s salt – 50 g/l;
B. A dye – 2 %;
C. An alkaline agent: Sodium carbonate – 5 g/l
Sodium hydroxide – 2.5 ml/l 38°Be (at 40°C), 1ml/l 38°Be (at 60°C);
D. Acetic acid – 1 ml/l;
E. Nonionogenic textile auxiliary – 0.5 g/l
2. Pad-batch dyeing process
The textile samples were padded with a dye solution containing a dye (10 g/l), urea (100 g/l), sodium carbonate (20 g/l), sodium alginate (10 g/l), Glauber’s salt (10 g/l) and water to reach a volume of 1000 ml.

The cold pad-batch method included padding at 20°C-25°C. This step was followed by placing the sample in a polyethylene bag to exclude drying. Then it was continuously rotated and batched for 2 h, 6 h, 12 h and 24 h. The drying was carried out for 5 min at 120°C. The fixing proceeded for 4 min at 160°C (for Pad-dry method), while that with steam - for 5 min at 102°C (for Pad-dry-stem method).

The washing of the dyed samples was carried out with 0.5 g/l solution of a nonionogenic surfactant for 5 min at 40°C. Then the samples were rinsed with cold water.

3. Printing
A printing paste containing dye (10 g/l), urea (100 g/l), sodium carbonate (20 g/l), water (100 ml) and sodium alginate to reach a volume of 1000 ml was used. The next step was printing and drying for 5 min at 105°C. The fixation was carried out with hot air for 4 min at 160°C, while that with saturated steam - for 5 min at 102°C. After the heat treatment, the samples were washed as described above.

The dyeing of wool was carried out at pH 4.5 - 5 with 2 % solution of the dye, Glauber’s salt (20 g/l), acetic acid (2 ml/l) and sodium carbonate (5 g/l) (Scheme 4).

The dyed samples were tested after washing-off using 0.5 g/l non-ionic detergent at 40°C for 5 min in accordance with ISO standard methods.

Color fastness to rubbing (BDS EN ISO 105-X12 (2004)), color fastness to washing (BDS EN ISO 105-C06/A1S (2010), color fastness to perspiration (BDS EN ISO 105-E04 (2013)) and color fastness to light (BDS EN ISO 105/ B02) were the specific tests carried out.

RESULTS AND DISCUSSION

Dyes spectral properties
The absorption maxima ($\lambda_{\text{max}}$) of dyes 1-3 are recorded in an aqueous solution. The $\lambda_{\text{max}}$ values refer to 500 nm (Dye 1), 480 nm (Dye 2) and 485 nm (Dye 3). The values of $\varepsilon$ (molar extinction coefficient) are in the range of 20160 mol$^{-1}$cm$^{-1}$ and 21300 mol$^{-1}$cm$^{-1}$, which indicates that the dyes have high absorption intensity.

Dyeing of cotton fabrics
Cotton fabrics are dyed with dyes 1-3 at 2 % depth o.w.f. according to the procedures mentioned above. Materials of an intense orange colour are obtained. Using the data color technique and associated software, the colour characteristics of the dyes are recorded.

1. Dye exhaustion at 40°C, 60°C and 80°C
The extent of dye exhaustion (%) is determined spectrophotometrically. The absorbance of each dyebath solution prior to and after dyeing is measured using 1 cm quartz cells housed in a visible scanning spectrophotometer at $\lambda_{\text{max}}$ of each dye. Because the temperature is considered a very important factor in textile dyeing, the influence of the temperature on the dye extraction and dye fixation is examined. It is found that the rate of dye exhaustion increases with temperature increase (for dyes 1 and 2). An inverse relationship (Fig. 1) is obtained for dye 3. The greatest dye exhaustion (90 %) is observed for dye 1 at 80°C. The influence of the temperature of dyeing on the dye fixation is also investigated. For this purpose the amount of dye in the washing bath (washing at 40°C) is determined spectrophotometrically (Fig. 2). It is found that the rate of fixation of the dye decreases.

![Scheme 4. Dying of wool at 80°C.](image-url)
with temperature increase. The best fixation is observed in case of dye 1 at 80°C.

Reflectance measurements on the dry dyed fabrics are carried out using the data color technique under a D65 lamp. The dyes color strength (K/S) and the color differences (DE) of the dyed samples after washing are measured. The values obtained are shown in Fig. 3.

It is seen that the values of K/S and DE are the highest for samples dyed at 80°C. The data for DE corresponds fully to those referring to the color strength of the samples dyed. All results mentioned show that monohlorotriazine dye 1 can be used for dyeing cellulosic textile materials by the process of exhaustion at a temperature of 80°C. At this temperature the color strength of the sample is increased significantly in comparison with those of the cotton samples dyed at 40°C and 60°C. The results obtained for dyes 2 and 3 show that the method used is inapplicable to them.

Fig. 1. The influence of the temperature of the dye bath on the dye exhaustion (%).

Fig. 2. Dependence of the amount of dye in the washing bath of the temperature of dyeing.

Fig. 3. Dependence of K/S (a) and DE (b) on the temperature of dyeing.
2. Padding
2.1. Cold pad-batch
The batching of the samples proceeds for 2 h, 6 h, 12 h and 24 h. (Method 2.1.1 - Method 2.1.4).

The dyeing ability of the dyes tested is estimated on the ground of the dye concentration in the washing bath (Fig. 4).

One can see that the batching time increase results in decrease of the dye concentration in the washing bath (dye 1). It is also seen that in case of dyes 2 and 3 the washing bath content of the dye is almost half of the initial one. The results referring to K/S and DE of the dyed samples after washing are shown in Fig. 5.

The results in Fig. 5 do not show high DE and K/S values of the cotton samples dyed. Compared to those dyed by the method of exhaustion at 80°C, they are about 5 times lower. This makes the method inapplicable to the dyes studied.

2.2. Pad-dry
The dyeing ability of the dyes tested is determined on the ground of the concentration of the dye in the washing bath (Fig. 6). The results for K/S and DE of the cotton samples dyed are shown in Fig. 7.

2.3. Pad-dry-steam
The dyeing ability of the dyes tested is determined on the ground of the concentration of the dye in the washing bath (Fig. 6). The values of K/S and DE of the cotton samples dyed are shown in Fig. 7.

Fig. 4. Concentration of the dye in washing bath at different time of cold pad-batch.

Fig. 5. Dependence of the K/S (a) and DE (b) on the duration of batching.

Fig. 6. Influence of the method of dyeing on the amount of dye in the washing bath - pad-dry (Method 2.2) and pad-dry-steam (Method 2.3).
It is seen that better results are obtained for samples dyed with dye 1. The comparison of the results obtained shows that method 2.3 is the better one because the concentration of dye in the washing bath is 2 times less (Fig. 6). The values of K/S and DE received by both methods are commensurable. (Fig. 7).

3. Printing
A hand printing using a laboratory sieve pattern of geometric shapes proceeds under pressure. The drying is accomplished at a temperature of 105 °C. The prints fixing is carried out with hot air at 160°C (Method 3.1) or with saturated steam at 102°C (Method 3.2). The efficiency of printing is evaluated on the ground of the color strength and color differences of printed cotton samples determined. It is found that the method of fixation of imprints does not affect significantly the color strength and does bring about color differences. The results obtained are illustrated in Fig. 8.

The juxtaposition of the data to those obtained by the method of padding shows that the values obtained by printing are higher.

The investigation carried out leads to the conclusion that dyes 2 and 3 do not qualitatively dye a cotton fabric. Most probably the allylamino and allyloxy reactive groups of the dyes do not pass into their active form, which is in fact required for the formation of a covalent bond with the cellulose hydroxyl groups. That is why tests are carried out with all dyes but on wool fibers in an acid media. Thus a woolen worsted tape is dyed by...
the method of exhaustion at 80°C. The effect of the dye nature on the exhaustion and dye fixation is examined. It is found that the dye exhaustion is better in case of dyes 2 and 3 (over 65%) in comparison with dye 1, where it is 40% (Fig. 9a). Fig. 9b shows that almost all of mono-chlorotriazine dye 1 is discharged from the wool fibers.

The color strength obtained with the application of dyes 2 and 3 is significant, unlike that reached with dye 1 (Fig. 10a). The color differences correspond to the saturation achieved (Fig. 10b).

The wool fibers dyeing with dye 2 and 3 is probably possible because of the acid medium required. The sulphonated groups make ionic bonds there with the wool amino groups. It is worth mentioning that dye 1 has three sulphonated groups in the chromophore like dyes 2 and 3, but the dyeing with it is somewhat hampered. This suggests that the allyl groups present display activity in the medium used. Further studies of the dyed samples with the application of other methods are required to elucidate the mechanism of allylic groups’ behavior.

**Fastness properties**

The fastness properties of dyed cotton and wool samples are assessed.

Dyes 1-3 show generally good light fastness properties. The washing, rubbing and perspiration fastness are good to excellent (Table 1). Dyes 1-3 show generally very good to excellent fastness properties on wool (Table 2).

Fig. 9. Dependence of the dye exhaustion (%) from the dye bath (Fig. 9a) and the amount of dye in the washing bath (Fig. 9b) at dyeing on wool by exhaustion at 80°C on the kind of the dye.

Fig. 10. Dependence of K/S (Fig. 10a) and DE (Fig. 10b) on the kind of the dye.
Table 1. Fastness properties data of the cotton fabrics dyed with dye 1 at different methods.

<table>
<thead>
<tr>
<th>Method for dyeing</th>
<th>Washing at 40°C</th>
<th>Perspiration</th>
<th>Rubbing</th>
<th>Light</th>
</tr>
</thead>
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<td></td>
<td></td>
<td>Alkaline</td>
<td>Acid</td>
<td>Dry</td>
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<tr>
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<td>5/3-4/5</td>
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<td>5</td>
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<tr>
<td>1.2</td>
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<td>5/3-4/4</td>
<td>5/4/4-5</td>
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<tr>
<td>3.1</td>
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<td>5/4/4-5</td>
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<td>5</td>
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<tr>
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<td>5/4/4-5</td>
<td>5/4/4-5</td>
<td>5</td>
</tr>
</tbody>
</table>

Light fastness: 1-poor, 2-slight, 3-moderate, 4-fair, 5-good, 6-very good, 7- excellent;  
Washing & Rubbing fastness: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent;  
Data x / y/ z indicate a change in color / staining wool / staining cotton.

Table 2. Fastness properties data of the wool fabrics dyed with dyes 1-3.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Washing at 40°C</th>
<th>Perspiration</th>
<th>Rubbing</th>
<th>Light</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Alkaline</td>
<td>Acid</td>
<td>Dry</td>
</tr>
<tr>
<td>1</td>
<td>5/4-5/5</td>
<td>5/5/4-5</td>
<td>5/5/5</td>
<td>5</td>
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<tr>
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<td>5/4-5/5</td>
<td>5/4-5/4-5</td>
<td>5/4-5/4-5</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>5/4-5/5</td>
<td>5/4-5/4-5</td>
<td>5/4-5/4-5</td>
<td>5</td>
</tr>
</tbody>
</table>

Light fastness: 1-poor, 2-slight, 3-moderate, 4-fair, 5-good, 6-very good, 7- excellent;  
Washing & Rubbing fastness: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent;  
Data x / y/ z indicate a change in color / staining wool / staining cotton.
CONCLUSIONS

The dying ability of three monofunctional reactive triazine dyes is investigated. The degree of exhaustion and fixation, the fastness properties of the dyed samples in respect to washing, acidic and alkaline perspiration, dry and wet rubbing, as well as the light fastness are assessed. The results obtained lead to the conclusion that the monochlorotriazine reactive dye 1 may be used for dyeing cellulosic textile materials. The methods of exhaustion at 80°C, pad-dry, pad-dry-steam and printing are the most suitable providing good light fastness properties. The dyes containing allylic group are applicable for dyeing wool using the method of exhaustion at 80°C.

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