

SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
16 (2010)

**USE OF NEW REACTIVE DYES FOR DYEING
OF POLYAMIDE 6 AND WOOL**

Vlasta LIŠKOVÁ^{a1}, Tiago A. D. PINTO^b and Ladislav BURGERT^a
and Radim HRDINA^c

^aInstitute of Chemistry and Technology of Macromolecular Materials,

^bDepartment of Chemistry, The University of Minho, PT-471 057 Braga,

^cInstitute of Organic Chemistry and Technology,

The University of Pardubice, CZ-532 10 Pardubice

Received January 5, 2010

This paper describes the research of newly designed and prepared reactive dyes for dyeing of polyamide 6 and wool. For this purpose, disazo reactive dyes with sulfatoethylsulfonyl group have been synthesized by the sequence of diazotation of aromatic amines and coupling reactions of formed diazonium compounds with secondary components (1-naftylaminesulfonic acids). In order to increase some colouristic properties of reactive dyes, such as fixation, exhaustion and wet fastness, the reactive group of the dyes was modified with sarcosine in several cases to form N-methyl-N-carboxymethyl-2-aminoethylsulfonyl group. In addition, dichloro-triazine dyes in modified and unmodified form have been tested as well. It was found out that the modification of reactive group with sarcosine improved significantly the colouristic properties of some reactive dyes applied to both

¹ To whom correspondence should be addressed.

investigated textile materials. Nevertheless, this method was not found to be universal for all the types of investigated reactive dyes. What can further be seen from the presented results is that among all the of investigated dyes some have been found to show especially high values of fixation that can overcome very frequent and common problems of low fixation occurring during the application of reactive dyes to dyeing of polyamide.

Introduction

At present, reactive dyes play an important role in textile chemistry. The term reactive dye normally refers to a dye applicable to cotton, because the technical importance of reactive dyes is essential for cotton. As the consequence of ecological limitations, reactive dyes are also applied to the wool and nylon to substitute metal complex dyes.

Commercial reactive dyes for wool and nylon are usually based on the reactive aliphatic double bond joined with an electron acceptor group, where double bond reacts with a nucleophilic group of a substrate "following antimarkovnikov rule". These are for example, derivatives of vinylsulfonyl group ($-\text{SO}_2\text{CH}_2\text{CH}_2-\text{X} = -\text{SO}_2\text{CH}=\text{CH}_2 + \text{HX}$) or the reactive group 2-bromoacryl amidyl ($-\text{NHCOCH}(\text{Br})=\text{CH}_2$) and its precursor 2,3-dibromopropionamidyl ($-\text{NHCOCH}(\text{Br})\text{CH}_2\text{Br}$), where the elimination of HBr takes place.

The vinylsulfonyl reactive dyes (VS) are well known as demonstrated by the patent publications [1-8]. The vinyl sulfone form is the proper reactive intermediate stage in the alkaline application of β -substituted ethyl sulfone dyes. VS dyes in the protected form (for example as β -sulfatoethyl sulfones) were originally developed for the reactive dyeing of wool by Hoechst chemists [9]. They are storage stable under standard conditions, and the reactive vinylsulfonyl dye (chromophore- $\text{SO}_2\text{CH}=\text{CH}_2$) is liberated by the reaction with an alkali in the dyebath. Vinylsulfonyl dye reacts subsequently with a nucleophilic group of a fibre by Michael addition. Hoechst also invented derivatives of VS dyes forming the reactive vinylsulfonyl group in an acid dyebath. A water soluble secondary amine such as *N*-methyltaurin is used for the protection of vinylsulfonyl group (commercial name, for example, Procilan E dyes of ICI) and the fixation reaction was described by Zollinger [10].

Precursors of vinylsulfonyl dyes can be generally described by the formula dye- $(\text{SO}_2\text{CH}_2\text{CH}_2-\text{Y})_n$, where Y represents a substituent that can be split off. For the acid dyeing this Y respectively HY can be every secondary aliphatic amine. Secondary amines without water-soluble group (such as diethylamine) [11] are hygienically dangerous because they volatilise with steam. Thus HY are water soluble secondary aliphatic amines of the formula $\text{HN}(\text{R})-(\text{CH}_2)_n-\text{A}$, where A represents the sulfonic or the carboxylic acid group or a their water soluble salt [12]. Patent literature also describes the dyeing mixtures for the reactive dyeing

of synthetic polyamides, where water soluble aliphatic amines containing sulfonic or carboxylic acid groups are used as “additives” to VS dyes [13]. Similarly, the reaction of vinylsulfonyl dyes with secondary aliphatic amines containing sulfonic or carboxylic acid groups is known [14].

The aim of this work was to prepare and study reactive dyes for dyeing of polyamide 6 and wool and to increase some colouristic properties such as fixation, exhaustion and wet fastness of the prepared VS dyes of the formula chromophore $-\text{SO}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$ where *N*-methylglycine (sarcosine) was used as secondary amine. Their evaluations are compared with other VS dyes.

Experimental

Instrumentation

All the dyeing experiments were carried out using laboratory dyeing machine Scourotester Computex (Budapest, Hungary) and Labomat Mathis (Mathis, Switzerland). Absorbance values were measured using UV/VIS spectrophotometer Helios Gamma Thermospectronic (UNICAM, England) working in a single beam arrangement within spectral range from 190 to 1100 nm and with the slit width 2 nm.

Reagents

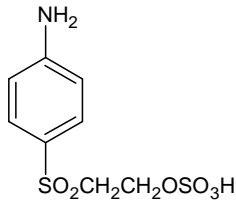
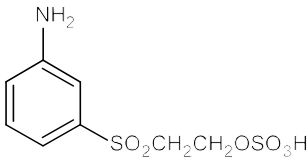
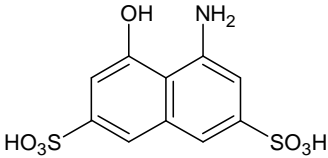
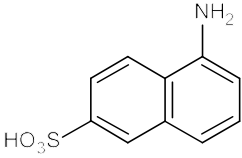
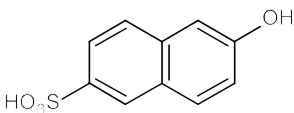
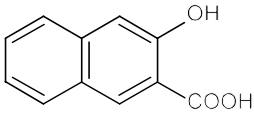
Propan-1-ol, propan-2-ol, ethyl acetate, NaCl, Na_2CO_3 , NaHCO_3 and NaNO_2 , all of pro analysis grade (p.a.), were obtained from Lachema, Pty. (Brno, the Czech Republic). *N*-methylpyrrolidon (p.a.) and PCl_3 (p.a.) were obtained from Merck (Darmstadt, Germany). Hydrochloric acid (35 % w/v, p.a.) from Lach-Ner, Ltd. (Neratovice, the Czech Republic), acetic acid (99 % w/v, p.a.) and NaOH (p.a.) from Penta, Ltd. (Chrudim, the Czech Republic) were also used. Other chemical reagents used for synthesis of dyes are listed in Table I.

Synthesis

The disazo dyes were prepared by the sequence of diazotization of aromatic amines and coupling reactions of formed diazonium compounds with secondary components (1-naphtylaminesulfonic acids). The next step was the diazotization of monoazo dye and the second coupling reaction with a secondary component. Reactive dyes contained 2-sulfatoethyl-sulfonyl ($-\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na}$) reactive group capable to liberate reactive vinyl group in the dye-bath under alkali conditions. The third synthetic step was the preparation of *N*-methyl-

N-carboxymethyl-2-aminoethyl-sulphonyl (–SO₂CH₂CH₂N(CH₃)CH₂COOH) reactive group capable to liberate reactive vinyl group in the application dye bath under acidic conditions.

Table I Reagents and chemicals used for preparation of dyes

Acronym	Formula	Supplier
PAFSES	 <p>2-[(4-aminophenyl)sulfonyl]ethylhydrogensulfate</p>	Synthesia, Ltd. (Pardubice, the Czech Republic)
MAFSES	 <p>2-[(3-aminophenyl)sulfonyl]ethylhydrogensulfate</p>	Spolchem, Pty. (Ústí nad Labem, the Czech Republic)
H-acid	 <p>4-amino-5-hydroxynaphthalene-2,7-disulfonic acid</p>	Synthesia, Ltd.
Cleve acid (1,6)	 <p>5-aminonaphthalene-2-sulphonic acid</p>	Synthesia, Ltd.
Schaeffer acid	 <p>6-hydroxynaphthalene-2-sulphonic acid</p>	Synthesia, Ltd.
BON acid	 <p>3-hydroxy-2-naphthoic acid</p>	Synthesia, Ltd.

Sarcosine	$\begin{array}{c} \text{H}_3\text{C}-\text{NH} \\ \\ \text{CH}_2\text{COOH} \end{array}$	Merck
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Preparation of Reactive Dye 1



Diazotization of PAFSES: PAFSES (C₈H₁₁NO₆S₂; $M = 281.3 \text{ g mol}^{-1}$; 96.6 %, 0.02 mole; 5.82 g) was mixed with 50 ml distilled water and 5.14 ml concentrated HCl (35 %). The dispersion was externally cooled (ice and acetone) to 0-5 °C under intensive stirring and then 4.1 ml 5 M NaNO₂ was added. The reaction time was approximately 20 min and the reaction was accelerated using an ultrasound bath (120 W, 1 min of dispergation). When the reaction was completed (checked by iodine starch paper) a small excess of HNO₂ was removed by addition of NH₂SO₃H. The dispersion of diazonium compound was immediately used for the next coupling reaction.

First Coupling Reaction: 1-Naphthylamine (C₁₀H₉N; $M = 143 \text{ g mol}^{-1}$; 0.02 mole; 2.86 g) was mixed with 30 ml water and 2 ml concentrated HCl (35 %) and the temperature was maintained at 0-5 °C (external cooling) under intensive stirring. Then the diazonium compound was gradually added and the reaction pH 5 was adjusted by an addition of 5 M NaOH. The reaction time was approximately 2 hours. When the reaction was completed (checked by the reaction with H-acid, drop reaction on filter paper), the monoazo dye MAD 1 (brownish red) was filtered off and the press cake was used without drying for the next diazotization.

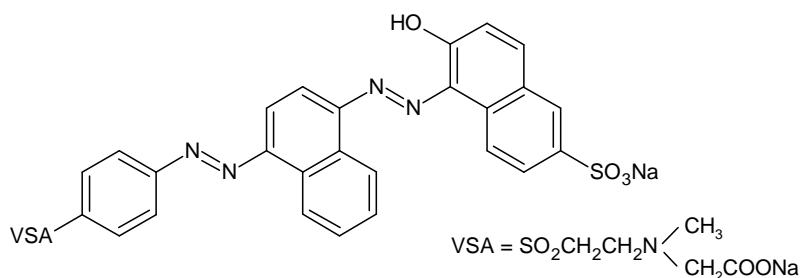
Diazotization of MAD 1: The monoazo dye MAD 1 was mixed with 80 ml water and 5.2 ml concentrated HCl (35 %). The dispersion was externally cooled to 0-5 °C and 4 ml 5 M NaNO₂ were added under intensive stirring. The reaction time of this diazotization was approximately 3 hours. When the reaction was completed, the dispersion of diazonium compound was used for the next coupling reaction.

Second Coupling Reaction: Schaeffer acid (C₁₀H₈O₄S; $M = 224.2 \text{ g mol}^{-1}$; 0.02 mol; 4.48 g) was mixed with 45 ml water and 4 ml 5 M NaOH to form solution. After that the temperature was set at 0-5 °C (external cooling) and the diazonium compound from the previous step was added under intensive stirring.

pH of the reaction mixture was adjusted at 8 by an addition of 5 M NaOH. The reaction time was approximately 30 min. When the reaction was completed, pH of the mixture was adjusted at 5 by an addition of concentrated HCl (35 %). After that, 40 g NaCl was added (precipitation of dye was checked by drop test on filter paper) and the mixture stirred for approximately 20 min. Finally, the dye was filtered off and carefully dried at 40 °C.

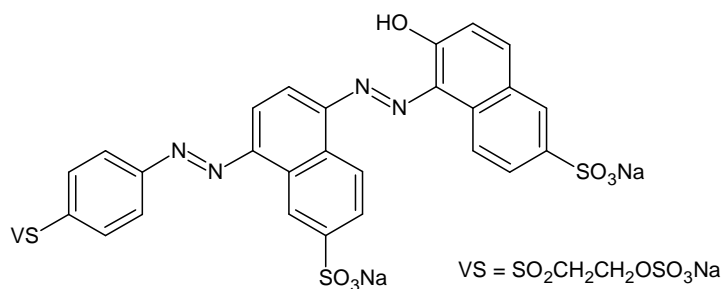
Thin layer chromatography (TLC) was used to check the composition of the prepared dye. (ALUGRAM SIL G/UV₂₅₄, mobile phase: propan-2-ol/propan-1-ol/ethylacetate/water = 2/4/1/3 by vol.).

Preparation of Reactive Dye 1A



The reactive dye 1 ($\text{C}_{28}\text{H}_{19}\text{N}_4\text{O}_{10}\text{S}_3\text{Na}_2$; $M = 714.7 \text{ g mol}^{-1}$; 0.01 mole, 7.14 g) was mixed with 50 ml water and with an excess of *N*-methylglycine ($\text{C}_3\text{H}_7\text{NO}_2$; $M = 89.1 \text{ g mol}^{-1}$; 0.02 mole; 1.78 g) which was added under intensive stirring. Then, pH of the reaction mixture was set at the value of 8 (5M NaOH), and the reaction mixture was stirred at the temperature of 60 °C for 3 hours. When the reaction was completed (checked by TLC, solid phase: ALUGRAM SIL G/UV₂₅₄, mobile phase: propan-2-ol/propan-1-ol/ethylacetate/water = 2/4/1/3 by vol.), the final dye was salted out by an addition of 20 g NaCl and carefully dried (40 °C)

Preparation of Reactive Dye 2



Diazotization of PAFSES: PAFSES ($C_8H_{11}NO_6S_2$; $M = 281.3 \text{ g mol}^{-1}$; 96.6 %; 0.02 mole; 5.82 g) was diazotized in the same way as in the case of the reactive dye 1.

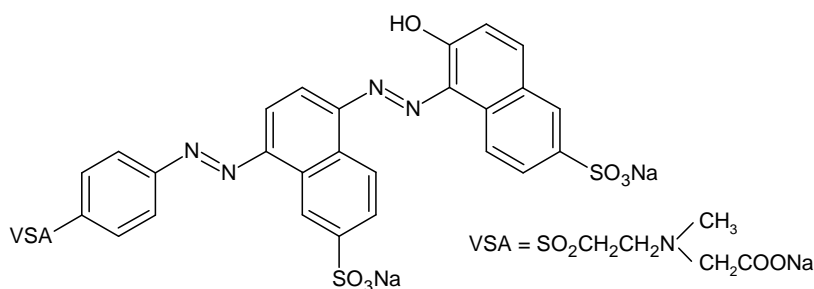
First Coupling Reaction: Cleve acid ($C_{10}H_9NO_3S$; $M = 223.2 \text{ g mol}^{-1}$; 0.02 mole; 4.46 g) was mixed with 40 ml water and 4 ml 5M NaOH, and the temperature was maintained at 0-5 °C (external cooling) under intensive stirring. Then the diazonium compound was gradually added and pH of the reaction was adjusted at 5 by an addition of 5M NaOH. The reaction time was approximately 2 hours. When the reaction was completed (checked by the reaction with H-acid, drop reaction on filter paper), the pH of the reaction mixture was increased to 8 by an addition of 5M NaOH and the red solution of monoazo dye MAD 2 was used for the next reaction step (diazotization).

Diazotization of MAD 2: The solution of monoazo dye MAD 2 was mixed with 5.2 ml concentrated HCl (35 %). The very fine suspension was externally cooled to 0-5 °C and 4.1 ml 5M $NaNO_2$ was added under intensive stirring. The reaction time of this diazotization was about 2 hours. When the reaction was completed, the suspension of diazonium compound was used for the next coupling reaction.

Second Coupling Reaction: Schaeffer acid ($C_{10}H_8O_4S$; $M = 224.2 \text{ g mol}^{-1}$; 0.02 mole; 4.48 g) was mixed with 45 ml water and 4 ml 5M NaOH. After that, the temperature was set to 0-5 °C (external cooling) and the diazonium compound from the previous step was added under intensive stirring. Thereafter, pH of the reaction was adjusted at 8 by an addition of 5M NaOH. The reaction time was approximately 30 min. When the reaction was completed, pH of the mixture was adjusted at the value of 5 by addition of concentrated HCl (35 %), and NaCl (40 g) was added (precipitation of dye was checked by drop test on filter paper). After 20 min of stirring the dye was filtered off and carefully dried (40 °C).

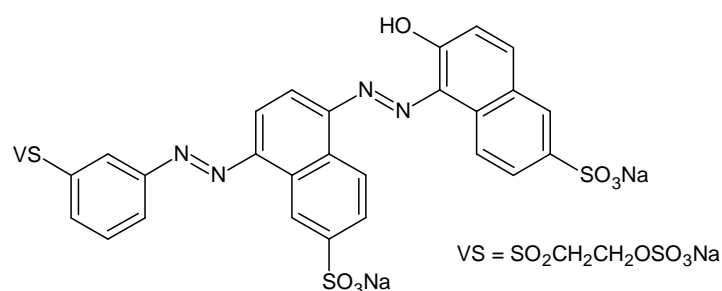
The purity of prepared dye was determined by TLC (solid phase: ALUGRAM SIL G/UV₂₅₄, mobile phase: propan-2-ol/propan-1-ol/ethyl-acetate/water = 2/4/1/3 by vol.).

Preparation of Reactive Dye 2A



The reactive dye 2 ($C_{28}H_{19}N_4O_{13}S_4Na_3$; $M = 816.7 \text{ g mol}^{-1}$; 0.01 mole; 8.16 g) was mixed with 50 ml water and an excess of *N*-methylglycine ($C_3H_7NO_2$; $M = 89.1 \text{ g mol}^{-1}$; 0.02 mole; 1.78 g) was added under intensive stirring. After that, pH of the reaction mixture was maintained at 8 (5M NaOH) and the reaction mixture was stirred at the temperature of 60 °C for 3 hours. When the reaction was completed (checked by TLC, solid phase: ALUGRAM SIL G/UV₂₅₄, mobile phase: propan-2-ol/propan-1-ol/ethylacetate/water = 2/4/1/3 by vol.), the final dye was salted out by the addition of 20 g NaCl and carefully dried at 40 °C.

Preparation of Reactive Dye 3



Diazotization of MAFSES: MAFSES ($C_8H_{11}NO_6S_2$; $M = 281.3 \text{ g mol}^{-1}$; 0.02 mole; 5.63 g) was mixed with 50 ml distilled water and with 5.14 ml concentrated HCl (35 %) and the dispersion was then cooled externally to 0-5 °C using a mixture of ice and acetone. After that, 4.1 ml 5M $NaNO_2$ was added under intensive stirring. The reaction took approximately 20 min; ultrasound bath was additionally used for dispergation (120 W, 1 minute of dispergation). When the reaction was completed (checked with iodine starch paper) a small excess of HNO_2 was removed by the addition of NH_2SO_3H . The dispersion of diazonium compound was immediately used for the next coupling reaction.

First Coupling Reaction: Cleve acid ($C_{10}H_9NO_3S$; $M = 223.2 \text{ g mol}^{-1}$; 0.02 mole; 4.46 g) was mixed with 40 ml water and 4 ml 5M NaOH, and the temperature of the reaction mixture was maintained at 0-5 °C (external cooling) under intensive stirring. Then the diazonium compound was gradually added and pH 5 of the reaction mixture was adjusted by an addition of 5M NaOH. After 2 hours, when the reaction was completed (checked by the reaction with H-acid, drop reaction on filter paper), pH of the reaction mixture was increased to 8 by addition of 5M NaOH, and the red solution of monoazo dye MAD 3 was used for the next reaction step (diazotization).

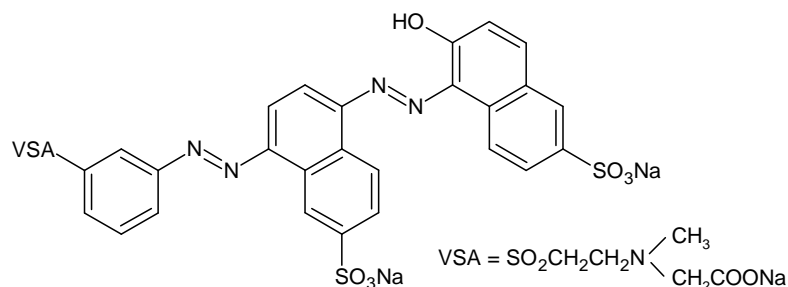
Diazotization of MAD 3: The solution of monoazo dye MAD 3 was mixed with 5.2 ml concentrated HCl (35 %). The very fine suspension was externally cooled

to 0-5 °C and 4.1 ml 5M NaNO₂ was added under intensive stirring. When the reaction was completed (after 2 hours), the suspension of diazonium compound was used for the next coupling reaction.

Second Coupling Reaction: Schaeffer acid (C₁₀H₈O₄S; *M* = 224.2 g mol⁻¹; 0.02 mole; 4.48 g) was mixed with 45 ml water and 4 ml 5M NaOH. Then the temperature of the mixture was set at 0-5 °C (external cooling) and the diazonium compound from the previous step was added under intensive stirring. After that, pH of the reaction was adjusted at 8 by addition of 5M NaOH, and the mixture was left to react for approx. 30 min. When the reaction was completed, pH 5 was adjusted by addition of concentrated HCl (35 %) and NaCl (40 g) was added (precipitation of dye was checked by drop test on filter paper). Finally, after 20 min of stirring the dye was filtered off and carefully dried (40 °C).

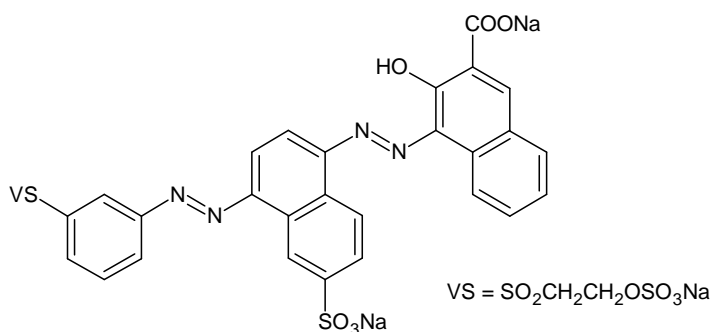
In order to check the purity of prepared dye, TLC was used (solid phase: ALUGRAM SIL G/UV₂₅₄, mobile phase: propan-2-ol/propan-1-ol/ethylacetate/water = 2/4/1/3 by vol.).

Preparation of Reactive Dye 3A



The reactive dye 3 (C₂₈H₁₉N₄O₁₃S₄Na₃; *M* = 816.7 g mol⁻¹; 0.01 mole; 8.16 g) was mixed with 50 ml water and with an excess of *N*-methylglycine (C₃H₇NO₂; *M* = 89.1 g mol⁻¹; 0.04 mole; 3.56 g) which was added under intensive stirring. Then, pH of the reaction was set at the value 8 (5M NaOH) and the reaction mixture was stirred at the temperature of 60 °C for 3 hours. When the reaction was completed (checked by TLC, solid phase: ALUGRAM SIL G/UV₂₅₄, mobile phase: propan-2-ol/propan-1-ol/ethylacetate/water = 2/4/1/3 by vol.), the final dye was salted out by an addition of 20 g NaCl and carefully dried (40 °C).

Preparation of Reactive Dye 4



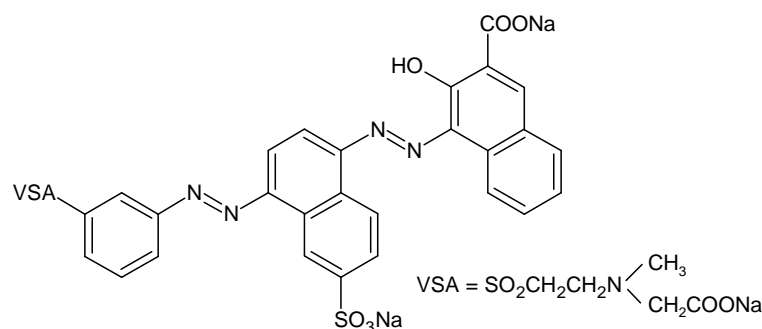
Diazotization of MAFSES: MAFSES ($\text{C}_8\text{H}_{11}\text{NO}_6\text{S}_2$; $M = 281.3 \text{ g mol}^{-1}$; 0.02 mole; 5.63 g) was diazotized in the same way as that described for dye 3.

First Coupling Reaction: Cleve acid ($\text{C}_{10}\text{H}_9\text{NO}_3\text{S}$; $M = 223.2 \text{ g mol}^{-1}$; 0.02 mole; 4.46 g) was coupled with diazonium compound by the procedure described for the preparation of dye 3.

Diazotization of MAD 4: The solution of mono azo dye MAD 4 was diazotized in the same way as that described for the preparation of reactive dye 3.

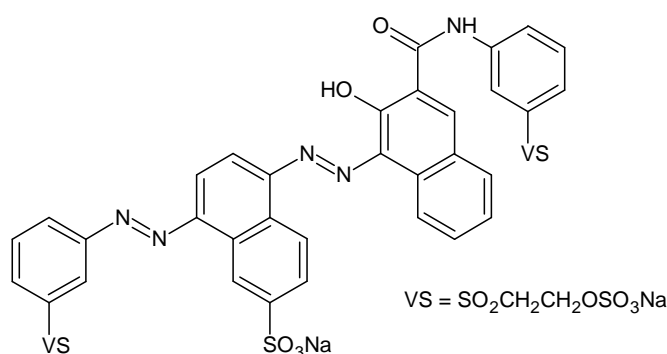
Second Coupling Reaction: BON Acid ($\text{C}_{11}\text{H}_8\text{O}_3$; $M = 188.18 \text{ g mol}^{-1}$; 0.02 mole; 3.76 g) was reconstituted with 40 ml water and 4 ml 5M NaOH. The solution was cooled externally to 0-5 °C under intensive stirring, and then solution of diazonium compound was added. The reaction mixture was kept at pH 8 (addition of 5M NaOH), and the reaction time was approx. 1 hour. When the coupling reaction was completed, the dye was precipitated by the addition of 40 g NaCl. The dye 4 was filtered off and carefully dried (40 °C).

Preparation of Reactive Dye 4A

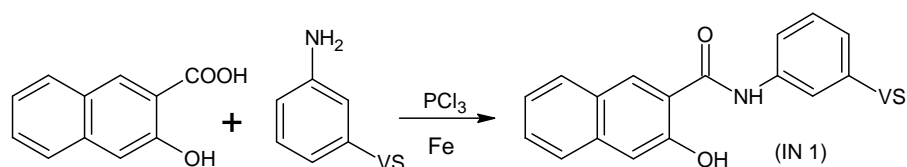


The reactive dye 4 ($C_{29}H_{19}N_4O_{12}Na_3S_3$; $M = 780.6 \text{ g mol}^{-1}$; 0.01 mole; 7.81 g) was mixed with 50 ml water, whereupon an excess of *N*-methylglycine ($C_3H_7NO_2$; $M = 89.1 \text{ g mol}^{-1}$; 0.04 mole; 3.56 g) was added under an intensive stirring. After that, pH of the mixture was set at 8 by addition of 5M NaOH, and the reaction mixture was stirred at the temperature of 60 °C for 3 hours. When the reaction was completed (checked by TLC, solid phase: ALUGRAM SIL G/UV₂₅₄, mobile phase: propan-2-ol/propan-1-ol/ethylacetate/water = 2/4/1/3 by vol.), the final dye was salted out by an addition of 20 g NaCl and carefully dried at 40 °C.

Preparation of Reactive Dye 5



Preparation of IN1: MAFSES ($C_8H_{11}NO_6S_2$; $M = 281.3 \text{ g mol}^{-1}$; 0.02 mole; 5.63 g) and BON Acid ($C_{10}H_8O_3$; $M = 188.18 \text{ g mol}^{-1}$; 0.02 mole; 3.76 g) were mixed with 20 ml *N*-methylpyrrolidone, 2 ml pyridine and powdered iron (0.1 g). Then phosphorus trichloride (PCl_3 ; $M = 137.33 \text{ g mol}^{-1}$; 0.02 mole; 1.74 g) was added under intensive stirring. The reaction mixture was refluxed (200 °C) for 3 hours. When the reaction was completed (checked by TLC, solid phase: ALUGRAM SIL G/UV₂₅₄, mobile phase: propan-2-ol/ammonia = 2/1 by vol.), the final reaction solution was mixed with 100 ml cold water (mixture with crushed ice) and intensively stirred. The precipitated intermediate IN1 was filtered off and mixed with 100 ml acetone. Then activated carbon (0.5 g) was added and the mixture was filtered (removing of carbon and impurities). The filtrate was diluted with water and the precipitated intermediate was filtered off and carefully dried (40 °C).



Diazotization of MAFSES: MAFSES ($C_8H_{10}NO_6S_2H$; $M = 281.3 \text{ g mol}^{-1}$; 0.02 mole; 5.63 g) was diazotized similarly as described for reactive dye 3.

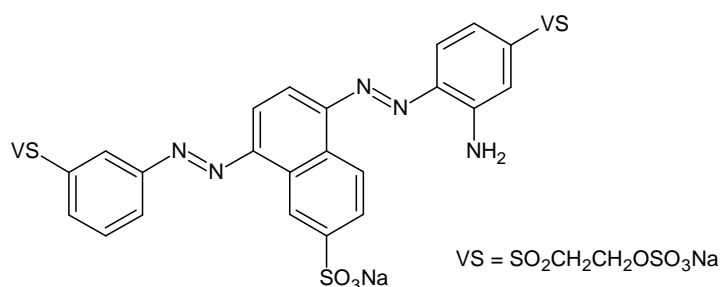
First Coupling Reaction: Cleve acid ($C_{10}H_9NO_3S$; $M = 223.2$; 0.02 mole; 4.46 g) was coupled with the diazonium compound in the same way as shown for reactive dye 3.

Diazotization of MAD 5: The solution of mono azo dye MAD 5 was diazotized in the same way as that described for reactive dye 3.

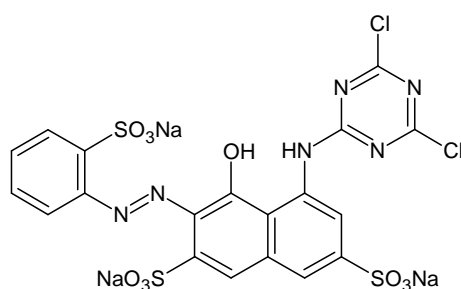
Second Coupling Reaction: Intermediate IN1 ($C_{19}H_{17}O_8S_2$; $M = 451.46 \text{ g mol}^{-1}$; 0.02 mole; 9.02 g) was dissolved in 40 ml water and 4 ml 5M NaOH. Then the mixture was cooled externally to 0-5 °C under intensive stirring, and the solution of diazonium compound was added. After that, pH of the reaction was set at 8 by means of 5M NaOH, and the reaction took approximately 1 hour. When the coupling reaction was completed, the dye was precipitated by addition of 40 g NaCl. The dye 5 was filtered off and carefully dried at 40 °C.

Structures of other investigated reactive dyes employed in this study are summarised below.

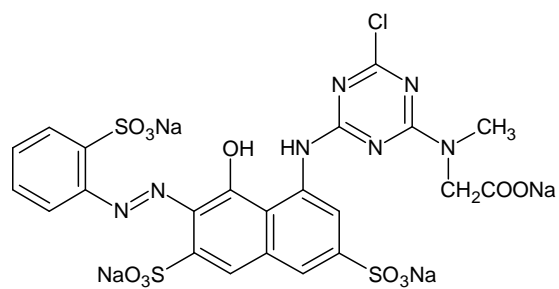
Reactive dye 6



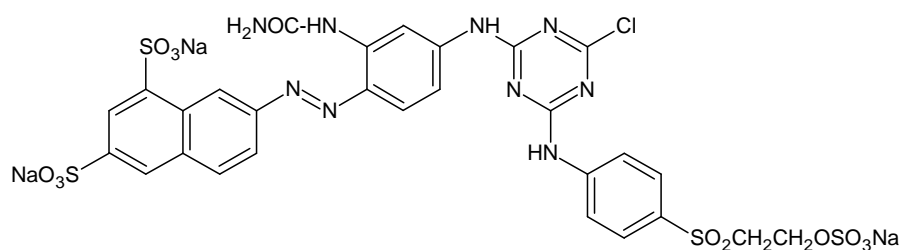
Reactive dye 7



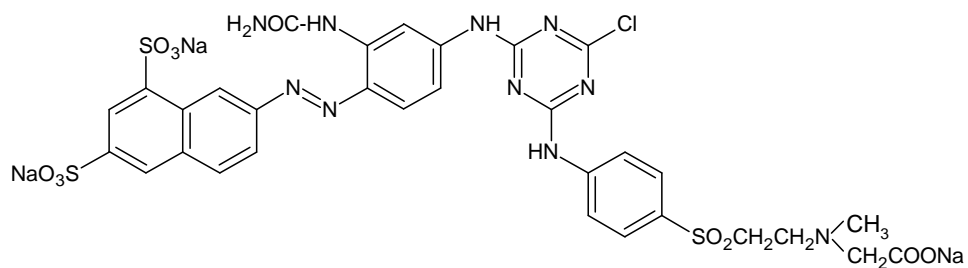
Reactive dye 7A



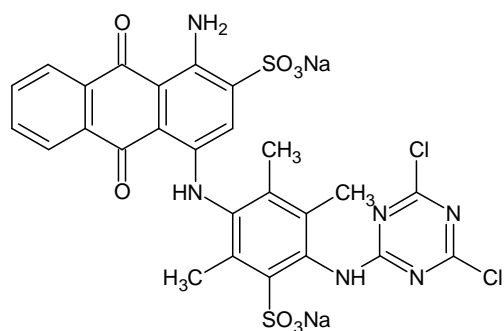
Reactive dye 8 (C.I. Reactive Yellow 145)



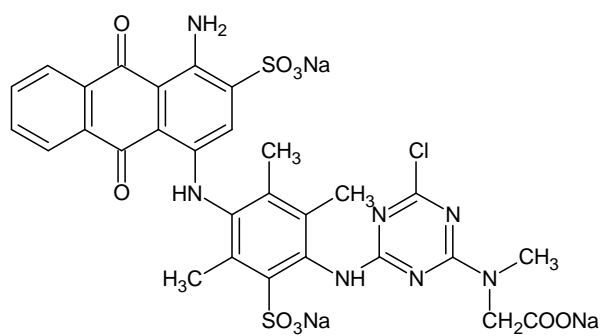
Reactive dye 8A



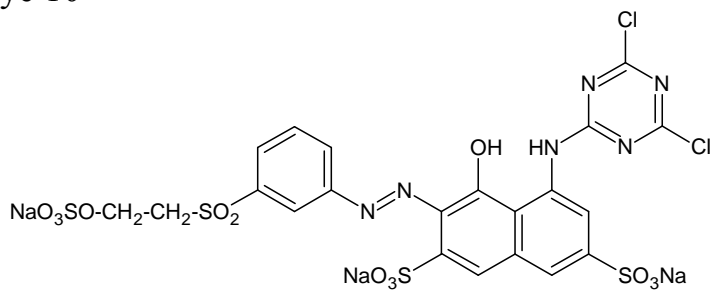
Reactive dye 9



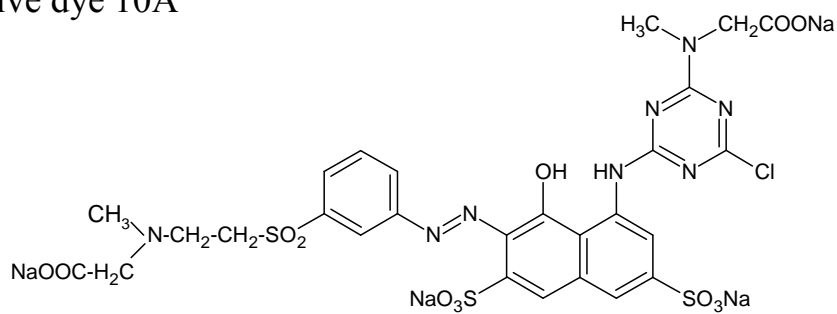
Reactive dye 9A



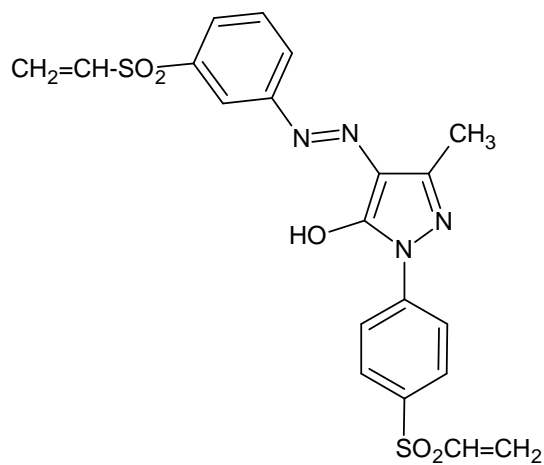
Reactive dye 10



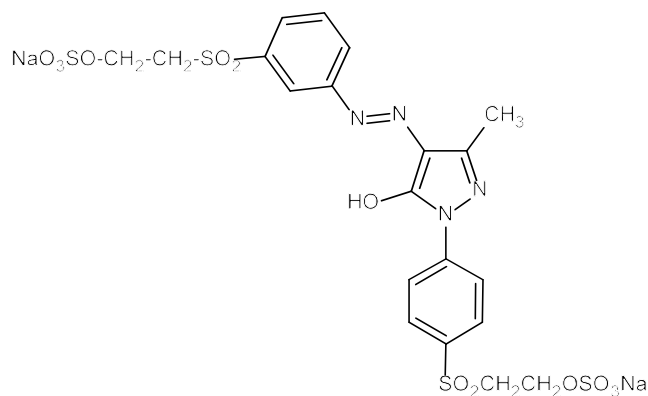
Reactive dye 10A



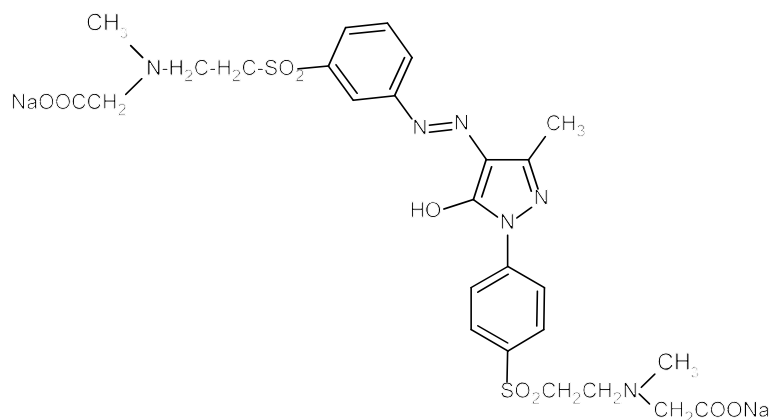
Reactive dye 11a



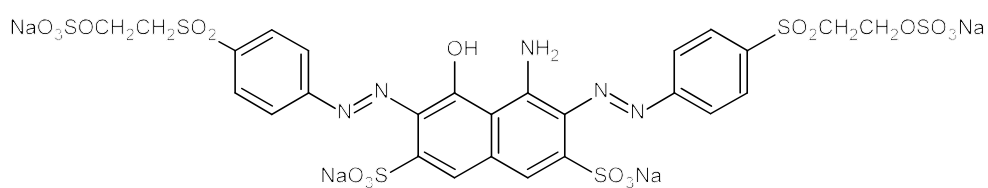
Reactive dye 11b



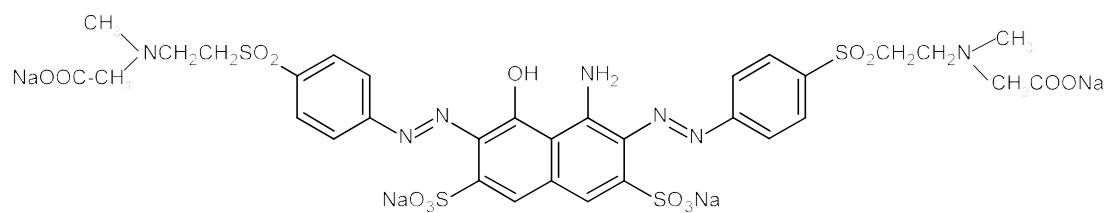
Reactive dye 11A



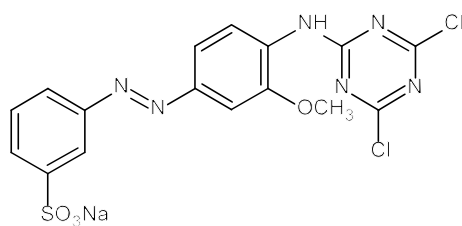
Reactive dye 12 (C.I. Reactive Black 5)



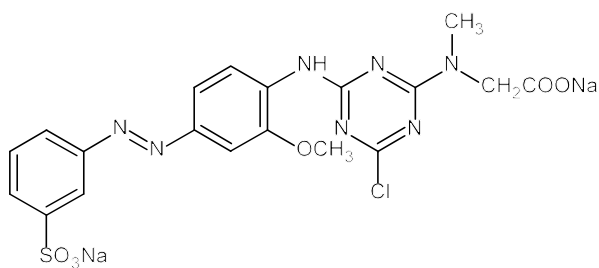
Reactive dye 12A



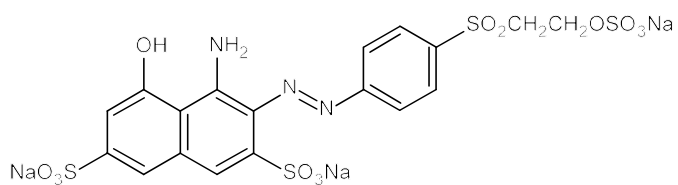
Reactive dye 13



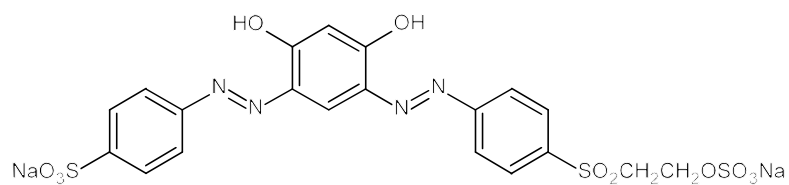
Reactive dye 13A



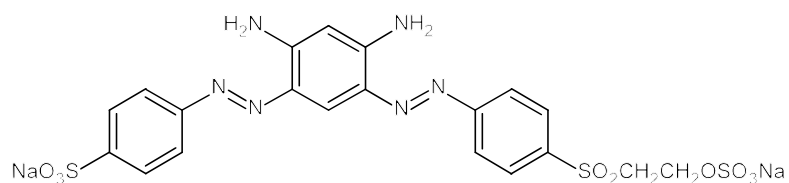
Reactive dye 14



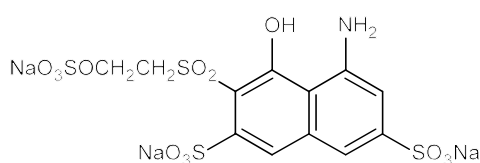
Reactive dye 15



Reactive dye 16



Reactive dye 17



TLC Identification of Sarcosine in Dyebath

Identification of sarcosine in dyebath was performed by thin layer chromatography. For this purpose, ALUGRAM SIL G/UV₂₅₄ and the mixture of propan-1-ol with NH₄OH (25 %) in 2:1 ratio (vol. parts) were used as the solid phase and mobile phase, respectively. Detection reaction was performed by spraying the chromatogram with ninhydrin (0.05 % solution in acetone) since ninhydrin forms with sarcosine violet colour. A solution containing 3 % of sarcosine in aqueous ethanol (1:1 by vol.) was used as reference sample.

NMR spectroscopy: The ¹H (360.13 MHz) and ¹³C (90.556 MHz) NMR spectra of compounds were recorded at 300 K on Bruker AMX 360 spectrometer equipped with a 5 mm broadband probe and Silicon Graphics Indy computer using the UXNMR software. The NMR spectra were measured in hexadeuteriodimethyl sulphoxide. The ¹H and ¹³C chemical shifts were referred to the signal of solvent ($\delta = 2.55$ ppm). Due to very large data quantity the NMR spectra are not shown here.

Dyeing procedure: Dyeing was carried out in pots placed in laboratory dyeing machine using a liquor ratio 1:20 for nylon fabric and 1:40 for wool. Dyeing of nylon fabric was performed at 2 % owf (wool 4% owf) in the presence of acetic acid (2 %) with the dyeing profile shown in Fig. 1.

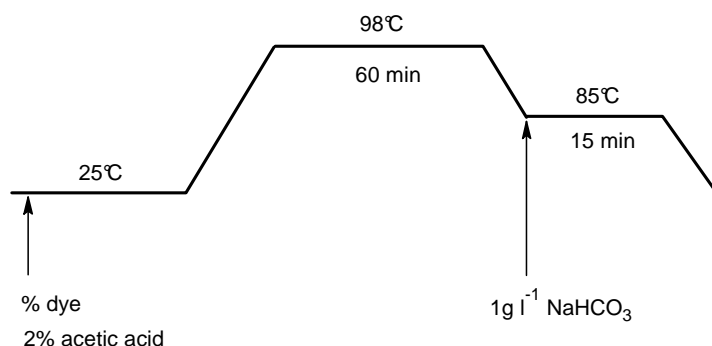


Fig. 1 Dyeing profile

Analysis of dyeing: Absorbance measurements of the original dyebath and the exhausted bath were carried out using UV/VIS spectrophotometer. Using a previously established absorbance/concentration relationship at the λ_{max} of the dye, the quantity of the dye in solution was calculated and the extent of dye exhaustion ($E\%$) achieved was determined using Eq. (1), where C_0 and C are the quantities of dye initially in the dyebath and of residual dye in the dyebath, respectively. C_{alkal} is a concentration of the dye after alkalization step. The calculation of the percentage covalent fixation was carried out as follows

$$E(\%) = \left(1 - \frac{C}{C_0} \right) 100 \quad (1)$$

$$F(\%) = \left(C_0 - C - \frac{C_{alkal}}{C_0 - C} \right) 100 \quad (2)$$

Table II Absorption wavelengths (λ_{max}) of all investigated dyes together with calibration ranges and regression parameters

Reactive dye	λ_{max} nm	Shade	Regression parameters ^a	Calibration range mg l ⁻¹
1, 1A	501.0	Red	$A = 0.0376 c; R^2 = 0.9997$	0-20
2, 2A	540.0	Red	$A = 0.0227 c; R^2 = 0.9993$	0-25
3, 3A	535.5	Red	$A = 0.0180 c; R^2 = 0.9999$	0-25
4, 4A	548.5	Red	$A = 0.0346 c; R^2 = 0.9997$	0-20
5	664.0	Brown	$A = 0.0031 c; R^2 = 0.9999$	0-200
6	659.0	Brown	$A = 0.0018 c; R^2 = 0.9997$	0-500
7	533.5	Red	$A = 0.0265 c; R^2 = 0.9999$	0-25
7A	538.5		$A = 0.0188 c; R^2 = 0.9993$	
8	414.0	Yellow	$A = 0.0118 c; R^2 = 0.9993$	0-50
8A	422.0		$A = 0.0117 c; R^2 = 0.9991$	
9	580.5	Blue	$A = 0.0134 c; R^2 = 0.9999$	0-50
9A	587.0		$A = 0.0066 c; R^2 = 0.9998$	

^aestimate of intercept was found to be insignificant

Table II — Continued

Reactive dye	λ_{max} nm	Shade	Regression parameters ^a	Calibration range mg l ⁻¹
10	516.5	Red	$A = 0.0166 c; R^2 = 0.9996$	0-50
10A	499.5		$A = 0.0108 c; R^2 = 0.9994$	
11a	380.5	Yellow	$A = 0.0286 c; R^2 = 0.9997$	0-25
11b	383.0		$A = 0.0308 c; R^2 = 0.9999$	
11A	382.0		$A = 0.0290 c; R^2 = 0.9994$	
12	597.5	Blue	$A = 0.0277 c; R^2 = 0.9991$	0-30
12A	598.5		$A = 0.0293 c; R^2 = 0.9999$	
13	349.5	Yellow	$A = 0.0250 c; R^2 = 0.9992$	0-30
13A	378.5		$A = 0.0119 c; R^2 = 0.9993$	
14	520.0	Red	$A = 0.0306 c; R^2 = 0.9998$	0-25
15	432.0	Yellow	$A = 0.0635 c; R^2 = 0.9993$	0-10
16	412.0	Yellow	$A = 0.0224 c; R^2 = 0.9992$	0-30
17	522.0	Red	$A = 0.0144 c; R^2 = 0.9995$	0-50

^aestimate of intercept was found to be insignificant

Results and Discussion

All the investigated dyes prepared in this study were applied to dyeing of polyamide 6 and wool. The wash fastness at 40 °C and 60 °C was tested according to the ISO 105-A10S/C01 (1994) and ISO 105-A10S/C03 (1994) procedure respectively. The wash fastness - potting - was tested according to the ISO 105-A10S/E09 (1994) procedure. The values obtained for dyeing of polyamide and wool are shown in Table III and Table IV, respectively. It can be seen from the results presented, that modification of reactive group by sarcosine improved significantly the colouristic properties of some of the synthesized dyes for dyeing of polyamide 6 and wool. The modification increased significantly colouristic results on wool in the case of reactive dyes 1 and 1A, 2 and 2A, 7 and 7A, 10 and 10A, 12 and 12A. The modification of reactive dyes 1, 2 and 12 applied to polyamide 6 was successful as well.

What can be further seen from the presented results is that regarding the dyeing of polyamide 6 the best colouristic properties were achieved in the pre-

Table III Exhaustion, fixation and fastness properties of reactive dyes on PAD 6

Reactive dye	Exhaustion, %	Fixation, %	Washing 40 °C	Washing 60 °C
1	97.4	89.6	4-5 ^a / 1-2 ^b , 3-4 ^c	4 / 1, 2
1A	90.7	99.3	4-5 / 4-5, 4-5	4-5 / 1-2, 4-5
2	37.3	97	4-5 / 5, 4	4-5 / 5, 4
2A	99.9	99.8	4-5 / 5, 4	4-5 / 5, 4
3	85.7	96.4	4-5 / 5, 4	4-5 / 5, 4
3A	35.5	81.3	4-5 / 5, 4	4-5 / 5, 4
4	98.2	76.7	4-5 / 5, 4	4-5 / 5, 4
4A	73.3	80.8	3-4 / 5, 3	3-4 / 4-5, 2-3
5	61.4	53.4	4 / 4-5, 4-5	4 / 4-5, 4-5
6	75.2	74.1	4-5 / 4-5, 4-5	4-5 / 4-5, 5
7	66.8	41.2	4-5 / 5, 5	4-5 / 5, 5
7A	69.4	39.8	4-5 / 5, 5	4-5 / 5, 4
8	100	91.2	5 / 5, 5	5 / 5, 5
8A	100	81.3	5 / 5, 5	5 / 5, 4
9	91.1	82.2	5 / 5, 5	5 / 5, 5
9A	93.3	78.2	4-5 / 5, 5	5 / 5, 5
10	92.1	83.8	4-5 / 5, 5	4-5 / 5, 5
10A	46.4	45.3	5 / 5, 5	4-5 / 5, 5
11a	97.6	82.1	5 / 5, 5	5 / 4, 4
11b	96.6	96.4	5 / 5, 4	5 / 5, 4
11A	65.2	59.5	5 / 5, 5	5 / 5, 5
12	79.4	63.6	5 / 5, 5	5 / 5, 5
12A	90.3	80.5	5 / 5, 5	5 / 5, 5
13	89.4	63.4	5 / 5, 5	5 / 5, 5
13A	98.0	48.4	5 / 5, 5	5 / 5, 3-5
14	80.7	67.0	4-5 / 4-5, 4-5	4-5 / 4-5, 4-5
15	87.8	98.9	4 / 4-5, 4-5	3 / 4-5, 4-5
16	95.2	99.0	4 / 4-5, 4-5	3 / 4-5, 4-5
17	89.5	88.4	4-5 / 4-5, 4-5	4 / 4-5, 4-5

^a colour change, ^b staining on polyamide, ^c staining on cotton

sence of dyes 8, 8A, 9, 9A, 10, 11a, 11A, 12, 12A, 13 and 13A. In the presence of these dyes typical values of exhaustion better than 90 % were obtained with the exception of those obtained for dyes 11A and 12 for which the exhaustion of only 60 and 80 %, respectively, was achieved. On the other hand, for both dyes, i.e. 11A and 12, excellent wetfastness values were obtained similarly as for the other above mentioned dyes (8, 8A, 9, 9A, 10, 11a, 12A, 13 and 13A). Fixation values of 80–90 % were achieved for the most of the above listed dyes; however regarding the employing of the dye 2A and 3 much better values (close to 100 %) were obtained. On the other hand, worse wetfastness characteristics for both the dye 2A and 3 were achieved in contrast to those obtained in the presence of others listed dyes. Regarding the dyeing of wool the best results were obtained in the presence of dyes 2A, 8, 8A, 9, 9A, 10, 10A, 11a, 11b, 12A and 13A. The

application of these reactive dyes gave excellent values of exhaustion close to 100 % and of fixation better or close to 90 % (reactive dye 13A). It is clearly evident, that reactive dyes 2A, 8, 8A, 9, 9A, 10, 10A, 11a, 11b, 12A a 13A ensured excellent colouristic characteristics for dyeing both investigated materials. These dyes thus may be universally recommended for dyeing of both polyamide and wool.

Table IV Exhaustion, fixation and fastness properties of reactive dyes on wool

Reactive dye	Exhaustion, %	Fixation, %	Washing 40 °C	Washing 60 °C
1	80	91	4 ^a / 1 ^b , 1-2 ^c	4-5 / 1, 2-3
1A	98.4	99.5	4 / 1, 3	4 / 1, 3
2	79.0	98	4-5 / 5, 3-4	4 / 1-2, 4
2A	100	98.8	4-5 /, 4-5, 4	4-5 / 1-2, 4-5
3	56.4	96.9	5 / 4-5, 4	5 / 1, 4-5
3A	92.1	89.6	4-5 / 4-5, 2-3	4-5 / 1, 4
4	63.7	90.7	4-5 / 2-3, 2	4-5 / 1, 4
4A	90.2	67.0	4-5 / 3, 2	4-5 / 2, 4-5
5	56.4	91.8	4 / 4, 4	2-3 / 2-3, 4-5
6	44.6	83.5	3 / 4, 4-5	3 / 2, 4-5
7	83.5	72.6	4 / 5, 4	4 / 1, 4
7A	100	80.9	4 / 5, 3-4	4 / 1, 4
8	100	92.7	5 / 5, 4	5 / 3-4, 4-5
8A	100	99.3	5 / 5, 3-5	4-5 / 3, 4-5
9	100	94.8	4-5 / 5, 5	5 / 1-5, 4
9A	100	94.0	4-5 / 5, 5	5 / 1-2, 4
10	99.4	90.0	4 / 5, 3-4	5 / 2, 4
10A	100	96.5	4-5 / 5, 3-4	4-5 / 3, 4
11a	99.2	96.8	4-5 / 5, 5	4-5 / 4-5, 5
11b	99.8	99.0	5 / 5, 5	5 / 4, 5
11A	81.1	79.8	5 / 5, 5	5 / 4, 5
12	81.0	56.1	4-5 / 4-5, 4-5	4-5 / 3, 4-5
12A	99.9	98.8	4-5 / 4-5, 4-5	4-5 / 3-4, 4-5
13	99.5	97.2	4-5 / 5, 4	3-4 / 2-3, 3-4
13A	99.6	87.9	3-4 / 4, 3-4	4-5 / 3-4, 4
14	35.6	85.7	2-3 / 2, 3	3-4 / 1, 3
15	89.9	92.7	2 / 1-2, 2	3-4 / 1, 3-5
16	68.4	98.3	4 / 4, 4-5	4 / 1-2, 4-5
17	60.3	98.7	3 / 4, 4	3-4 / 1-2, 4-5

^a colour change, ^b staining on wool, ^c staining on cotton

Conclusion

It can be concluded from the presented results that reactive dyes for polyamide 6 offer real potential for producing dyeings of higher fixation and wetfastness than those produced from acid and disperse dyes without limitation regarding shade. The prepared reactive azo dyes based on *N*-methyl-*N*-carboxymethyl-2-aminoethyl-sulfonyl group are suitable for the reactive dyeing of both polyamide 6 and wool. The dyeing procedure is the sequence of acid dyeing at pH 3, alkali treatment at pH 8 and washing. Due to high fixation and very good wetfastness values achieved with some of these newly designed reactive dyes their successful application in routine practice may be expected.

Acknowledgements

The study was performed with financial support of the Ministry of Education, Youth and Sports of the Czech Republic (project No. 0021627501).

References

- [1] U.S. Patent, 4,336,190.
- [2] U.S. Patent, 4,492,654.
- [3] U.S. Patent, 4,064,754.
- [4] U.S. Patent, 4,577,015.
- [5] U.S. Patent, 4,049,656.
- [6] U.S. Patent, 3,359,286.
- [7] U.S. Patent, 3,268,548.
- [8] U.S. Patent, 3,385,843.
- [9] Heyna J, Schumacher W.: DBP 965, 902, Hoechst, 1949.
- [10] Zollinger H.: *Textilveredlung* **6**, 57 (1971).
- [11] DAS 1,103,883, Hoechst, 1958.
- [12] BP 880,886, ICI, 1988.
- [13] EP Patent, 0, 277,624 A2, Hoechst, 1988.
- [14] U.S. Patent, 3,802,837.