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# Reactive Dyes for Cellulose Fibres Including UV Absorbers

**Abstract**
*Several reactive dyes derivatives of C.I. Reactive Red 198 have been prepared. Three of these dyes included additional UV-absorber systems based on 2'-hydroxy-benzotriazole. The spectrophotometric properties of the dyes obtained were measured, and their application properties on three different types of cotton fabric were examined. It was found that newly-prepared dyes could be applied to the cotton fabric by the pad dyeing method, which gives a higher dyeing efficiency than the exhaustion method. As in previous works, it was found that the type of the fabric used has a significant influence on the measured UPF value. It was found that the new products gave excellent UV protection properties to dyed textiles, although only minor improvement was observed in comparison with the reference dye.*

**Key words:** *reactive dyes for cellulose, 2'-hydroxybenzotriazole UV-absorbers, UPF factor of cotton fabrics.*

## ■ Introduction

In recent years, people have been spending much more time outdoors, and thus they are more exposed to solar radiation. It is obvious, that light is necessary for the proper growth and life of human beings and the whole planet. However, too much exposure to the short-wave range of the sunlight (UV radiation) can result in skin damage such as inflammations, and sunburns, especially for children and people with light-sensitive skin. These factors can cause premature ageing and even skin cancer. According to the protection measures against UV radiation established by the WHO, the use of tightly-woven loose-fitting full-length clothes is recommended, inter alia [1]. It is very important to consider what kind of textiles should be used, because most of the garments worn during summer do not provide sufficient protection.

In practice, the UV protection properties of textiles are characterised by the UPF value of a particular fabric. UPF is the abbreviation of the Ultraviolet Protection Factor, and is calculated on the base of transmitted UV radiation through the textile article (similar to the SPF of cosmetics). It shows how much longer a person wearing the particular garment can stay out in the sun before the onset of skin reddening, compared to an unprotected person. According to the following classification system, a UPF range of 15 to 24 (effective UV transmission 6.7 to 4.2%) gives good protection, a UPF of 25-39 very good protection, and a UPF of 40-50 and more gives excellent protection [2,3].

The UPF of textiles depends on their chemical composition and physical structure (thickness, porosity, method of manufacturing). The second important factor which affects the UPF of textiles is the presence on the fabric of various chemicals such as dyes and other auxiliaries. It was experimentally found that among natural fibres the best protection against UV radiation is given by wool. On the other hand, from the practical and aesthetic viewpoints, in summer we usually wear clothes which are made from undyed cotton, a natural fibre which provides only little protection from the ultraviolet radiation. The introduction of dyes and other auxiliaries which possess their own significant absorption in the UV region can increase the protection properties of this fibre.

In practice, a series of special UV absorbers are used in order to protect textiles and to improve the light-fastness of the coloured fabrics. These compounds absorb the harmful UV radiation in the region of 250-400 nm and rapidly convert it to harmless heat. Among various chemical structures, one of the most important groups are 2'-hydroxyphenyl-benzotriazoles such as Tinuvin 326 (Figure 1), commercialised by Ciba-Geigy [4]. This product is widely used for polyester fibres dyed by the exhaustion method. The specific nature of the hydrogen bridge formed in the molecule is responsible for its protective properties. In the excited state of the molecule, after absorbing the part of radiation, the proton from the bridge is transferred from the oxygen atom of the hydroxyl group to the nitrogen atom of the benzotriazole ring. This leads to a new excited state with lower energy, from which the molecule can easily return to the first basic state [5].

A similar absorber (Figure 2) was designed to improve the photostability of the anionic dyes applied while dyeing the wool. The sulphonic group in its molecule gives solubility in water and allows fixation of the absorber onto the fibre [6].

At present, other special compounds are also used to increase the protective properties of coloured or undyed fabrics against UV radiation. For example, for
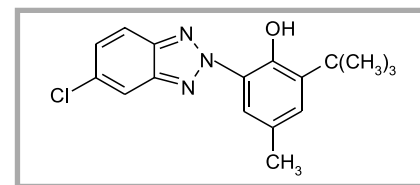


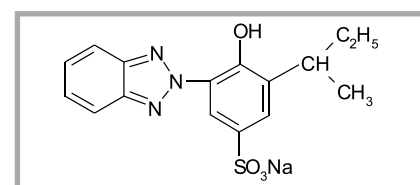**Figure 1.** *Chemical structure of the UV absorber 'Tinuvin 326'.*



**Figure 2.** *Water-soluble UV absorber of the benzotriazole-type.*

cotton and cotton blends, studies recommend Cibatex UPF, a water-soluble oxalic acid dianilide with two reactive groups (no structure details known). It is applied by the exhaustion (1-4%) or pad batch methods (15-50 g/dm³) with reactive or direct dyes [3].

One interesting experiment in this area was an attempt to incorporate the UV-absorbers system (of the benzophenone and benzotriazole type) to the molecule of dispersed dye (Disperse Yellow 42) used in polyester fabric. One example of such a prepared dye is presented in Figure 3. A slight improvement of light fastness in the dyeing fabric was observed in some cases of these dyes [7].

At the present moment, there is no information of such works in the field of the reactive dyes for cellulose fibres. Thus, the purpose of our research was the synthesis and examination of the application properties of bifunctional reactive dyes for cellulose fibres which included an additional UV absorber fragment in their molecule. The structure of these dyes is presented in Figure 4.

In this formula, A was a typical moderator used in the synthesis of reactive dyes such as metanilic acid (A1) in the case of the standard reference dye (C.I. Reactive Red 198), or the amino group (A2). In the case of other dyes, we used as A specially prepared water-soluble UV-absorbers, derivatives of the 2'-hydroxyphenyl-benzotriazole presented by structures (A3, A4, and A5) in Table 1.

In our earlier work [8], the same absorbers were successfully used as components of colourless UV-absorbers for undyed cellulose fibres. In the present work, it was anticipated that cotton fabric coloured with some of the synthesised dyes would also exhibit increasing protective properties in comparison with fabric dyed with the standard dye.

## ■ Experimental

The UV absorbers were prepared by the methods usually used in the case of other benzotriazole derivatives [9].

**Absorber A3** was prepared by a coupling reaction of diazotized 3-amino-4-nitrobenzenesulphonic acid with 4-hydroxyacetanilide, followed by the reduction of the nitro group of the monoazo dye to the triazole ring with simultaneous
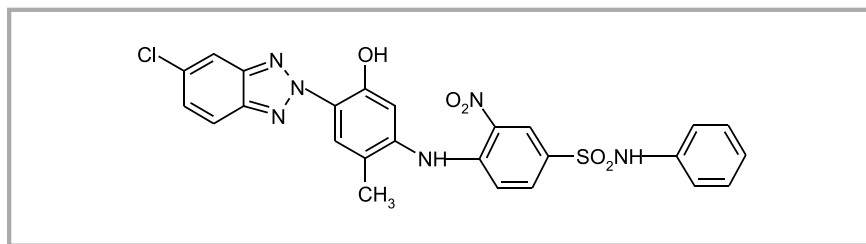


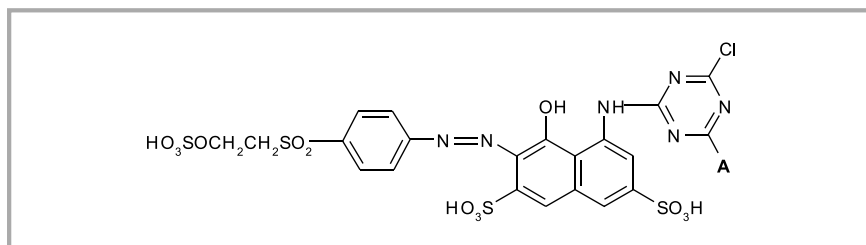*Figure 3. Disperse Yellow 42 with built-up UV absorber.*



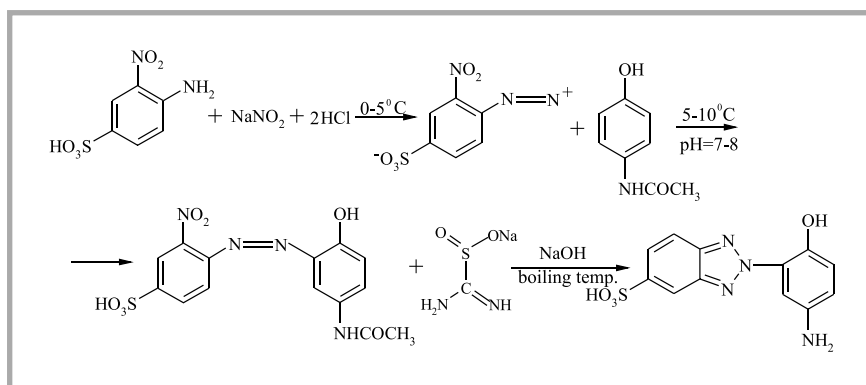*Figure 4. The general structure of the prepared dyes.*



*Figure 5. The synthesis route of the absorber A3.*

*Table 1. Results of ¹H NMR analysis of prepared UV-absorbers (A3, A4, and A5).*

| The structure of the absorber | Results of ¹H NMR analysis |
|---|---|
|  A3 | 1, 2  7.77-7.89 ppm (m, 2H); <br> 3  8.19 ppm (s, 1H); <br> 4  7.07 ppm (s, 1H); <br> 5,6  6.55-6.66 ppm (m, 2H). |
|  A4 | 1, 2  7.75-7.86 ppm (m, 2H); <br> 3  8.14 ppm (s, 1H); <br> 4  6.80 ppm (s, 1H); <br> 5  6.27 ppm (s, 1H). |
|  A5 | 1  6.64 ppm (s, 1H); <br> 2  6.85 ppm (d, $^3J_{2,3}$=9.11 Hz; 1H); <br> 3  7.43 ppm (d, $^3J_{3,2}$=9.11 Hz; 1H); <br> 4  8.12 ppm (s, 1H); <br> 5  7.66 ppm (d, $^3J_{5,6}$=8.43 Hz); <br> 6  7.08 ppm (d, $^3J_{6,5}$=8.43 Hz). |

**Table 2.** *Spectrophotometric properties of absorbers A3-A5.*

| UV-absorber | $\lambda_{max}$, nm | $B_{max}$ | $\varepsilon_{max}$, dm³/mol×cm |
|---|---|---|---|
| A3 | 300 | 0.72199 | 1,44×10⁴ |
| A4 | 310 | 0.52593 | 1,05×10⁴ |
| A5 | 351 | 0.62234 | 1,12×10⁴ |

**Table 3.** *The structure of prepared dyes and their colouring efficiency (*Reactive Red 198).*

| Symbol of the dye | Moderator A | $\varepsilon_{max}$×10⁻⁴, dm³/mol×cm |
|---|---|---|
| P1* | A1 | 3.13 |
| P2 | A2 | 2.46 |
| P3 | A3 | 2.38 |
| P4 | A4 | 2.77 |
| P5 | A5 | 2.17 |

**Table 4.** *The exhaustion degree, fixation degree and total dyeing efficiency of prepared dyes.*

| Symbol of the dye | Dyeings 1%, Fabric X | | | Dyeings 2% | | | Pad dyeing |
|---|---|---|---|---|---|---|---|
| | Degree of exhaustion, % | Degree of fixation, % | Dyeing efficiency, % | Degree of exhaustion, % | | | Dyeing efficiency, % Fabric X |
| | | | | Fabric X | Fabric Y | Fabric Z | |
| P1 | 79.1 | 86.3 | 68.3 | 64.2 | 67.5 | 64.9 | 92.1 |
| P2 | 79.6 | 82.0 | 65.2 | 62.8 | 66.8 | 65.8 | 85.8 |
| P3 | 80.8 | 77.5 | 62.6 | 61.8 | 62.6 | 63.6 | 81.8 |
| P4 | 50.5 | 89.1 | 45.0 | 39.7 | 40.8 | 39.1 | 83.5 |
| P5 | 79.0 | 83.6 | 66.0 | 63.4 | 64.0 | 62.5 | 86.1 |

hydrolysis of the acetylamino group (scheme shown in Figure 5):

**Absorber A4** was prepared in a similar way to A3, but 4-methylphenol was used as a coupling agent. The resultant 2'-hydroxy-4'-methylphenylbenzotriazole-6-sulphonic acid was then coupled with diazotized metanilic acid, and the azo bond was reduced to the amino group.

**Absorber A5** was prepared by coupling diazotized 2-aminophenol-4-sulphonic acid with 1,3-phenylenediamine, and the oxidation of the resultant o-aminoazo dye with copper salts in a boiling aqueous-ammonia environment [10].

The structure of the prepared absorbers A3-A5 were confirmed by ¹H NMR analysis on the Bruker DPX-250 Avance

spectrometer at a frequency of 250 MHz. The analysed compounds were dissolved in $D_2O$. The results of this analysis are listed in Table 1.

All the prepared absorbers A3-A5 were examined after the removal of mineral salt impurities for UV spectra on the UV-VIS Perkin Elmer Lambda 40 spectrophotometer in water solutions. The results of these measurements are listed in Table 2 and Figure 7.

Reactive dyes P1-P5 were prepared by the condensation of 1,3,5-trichloro-s-triazine (cyjanuric chloride) with 1-amine-8-hydroxy-3,6-naphtalenedisulphonic acid (H acid) at the temperature of 0-5°C and pH=1.0±0.2. The completiong of this reaction was confirmed by testing each sample on filter paper with an Ehrlich reagent. No colour present means that all the aromatic amine had overreacted with the cyjanuric chloride. Such prepared 'triazinyl-H' acid was then coupled with diazotized 4-(β-sulphatoethyl)sulphony laniline ('paraester') at the temperature of 0-5°C and pH=7.0±0.2. The last step of the synthesis was the condensation of dichlorotriazinyl dye with amine A at the temperature of 35-40°C and pH=7.0±0.2. The latter step was monitored by paper chromatography (Whatman 3 paper, developing phase 1% aqueous NaCl). The synthesis route of the reactive dyes is presented in the scheme in Figure 6. Synthesised dyes P1-P5 were examined for their UV spectra in the UV-VIS region.
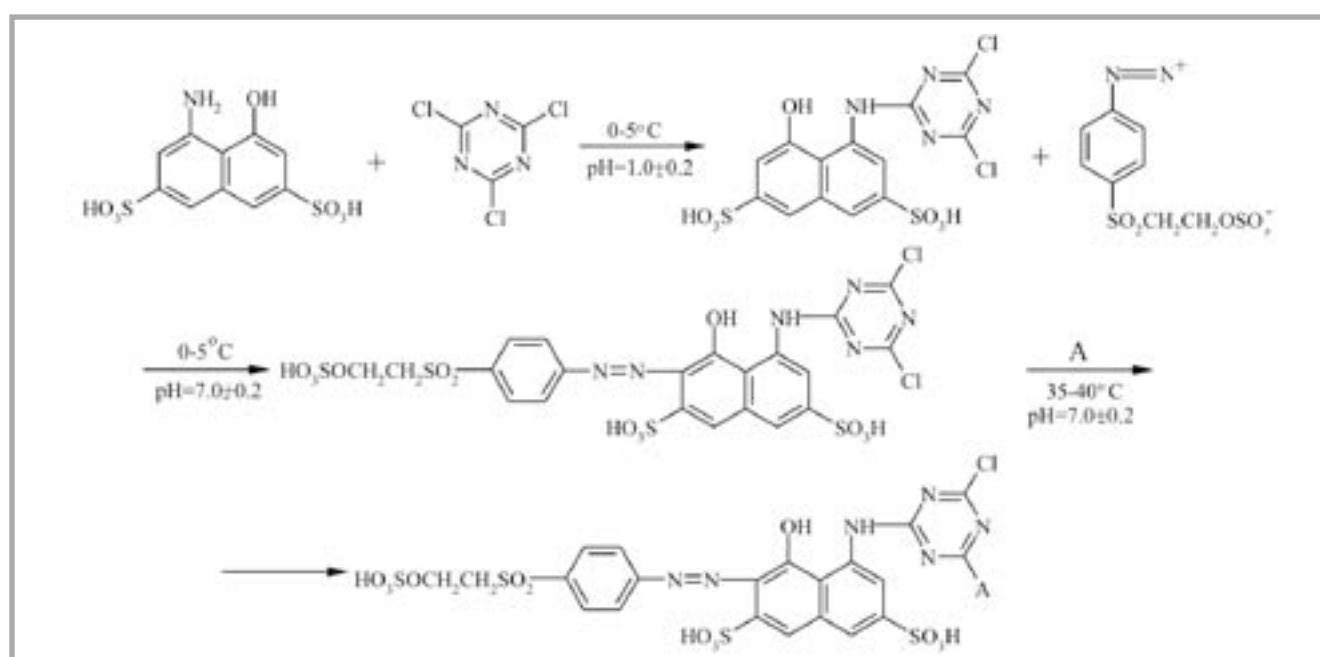


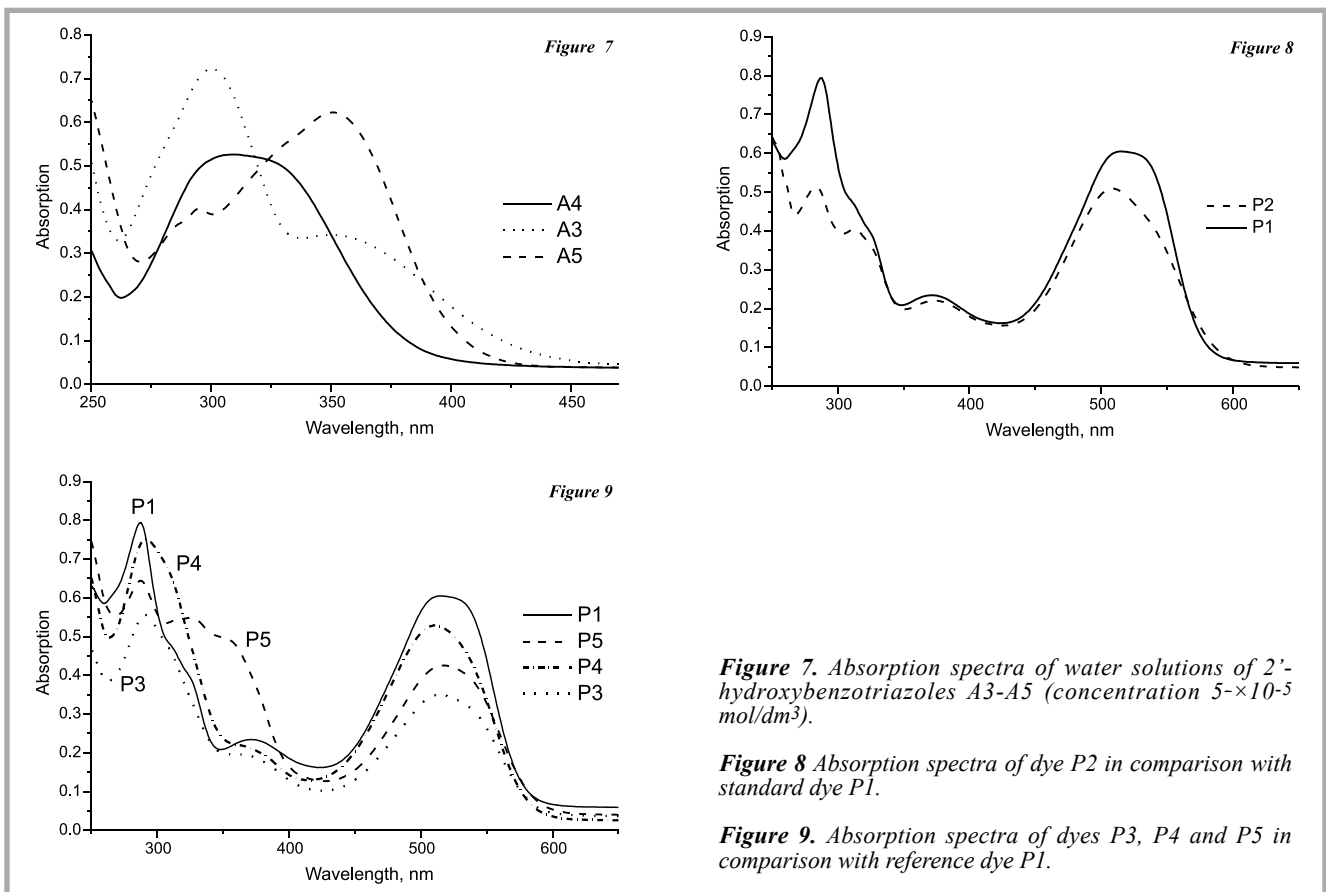**Figure 6.** *The synthesis route of prepared dyes, derivatives of C.I. Reactive Red 198.*

**Figure 7.** *Absorption spectra of water solutions of 2'-hydroxybenzotriazoles A3-A5 (concentration 5-×10-5 mol/dm3).*

**Figure 8** *Absorption spectra of dye P2 in comparison with standard dye P1.*

**Figure 9.** *Absorption spectra of dyes P3, P4 and P5 in comparison with reference dye P1.*

Measurements were made in water solutions with the use of a UV-VIS Perkin Elmer Lambda 40 spectrophotometer. The results of these measurements are listed in Table 3 and presented in Figures 8 and 9.

All the prepared dyes were subjected to application examinations, during which the following cellulose fabrics were used:

■ bleached cotton fabric with linen weave, weight 107 g/m2 (Fabric X);

■ bleached cotton with linen weave, weight 104 g/m2 (Fabric Y);

■ bleached cotton satin, weight 119 g/m2 (Fabric Z).

Dyeing was carried out by the exhaustion method (1% and 2% dyeings, dyebath ratio 1:20 in the presence of 50 g/dm3 sodium chloride and 20 g/dm3 sodium carbonate). The percentage degree of exhaustion was calculated from spectrophotometric measurements according to formula (1):

$$E = (1 - \frac{B_2}{B_1}) \times 100\% \quad (1)$$

where:

$B_1$ – the absorption of the dyebath at $\lambda_{max}$ before dyeing;

$B_2$ – the absorption of the dyebath at $\lambda_{max}$ after dyeing.

The results of these measurements are listed in Table 4.

Each fabrics was also coloured with the same dyes by the use of the pad dyeing method. Each bath contained the following elements: 1 g dye, 10 g of urea, 1 g NaHCO$_3$ , 5 cm3 10% solution of 3-nitrobenzenesulphonic acid sodium salt (Nitrole S), 5 cm3 5% solution of sodium alginate, and was completed to 50 cm3 with distilled water). The fixation of the dyes was carried out at the temperature of 130°C over 5 minutes.

In order to more precisely characterise the prepared dyes, their fixation on the fabric X was measured. Any unfixed dye was stripped from a sample of dyed fabric by repeated hot extraction with pyridine-water azeotrope. After drying, the fabric sample was then dissolved in concentrate sulphuric acid and poured onto a water-ice mixture. The concentration of dyes in these solutions were measured spectrophotometrically. The same procedure was repeated with the samples of the dyed fibre which were not extracted with the water-pyridine system. The percentage degree of fixation was then calculated from formula (2):

$$Z = \frac{C_2}{C_1} \times 100\% \quad (2)$$

where:

$C_1$ – the absorption of the dissolved sample of the fabric without extraction with the pyridine-water azeotrope,

$C_2$ – the absorption of the dissolved sample of the fabric extracted by the pyridine-water azeotrope.

The total efficiency of the dyeing process was calculated from formula (3):

$$W = \frac{E \times Z}{100}\% \quad (3)$$

The results of these measurements are listed in Table 4.

Finally, the dyeing textiles were examined for their protective properties according to the European Standard [11]. The measurements of UV transmittance were carried out with the double beam Beckman DK-2A spectrophotometer equipped with an Ulbricht sphere and powered by a hydrogen lamp. The *UPF* factor was calculated from formula (4):
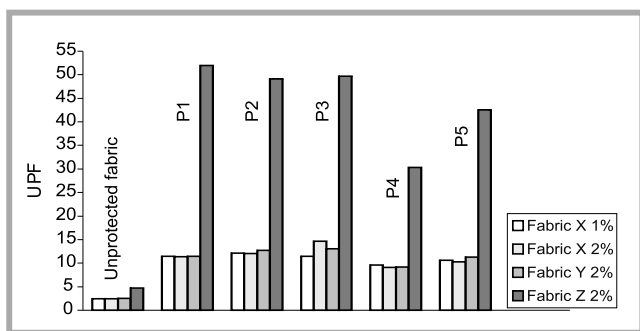
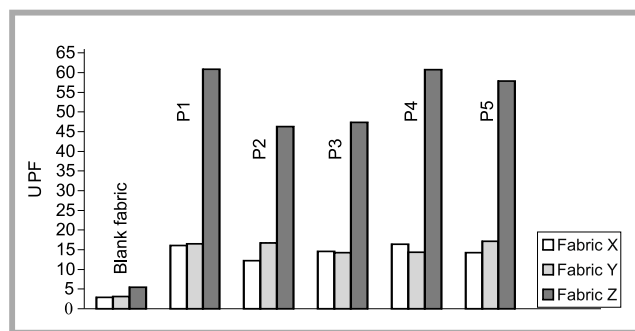**Figure 10.** *UPF factor of fabrics dyed by the exhaustion method.*



**Figure 11.** *UPF factor of fabrics coloured by pad dyeing method.*

$$UPF = \frac{\sum_{\lambda=280}^{\lambda=400} E(\lambda) \varepsilon(\lambda) \Delta\lambda}{\sum_{\lambda=280}^{\lambda=400} E(\lambda) T_i(\lambda) \varepsilon(\lambda) \Delta\lambda} \qquad (4)$$

where:

$E(\lambda)$ - the solar spectral irradiance, W/m$^2$nm;

$\varepsilon(\lambda)$ - the erythema action spectrum;

$T_i(\lambda)$ - the spectral transmittance sample $i$ at the wavelength $\lambda$;

$\Delta\lambda$ - the interval of the wavelength, nm.

The results obtained are presented graphically in Figures 10 and 11.

## ■ Results and Conclusions

As can be seen from the results presented in Figure 7 (page 79) and Table 2, all the examined absorbers exhibit significant absorption in the near UV region, as was expected. The A4 absorber has the broadest absorption band, so one may expect the best increase in UV protecting properties after building it up to the dye molecule. Similar properties might also be expected in the case of absorber A3, which possesses the highest value of the molar absorption coefficient.

The analysis of the data presented in Figure 8 (page 79) and in Table 3 show that introducing other moderators than methanilic acid to the dye molecule, such as ammonia, results in only a small decrease in their molar absorption coefficients $\varepsilon_{max}$, in comparison with the standard dye P1. Some decrease in the absorption intensity in the UV-B ultraviolet region absorption spectra (280-315 nm) is also visible, probably due to the absence of the aromatic ring of the methanilic acid in P2.

The absorption curves of the dyes P3-P5 presented in Figure 9 show that incorporating the 2'-hydroxybenzotriazole system into the dye molecule results in the increase in absorption in the UV region, which is especially visible in the

case of dye P5, and also in the case of dye P4. On the other hand, due to the radical increase in the molecular weight of these dyes, their molar absorption in the visible region is much lower than in the case of the reference dye P1. The decrease in colour intensity of the newly-prepared dyes is much greater than was expected.

All the factors mentioned above also influence the application properties of the prepared dyes. As can be seen from the data presented in Table 4, in several cases (Dye P4), probably due to the structural disturbance of the dye molecule, the degree of exhaustion on the coloured fabric is visibly decreased. More comparable results were obtained during the pad dyeing method with an average dyeing efficiency of 80–90%. For this reason, prepared dyes could more readily be used in this method, or in the printing of cellulose fibres.

Figures 10 and 11 present the values of the UPF factor calculated from the measurements of transmitted UV radiation through the cotton fabrics used. As it mentioned earlier, the results again show that the physical properties of the examined fabrics have a crucial influence on their UPF factor. The higher protection properties of the uncoloured fabric are increased to a much greater extent after the dyeing process. This is especially visible in the case of Fabric X and Fabric Z, where an increase from 'moderate' and 'good' to 'excellent' protection can be observed for several dyes.

Comparing the new dyes with the reference C.I. Reactive Red 198 (P1), one may note that dye P3 gives the best UPF factor for the exhaustiong method, while in the pad dyeing method the best results are obtained for the dye P4, although both these values are practically very close to those of the reference dye. However, if one considers the fixation degree on the

fibre of the reference dye in comparison with the new dyes, improvement of up to 10% of the UV-protecting properties may be observed in the latter case. This result is however rather unimportant from the practical point of view, so one may rather consider the use of new benzotriazoles as the components of fibre-reactive, colourless UV absorbers, as we suggested in our earlier work [8].

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