

Iron complexes of reactive azo dyes

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A set of reactive mordant azo dyes was prepared by diazotisation of aromatic amines and their subsequent coupling reaction with secondary components. The reactive dyes thus formed contained 2-sulfatoethyl-sulfonyl ($-\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na}$), *N*-methyl-*N*-carboxymethyl-2-aminoethyl-sulfonyl ($-\text{SO}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$) and 2,3-dibromopropionamidyl ($-\text{NHCOCH}(\text{Br})\text{CH}_2\text{Br}$) reactive groups, capable of liberating reactive vinyl groups in the application dyebath. Negative-Ion Electrospray Ionisation Mass Spectrometry, UV/VIS spectroscopy and elemental analysis confirmed the structure of the prepared dyes. Dyed wool samples (combination of acid and reactive dyeing conditions) were treated (mordanted) with iron salts ($\text{Fe}(\text{II})$, $\text{Fe}(\text{III})$) and a chromium salt (CrF_3). The iron mordant dyeing showed acceptable wash fastness and light fastness comparable with chromium complexed dyes.

Keywords: azo dyes, reactive dyes, iron mordant dyes, wool, wash fastness, light fastness

INTRODUCTION

Metal complex dyes play very a important role in the textile industry. Chromium $\text{Cr}(\text{III})$ and cobalt $\text{Co}(\text{III})$ complexes are used most frequently for the dyeing of wool and synthetic polyamides. Metal complex dyes are applied to the wool either in the pre-metallised form or a complex is prepared "in situ" in the fibre by the treatment of dyed wool with chromate or dichromate ($\text{Cr}(\text{VI})$) salts [1, 2].

The aim of our work was to prepare iron mordant azo dyes in order to replace the ecologically and toxicologically problematic chromium and cobalt dyes [3–5]. Traditionally used cobalt and chromium complex dyes have very good wet fastness (rating 4 – 5 in ISO five member "grey scale") and also light fastness (rating 6 – 7 in ISO eight member "blue scale") [6]. It is known [7–16] that some iron ($\text{Fe}(\text{II})$, $\text{Fe}(\text{III})$) complex dyes have comparable fastness properties. Since iron salts are not considered toxic, they present little or no pollution problems for the users [17 – 21]. In spite of this, mordant dyes are used still for "deep" black shades, because they exhibit extremely high wash fastness (all wet fastness have grade 5) and are practically irreplaceable (Mordant Black 9, 11). These remarkable fastness properties arise from the oxidation of the mordant dye by the $\text{Cr}(\text{VI})$ salt, whereby a new molecule (chromophore) comes into existence. Probably, the key fact is, that the sulfo group is eliminated during the oxidation, so that this new chromophore and subsequently its chromium complex are insoluble in water (formation of black pigment) [22 – 25].

For this reason, a reactive group was incorporated into the dye molecule, able to react with a nucleophilic group of animal fibre (mainly with

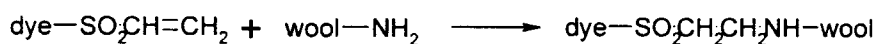
amino group) forming a fast covalent bond between dye and fibre. In this way, the intention was to prepare dyes with excellent wash fastness, and by consequent iron treatment (mordanting) to increase the light fastness significantly.

Thus, the prepared dyes in this work contained in the molecule three different types of reactive group (Table 1), where RG^1 and RG^2 were precursors of the vinylsulfonyl group ($-\text{SO}_2\text{CH}=\text{CH}_2$) and RG^3 was a precursor of the α -bromoacryloamidyl ($-\text{NHCOCH}(\text{Br})=\text{CH}_2$) reactive group.

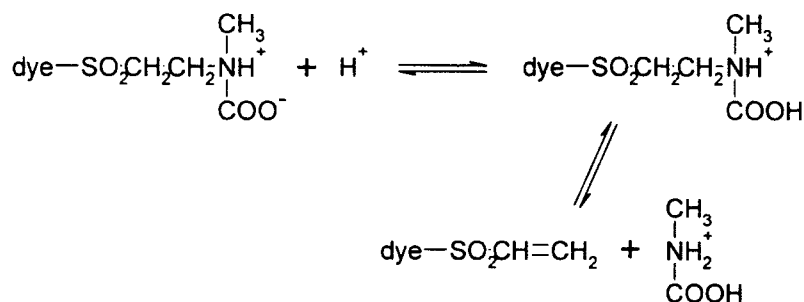
Vinylsulfonyl dyes (VS) in the protected form (as β -sulfatoethyl sulfones) were originally developed for the reactive dyeing of wool by Hoechst [26]. They are storage stable under standard conditions, and the reactive vinylsulfonyl dye (chromophore- $\text{SO}_2\text{CH}=\text{CH}_2$) is liberated by reaction with an alkali in the dyebath. The vinylsulfonyl dye reacts subsequently with a nucleophilic group in the fibre by Michael addition (Figure 1). 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 protection of the vinyl sulfonyl group and the fixation reaction described by Zollinger [27]. In this work sarcosine (*N*-methyl glycine) was used. This type of reactive group has been developed in previous work [28] and the reaction with the wool fibre is shown in Figure 1. Dyes based on the 2,3-dibromo-propionamidyl reactive group were introduced to the dyestuff market by BASF [29] and Ciba-Geigy [30], and the fixation reaction with wool has been explained in the literature [31, 32].

Figure 1: Reactions of reactive dyes in dye bath

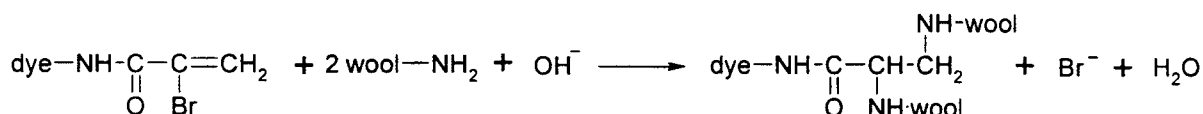
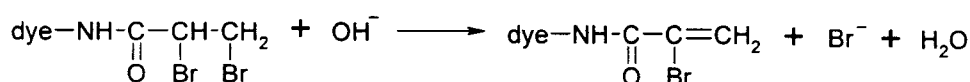
Dyes with RG¹



Dyes with RG²



Dyes with RG³



The idea to prepare reactive iron complex dyes is not new [33–36], but it is believed that the area of mordant dyes can bring new opportunities to solve environmental problems without compromising fastness properties.

EXPERIMENTAL

Preparation of 2,3-dibromo-propionyl chloride

Acrylic acid (99%, 13.9 cm³, 0.2 mol, ρ 1.051 g·cm⁻³, MW 72.06) was cooled (external cooling bath with ice) to 15 °C and bromine (11.3 cm³, 0.22 mol, MW 79.90) was slowly added dropwise under stirring and cooling. The reaction temperature ranged between 15 – 20 °C. When all the bromine was added, the reaction mixture became slightly red and solid. The solid (2,3-dibromo-propionic acid) was dissolved in thionylchloride SOCl₂ (29.4 cm³, 0.4 mol, MW 118.96) and FeCl₃ (1 cm³ 40% aqueous solution) was added. The reaction mixture was refluxed for 8 hours and then the excess of thionylchloride was removed by distillation (b.p. 79 °C). Raw 2,3-dibromo-propionyl chloride was purified by vacuum distillation (4.9 kPa, 97–99 °C). The yield of 2,3-dibromo-propionyl chloride was 22.9 cm³ (purity 98%, 0.19 mol, ρ 2.1 g·cm⁻³, MW 250.31).

Diazotisation of 2-aminophenol

2-Aminophenol (26.2 g, 0.24 mol, MW 109.12) was dissolved in 20 cm³ water, 20 g crushed ice and 53 cm³ concentrated HCl (35%, 0.6 mol). Then an aqueous solution of NaNO₂ (4N, 60 cm³, 0.24 mol) was slowly added dropwise under intensive stirring and external cooling (ice, acetone). The diazotisation temperature was 0 – 5 °C, and the reaction time was approximately 10 minutes. When the reaction was completed (checked by iodine starch paper), the small excess of HNO₂ was removed by the addition of NH₂SO₃H. The solution of diazonium compound was used for the next coupling reaction.

Diazotisation of 2-[(4-aminophenyl)-sulfonyl]ethyl hydrogen sulfate

PAFSES (95.5%, 73.6 g, 0.25 mol, MW 81.29, commercial sample from Spolek pro chemickou a hutní výrobu, a.s. Ústí nad Labem, Czech Republic) was mixed with 40 cm³ water, 10 g ice and 55.2 cm³ HCl (35%, 0.625 mol) under intensive stirring and external cooling (ice, acetone). Then NaNO₂ (4N, 62.5 cm³, 0.25 mol) was slowly added dropwise. The diazotisation temperature was 0 – 5 °C, and the reaction time was approximately 40 minutes. When the reaction was completed (checked by iodine starch paper), the small excess of HNO₂ was removed by the addition of NH₂SO₃H. The solution of diazonium compound

was immediately used for the next coupling reaction.

Bis-diazotisation of 4-amino-*N*-(4-amino-phenyl)benzenesulfonamide

DASA (94.0%, 9.8 g, 0.035 mol, MW 263.31, sample from [28]) was dissolved in a mixture of 30 cm³ water, 5 g ice and 15 cm³ HCl (35%, 0.17 mol) under intensive stirring and external cooling (ice, acetone). Then NaNO₂ (4N, 17.5 cm³, 0.07 mol) was slowly added dropwise. The diazotisation temperature was 0 - 5 °C, and the reaction time was approximately 10 minutes. When the reaction was completed (checked by iodine starch paper), the small excess of HNO₂ was removed by the addition of NH₂SO₃H. The solution of bis-diazonium compound was immediately used for the next coupling reactions.

Preparation of 4-hydroxy-5-(4-nitro-benzoylamino)-naphthalene-2,7-disulfonic acid (monosodium salt)

H-acid (83.5%, 15.3 g, 0.04 mol, MW 319.3) was mixed with 100 cm³ water and cooled to 0 - 5 °C. Then sodium acetate (20% aqueous solution) was added to maintain pH 2 - 3. Following this the solution of 4-nitrobenzoyl chloride (7.42 g dissolved in 28 cm³ dipropylene glycol monomethyl ether - Dowanol DPM, 0.04 mol) was slowly added dropwise to the suspension of H-acid under intensive stirring and cooling. The reaction temperature was 5 - 10 °C, and the reaction pH 2 - 3 was maintained by the addition of sodium acetate over the reaction time of 2 hours. Following this the cooling bath was removed and the suspension was stirred overnight (approx. 16 hours) at the laboratory temperature (approx. 20 °C). Then 4-nitrobenzoyl chloride (1 g dissolved in 5 cm³ of Dowanol DPM, 0.0054 mol) was added again and the suspension stirred for 3 hours, the reaction pH being held at 3.5 (with the addition of 5N NaOH). Yellow product was then filtered off and dried at 80 °C. The yield was 17.5 g monosodium salt (0.036 mol, MW 490.39).

Preparation of 4-hydroxy-5-(4-amino-benzoylamino)-naphthalene-2,7-disulfonic acid (Bechamp reduction)

Iron filings (2.6 g, 0.047 mol) were mixed with 30 cm³ water and 0.26 cm³ concentrated HCl (35%). The mixture was heated to the boiling point and stirred for 10 minutes. Then the mixture was cooled to the temperature 65 °C and the solution of 4-hydroxy-5-(4-nitro-benzoylamino)-naphthalene-2,7-disulfonic acid (4.9 g dissolved in 30 cm³ water, pH maintained at value 8.5, 0.01 mol) was slowly added. After all the nitro compound had been added, the reaction mixture was stirred for 2 hours. When the reduction was completed (colourless solution), the reaction mixture was

cooled to 20 °C and iron oxides were filtered off (clearing). The filtrate was acidified with concentrated HCl to pH 1 and the precipitated white product was filtered off and dried at 60 °C. The yield was 4.0 g (0.0091 mol, MW 438.42).

Preparation of Dye I

Resorcinol (25.3 g, 0.23 mol, MW 110.11) was dissolved in 30 cm³ water and the solution pH was maintained at value 8-9 by the addition of 4N NaOH. Then the diazonium salt of 2-aminophenol (0.23 mol) was slowly poured in under intensive stirring and external cooling (reaction temperature 10 °C, reaction pH 8-9, reaction time 4 hours). The coupling reaction was checked by TLC (Silufol UV 254, mobile phase: water/ethylacetate/propan-1-ol/propan-2-ol = 3/1/4/2). When the first coupling reaction was completed, the diazonium salt prepared from PAFSES (0.25 mol) was slowly added under stirring and cooling (reaction temperature 5 °C, reaction pH 8-9, reaction time 12 hours). The target dye was salted out of solution using 40 g NaCl and dried (60 °C). The yield was 120 g crude Dye I.

Preparation of Dye V

H-acid (15 g, 68.65%, 0.032 mol, MW 319.3) was mixed with 50 cm³ water and 10 g crushed ice. The diazonium salt prepared from PAFSES (0.035 mol) was then slowly added dropwise under intensive stirring and cooling (reaction temperature 5 °C). The reaction pH was brought to 1 by addition of an aqueous solution of CH₃COONa (20% solution) and the reaction mixture stirred for 24 hours. When the first coupling reaction was completed (checked by TLC as above), the pH was maintained at 6 (addition of 5N NaOH) and the *bis*-diazonium salt prepared from DASA (0.034 mol) was added all at once. The reaction pH 6-7 was maintained by the addition of 5N NaOH. The reaction temperature was 5 °C. The reaction mixture was stirred for 10 minutes (formation of *bis*-azo dye) and then an alkaline solution of salicylic acid (0.035 mol, 4.8 g dissolved in 10 cm³ water and 14 cm³ 5N NaOH) was added all at once. The reaction mixture was stirred for 1 hour at reaction pH 8-9 and reaction temperature 5 °C. The target dye was salted out of solution using 40 g NaCl and dried (60 °C). The yield was 34 g crude Dye V.

Preparation of Dye VI

1-[-[(2-Hydroxyethyl)sulfonyl]phenyl]-3-methyl-5-pyrazolone (15 g, 83.2%, 0.044 mol, MW 282.31, sample from [28]) was dissolved in 20 cm³ water, 15 g crushed ice and 9 cm³ 5N NaOH. The diazonium salt prepared from 2-aminophenol (0.046 mole) was then added dropwise to the solution under intensive stirring, with reaction pH 8-9 and reaction temperature 5 °C (external cooling). TLC was used to check the coupling

reaction. The reaction mixture was stirred for 4 hours and the dye was salted out of solution using 20 g NaCl and dried (80 °C). The yield was 17 g crude mono-azo dye.

Dry mono-azo dye (15 g) was slowly added (partwise) to stirred and externally cooled HSO_3Cl (50 cm³). The formed solution was stirred for 2 hours at 25 °C. Then the solution was added dropwise to a mixture of 50 cm³ water and 50 g crushed ice. The precipitated dye was filtered off and carefully dried (IR lamp). The yield was 14 g of crude reactive dye.

Reactive dye (14 g) was mixed with 30 cm³ water and with *N*-methylglycine (3.6 g, 0.04 mol, MW 89.09) under intensive stirring. Then 5N NaOH was added to obtain pH 8–9 and the reaction mixture was stirred for 2 hours at the reaction temperature 50 °C. The dye was salted out of solution using 20 g NaCl and dried (60 °C). The yield was 17.5 g crude Dye VI.

Preparation of Dye X

4-Hydroxy-5-(4-amino-benzoylamino)-naphthalene-2,7-disulfonic acid (10 g, 0.023 mol, MW 438.42) was mixed with 20 cm³ water. The diazonium salt prepared from 2-aminophenol (0.024 mol) was then slowly added under intensive stirring and external cooling. The reaction pH was maintained at 6 by the addition of 5N NaOH. The reaction temperature was 5 °C and the reaction time was 4 hours. When the coupling reaction was completed (checked by TLC) the formed azo dye was salted out of reaction mixture using 15 g NaCl and dried (80 °C). The yield of azo dye was 12 g.

12 g of azo dye was mixed with 20 cm³ water and 10 cm³ phosphorus buffer added (buffer: 1 cm³ concentrated H_3PO_4 diluted with 9 cm³ water and neutralised with 5N NaOH at pH 6). The solution was externally cooled to 1 °C and 2,3-dibromopropionyl chloride (98%, 2.7 cm³, 0.022 mol) was slowly added under intensive stirring. The reaction pH was kept at 4–5 using 5M NaOH. When the reaction was completed, the dye was salted out of solution using 15 g NaCl. The yield was 18 g crude Dye X.

Application procedures (Dyeing)

Dyeings of wool with reactive mordant dyes I – XII were carried out from an acid dyebath (pH 3, acetic acid), with liquor ratio 20:1 and 4% mass concentration of dye (on mass of fabric) using a Linitest laboratory dyeing machine (Hanau, FRG). The dyeing cycle was 30 min from 20 °C to 100 °C, 60 min at 100 °C, 15 min cooling to 70 °C. After this the metal salt was added (metallisation factor Crf was 0.35; mass of metal salt = mass of dye \times Crf) and the dyebath heated to 100 °C over 15 min, held for 45 min at 100 °C, and cooled over 15 min to 25 °C. The fabrics were removed and treated

with alkali (NaHCO_3) for 15 min at 40 °C in a wash-bath, at pH 8.5, and then the fabrics were removed, washed with water at 20 °C and air-dried at room temperature.

Comparison dyeings of wool with Mordant Black 9 and Mordant Black 11 were carried out from an acid dyebath (pH 3, acetic acid), with liquor ratio 20:1 and 4% mass concentration of dye (on mass of fabric) using a Linitest laboratory dyeing machine (Hanau, FRG). The dyeing cycle was 30 min from 20 °C to 100 °C, 60 min at 100 °C, 15 min cooling to 70 °C. Then HCOOH (2 % on mass of fabric) was added and the dyebath heated 100 °C over 15 min, held for 15 min at 100 °C, and cooled over 15 min to 70 °C. After this $\text{K}_2\text{Cr}_2\text{O}_7$ was added (metallisation factor Crf was 0.25) and the dyebath heated over 15 min 100 °C, held for 45 min at 100 °C, and cooled over 15 min to 25 °C. The fabrics were removed and washed with water at 20 °C and air-dried at room temperature.

Measurements of absorption spectra of the dyes and of the exhaustion of dye from the dyebath were carried out using an HP 8453 diode array absorption spectrophotometer (Hewlett Packard).

Fastness tests

The wash fastness at 60 °C was tested according to the ISO 105-A10S/C03(1994) procedure.

The wash fastness - potting - was tested according to the ISO 105-A10S/E09(1994) procedure.

Light fastness was evaluated on Xenotest 450 (Hanau, FRG) according to the ISO 105:B02 (method 2) (normal climate conditions) procedure.

Electrospray ionisation mass spectrometry (ESI-MS)

Mass spectra were measured on an ion trap analyser Esquire 3000 (Bruker Daltonics, Bremen, Germany). The samples were dissolved in 50% aqueous acetonitrile and analysed by direct infusion at flow rate 3 $\mu\text{L}\cdot\text{min}^{-1}$. Mass spectra were recorded in the range m/z 50 – 1000 using electrospray ionisation (ESI) in the negative-ion mode and averaged over 10 scans. The mass spectrometer was tuned to obtain an optimum response for m/z 500 (except for dye XII, where the spectrometer was tuned to m/z 800). The pressure and flow rate of nitrogen were 10 psi and 4 $\text{dm}^3\cdot\text{min}^{-1}$, respectively. The isolation width of the precursor ion for MS^n measurements was $\Delta m/z=4$ (except for bromine containing compounds, where the isolation width was $\Delta m/z=6$). For measurement of dye XII, the tuning parameter "compound stability" was set to a lower value (50%) to increase the relative abundance of the deprotonated molecule.

RESULTS AND DISCUSSION

Synthesis of the dyes

All dyes I – XII were prepared by diazotisation of the primary component (aromatic amine) followed by coupling with the secondary component under weak alkaline conditions. The synthetic route for each dye is in Table 1 and the structures of the prepared dyes are summarised in Table 2. The dyes are drawn in the azo form in spite of the fact that the hydrazone form probably dominates [43-47].

Dyes I – V were prepared from 2-[(4-aminophenyl)sulfonyl]ethyl hydrogen sulfate (PAFSES) as the primary component, which was diazotised with an aqueous solution of NaNO_2 in the presence of diluted mineral acid. The secondary component for the coupling reaction was a monoazo or disazo dye prepared by standard procedures [37]. The preparation of Dye I is described in Figure 2; Dyes II – IV were prepared in a similar way. Since the preparation of Dye V is more complicated, its synthesis is shown separately in Figure 3.

Table 1: Preparation of mordant reactive dyes

Dyes I – V	Reactive group $\text{RG}^1 =$	$\text{—SO}_2\text{CH}_2\text{CH}_2\text{O—SO}_3\text{Na}$	(2-sulfatoethyl-sulfonyl)
Dyes VI – IX	Reactive group $\text{RG}^2 =$	$\text{—SO}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{COOH}$	(<i>N</i> -methyl- <i>N</i> -carboxymethyl-2-aminoethyl-sulfonyl)
Dyes X – XII	Reactive group $\text{RG}^3 =$	$\text{—NH—C(=O)—CH(Br)—CH}_2\text{Br}$	(2,3-dibromopropionamidyl)

Dye	Synthetic route
I	2-aminophenol $\xrightarrow{1}$ resorcinol $\xleftarrow{2}$ PAFSES
II	4-amino-3-hydroxy-7-nitro-naphthalene-1-sulfonic acid $\xrightarrow{1}$ resorcinol $\xleftarrow{2}$ PAFSES
III	5-aminosalicylic acid $\xrightarrow{1}$ resorcinol $\xleftarrow{2}$ PAFSES
IV	2-aminophenol-4-sulfonic acid $\xrightarrow{1}$ 1,5-dihydroxynaphthalene $\xleftarrow{2}$ PAFSES
V	PAFSES $\xrightarrow{1}$ H-acid $\xleftarrow{2}$ DASA $\xrightarrow{3}$ salicylic acid
VI	2-aminophenol $\xrightarrow{1}$ PYRAZ $\xleftarrow{2}$ dehydration with HSO_3Cl \rightarrow addition of sarcosine
VII	2-aminophenol-4-sulfonic acid $\xrightarrow{1}$ PYRAZ $\xleftarrow{2}$ dehydration with HSO_3Cl \rightarrow addition of sarcosine
VIII	4-amino-3-hydroxy-7-nitro-naphthalene-1-sulfonic acid $\xrightarrow{1}$ PYRAZ $\xleftarrow{2}$ dehydration with HSO_3Cl \rightarrow addition of sarcosine
IX	5-aminosalicylic acid $\xrightarrow{1}$ PYRAZ $\xleftarrow{2}$ dehydration with HSO_3Cl \rightarrow addition of sarcosine
X	2-aminophenol $\xrightarrow{1}$ 4-hydroxy-5-(4-amino-benzoylamino)-naphthalene-2,7-disulfonic acid $\xrightarrow{2}$ treat with 2,3-dibromo-propionyl chloride
XI	2-aminophenol-4 sulfonic acid $\xrightarrow{1}$ 4-hydroxy-5-(4-amino-benzoylamino)-naphthalene-2,7-disulfonic acid $\xrightarrow{2}$ treat with 2,3-dibromopropionyl chloride
XII	2-amino-5-nitro-phenol $\xrightarrow{1}$ 4-hydroxy-5-(4-amino-benzoylamino)-naphthalene-2,7-disulfonic acid $\xrightarrow{2}$ treat with 2,3-dibromopropionyl chloride

PAFSES = 2-[(4-aminophenyl)sulfonyl]ethyl hydrogen sulfate

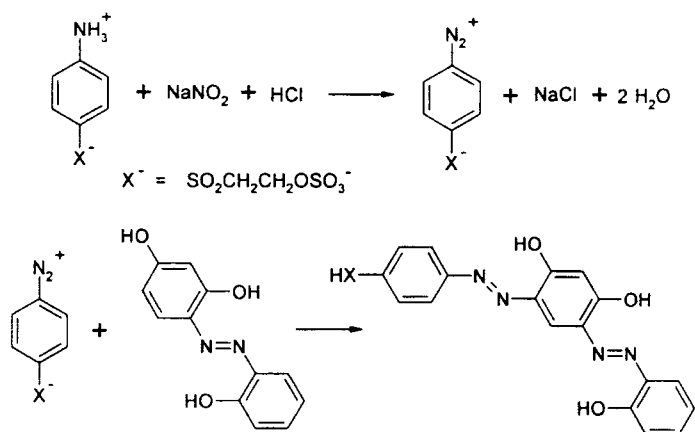
DASA = 4-amino-*N*-(4-aminophenyl)benzenesulfonamide

PYRAZ = 1-[(2-hydroxyethyl)sulfonyl]phenyl]-3-methyl-5-pyrazolone

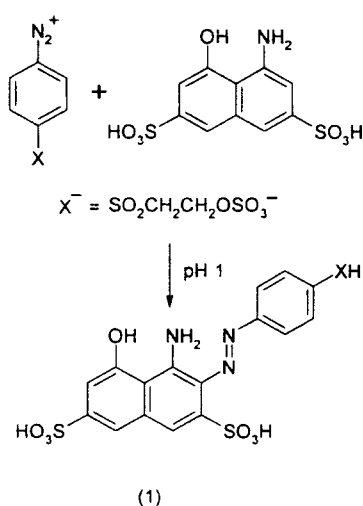
Table 2: Molecular structure of prepared mordant dyes

Dye	Structure
I	
II	
III	
IV	
V	
VI	

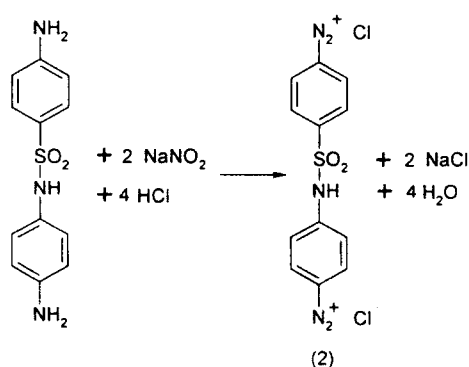
Dye	Structure
VII	
VIII	
IX	
X	
XI	
XII	

Figure 2: Synthesis of Dye I**Figure 3: Synthesis of Dye V**

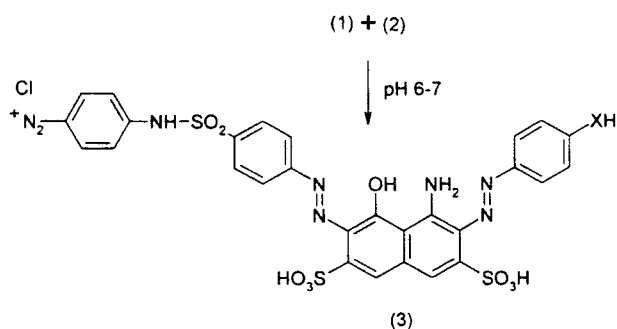
First coupling reaction



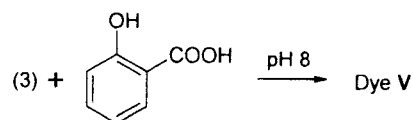
Bis-diazotisation of DASA



Second coupling reaction

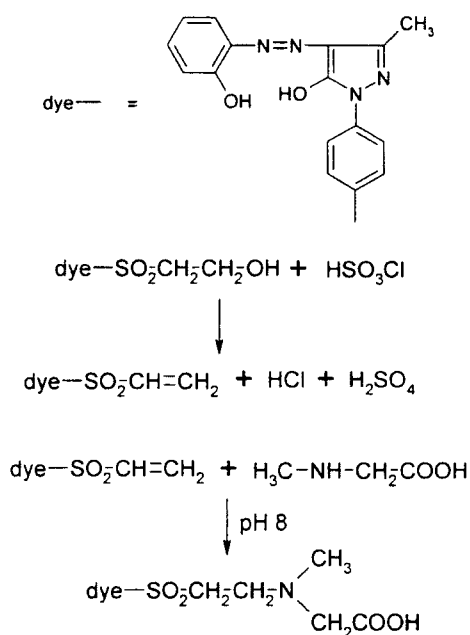


Third coupling reaction



Dyes VI – IX were prepared by diazotisation of an aromatic amine and coupling with 1-[-[(2-hydroxy-ethyl) sulfonyl] phenyl]-3-methyl-5-pyrazolone (PYRAZ). Attempts to accomplish the esterification of the aliphatic hydroxyl group ($-\text{SO}_2\text{CH}_2\text{CH}_2\text{OH}$) with sulfuric acid and oleum were unsuccessful. Thus, chlorosulfuric acid (HSO_3Cl) was used, whereupon the dehydration took place and vinylsulfonyl dye (chromophore- $\text{SO}_2\text{CH}=\text{CH}_2$) was prepared (Figure 4).

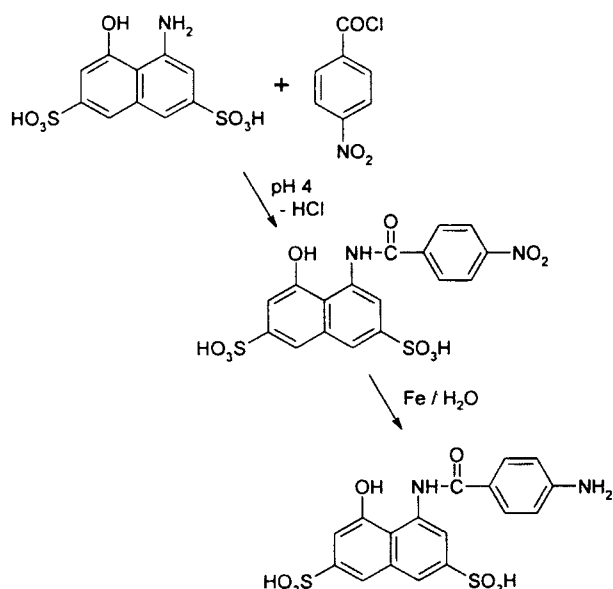
The dye in this form is very reactive and can be used for wool dyeing directly [38].

Figure 4: Preparation of Dye VI

Dyes X – XII are based on the 2,3-dibromopropionamidyl reactive group (RG^3) and on the coupling component 4-hydroxy-5-(4-amino-benzoylamino)-naphthalene-2,7-disulfonic acid.

Synthesis of synthetically pure secondary component (4-hydroxy-5-(4-amino-benzoylamino)-naphthalene-2,7-disulfonic acid) is crucial for the successful synthesis of the reactive dye. The starting compound for the synthesis was H-acid, which was condensed with 4-nitro-benzoylchloride [39] and then the nitro group reduced to the amino group (Figure 5).

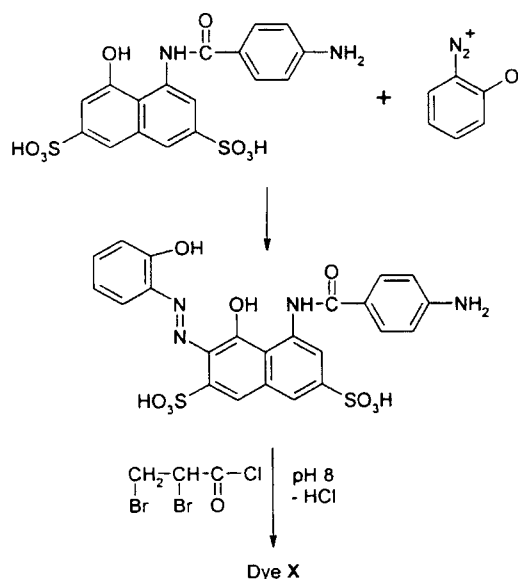
Figure 5: Preparation of 4-hydroxy-5-(4-amino-benzoylamino)-naphthalene-2,7-disulfonic acid



Bechamp reduction of 4-hydroxy-5-(4-nitro-benzoylamino)-naphthalene-2,7-disulfonic was better than reduction with sodium sulfides (NaSH, Na₂S), where azoxy impurities were formed and the purification procedure was very difficult. The nitro compound can be also reduced successfully by FeCl₂ [40].

Dyes **X** – **XII** were prepared by the classical diazotisation of *o*-aminophenols and consecutive coupling reaction with 4-hydroxy-5-(4-amino-benzoylamino)-naphthalene-2,7-disulfonic acid followed by the condensation of the dye (amino group) with 2,3-dibromo-propionyl chloride (Figure 6) [29, 30, 41].

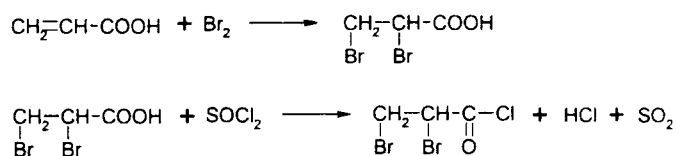
Figure 6: Synthesis of Dye **X**



2,3-Dibromo-propionyl chloride was prepared by the procedure described in the patent literature [42], that is, the reaction of acrylic acid with bromine and treatment with thionylchloride under

catalysis of FeCl₃ (Figure 7). The product was purified by vacuum distillation.

Figure 7: Preparation 2,3-dibromo-propionyl chloride



Prepared Dyes **I** – **XII** were salted out of the reaction mixture, meaning that every dye contained some amount of inorganic salt. Since Dyes **I** – **XII** were chromatographically pure, the content of dye was approximately determined by elemental analysis. Spectral properties of the dyes are summarised in Table 3.

Table 3: Tinctorial strength of synthesised mordant reactive dyes (aqueous solution)

Dye	Conc of dye / (mass %)	λ_{max} / nm	ϵ_{max}^* / $\text{dm}^3 \cdot \text{g}^{-1} \cdot \text{cm}^{-1}$
I	63	420	44
II	62	420	34
III	66	412	40
IV	66	490	62
V	69	600, 392	34, 10
VI	41	411	92
VII	42	396	82
VIII	43	445	55
IX	43	417	21
X	85	530	28
XI	87	516	25
XII	88	520	25

* absorption coefficient was measured for the dye precipitated from the reaction mixture (nonpurified)

Structure confirmation by electrospray ionisation mass spectrometry

The structures of some representative compounds were confirmed by ESI-MS spectrometry.

Dye IV, MW (C₂₄H₂₀O₁₂N₄S₃) = 652

MS: m/z 689, 20%, [M-2H+K]⁻; m/z 673, 31%, [M-2H+Na]⁻; m/z 651, 58%, [M-H]⁻; m/z 571, 98%, [M-H-SO₃]⁻; m/z 553, 100%, [M-H-H₂SO₄]⁻.

MS/MS of 651 (collision amplitude, CA = 0.8 V): m/z 593, 5%, [M-2H+Na-SO₃]⁻; m/z 571, 100%, [M-H-SO₃]⁻.

MS/MS of 571 (CA = 1 V): m/z 553, 45%, [M-H-H₂SO₄]⁻; m/z 525, 18%, [M-H-H₂SO₄-CH₂CH₂]⁻; m/z 491, 61%, [M-H-2SO₃]⁻; m/z 462, 31%, [M-H-SO₃-HSO₃-CH₂CH₂]⁻; m/z 186, 100%, [(NH)(O)C₆H₃SO₃]⁻.

The peaks of deprotonated molecule [M-H]⁻ and the characteristic adducts for sulfonic acids ([M-2H+Na]⁻ and [M-2H+K]⁻ ions) confirm unambiguously the expected molecular weight MW 652 Da. The neutral losses of SO₃ and H₂SO₄

observed in both MS and MS/MS spectra show the presence of sulfonic and sulfate groups, respectively. The loss of CH₂CH₂ can be also correlated with the structure, because this functionality is adjacent to the initially cleaved -OSO₃H group.

Dye VII, MW (C₂₁H₂₃O₉N₅S₂) = 553

MS: m/z 552, 100%, [M-H]⁻; m/z 508, 16%, [M-H-CO₂]⁻.

MS/MS of 552 (CA = 0.9 V):

m/z 472, 25%, [M-H-SO₃]⁻; m/z 352, 31%, [M-(OH)(N₂)C₆H₃SO₃H]⁻; m/z 199, 50%, [HOC₆H₂(N₂)SO₃]⁻; m/z 186, 12%, [HOC₆H₂(NH)SO₃]⁻; m/z 171, 100%, [HOC₆H₂SO₃]⁻.

The deprotonated molecule at m/z 552 is the base peak of the spectrum, which is in accordance with the expected molecular weight, MW 553 Da. The fragment ion at m/z 508 is a typical loss for carboxylic acids (Δm/z = 44, CO₂). The important fragment ions in MS/MS spectrum are again the products of the cleavage of azo bond and neighbouring C-N bonds at m/z 171, 186 and 199. The presence of a sulfonic acid group is confirmed by the typical neutral loss of SO₃.

Dye VIII, MW (C₂₅H₂₄O₁₁N₆S₂) = 648

MS: m/z 647, 100%, [M-H]⁻; m/z 558, 15%, [M-H-CH₃NHCH₂COOH]⁻; m/z 294, 5%, [(NO₂)(OH)(N₂)C₁₀H₃SO₃]⁻; m/z 281, 13%, [(NO₂)(OH)(N)C₁₀H₄SO₃]⁻; m/z 268, 4%, [(NO₂)(OH)C₁₀H₅SO₃]⁻; m/z 266, 15%, [(NO₂)(OH)C₁₀H₃SO₃]⁻.

MS/MS of 647, collision amplitude (CA) = 0.6 V: m/z 619, 3%, [M-H-N₂]⁻; m/z 352, 3%, [M-(NO₂)(OH)(N₂)C₁₀H₄SO₃H]⁻; m/z 294, 43%, [(NO₂)(OH)(N₂)C₁₀H₃SO₃]⁻; m/z 281, 13%, [(NO₂)(OH)(N)C₁₀H₄SO₃]⁻; m/z 268, 100%, [(NO₂)(OH)C₁₀H₅SO₃]⁻; m/z 266, 91%, [(NO₂)(OH)C₁₀H₃SO₃]⁻; m/z 238, 4%, [(O)(OH)C₁₀H₅SO₃]⁻; m/z 220, 1%, [(OH)C₁₀H₃SO₃]⁻; m/z 204, 5%, [(NO₂)(OH)C₁₀H₃O]⁻.

The deprotonated molecule [M-H]⁻ is the base peak in the negative-ion ESI mass spectrum which makes it possible to confirm the expected molecular weight, MW 648 Da. Some fragment ions with relative abundances lower than 20% are also observed in the first stage mass spectrum such as [M-H-CH₃NHCH₂COOH]⁻ and ions resulting from the cleavage of the azo bond (m/z 281) and of neighbouring C-N bonds to azo bond (m/z 266 and 294). These ions are also apparent in the MS/MS spectrum of m/z 647, where the characteristic neutral losses confirm the presence of a sulfonic acid group (Δm/z = 64, SO₂) and of a nitro group (Δm/z = 30, NO and Δm/z = 46, NO₂) yielding the fragment ions at m/z 238, 220 and 204.

Dye IX, MW (C₂₂H₂₃O₈N₅S) = 517

MS: m/z 516, 100%, [M-H]⁻; m/z 427, 12%, [M-H-CH₃NHCH₂COOH]⁻.

MS/MS of 516 (CA = 1 V):

m/z 458, 9%, [M-H-CH₂COO]⁻; m/z 427, 100%, [M-H-CH₃NHCH₂COOH]⁻; m/z 383, 52%, [M-H-CH₃NHCH₂COOH-CO₂]⁻; m/z 263, 74%, [CH₂=CHSO₂C₆H₄C₃N₂H(CH₃)O]⁻.

The molecular weight MW 517 Da can be easily confirmed by the presence of deprotonated molecule as the base peak of the MS spectrum. The neutral losses of CH₃NHCH₂COOH and CO₂ show the presence of these functionalities in the molecule and other structural subunits are confirmed by the fragment ions, for example m/z 263.

Dye X, MW (C₂₆H₂₀O₁₀N₄S₂Br₂) = 770

MS: m/z 689, 66%, [M-H-HBr]⁻; m/z 599, 100%, [M-H-2HBr]⁻.

MS/MS of 689 (CA = 1 V):

m/z 582, 87%, [M-H-HBr-HOC₆H₄N]⁻; m/z 569, 100%, [M-H-HBr-HOC₆H₄N=NH]⁻; m/z 518, 94%, [M-H-HBr-HOC₆H₄N-SO₂]⁻; m/z 489, 9%, [M-H-HBr-HOC₆H₄N=NH-SO₃]⁻; m/z 438, 11%, [M-H-2HBr-HOC₆H₄N-SO₂]⁻.

HBr is cleaved from the molecule so easily that the molecular ion is not apparent, but the identity is confirmed by the characteristic ions [M-H-HBr]⁻ and [M-H-2HBr]⁻ with appropriate isotopic ratios for one or zero bromine atoms. The MS/MS spectrum shows typical neutral losses for sulfonic acid group (SO₃ and SO₂) and also the cleavage of HBr.

Dye XI, MW (C₂₆H₂₀O₁₃N₄S₃Br₂) = 850

MS: m/z 851, 52%, [M-H]⁻; m/z 769, 100%, [M-H-HBr]⁻; m/z 679, 79%, [M-HBr-CHBr]⁻; m/z 637, 68%, [M-BrCH(Br)CCO]⁻.

Surprisingly, the molecular ion [M-H]⁻ is present with a relatively high intensity and some further neutral losses related to the bromine-containing part of the molecule are observed in accordance with the structure (m/z 769, 679 and 637).

Dye XII, MW (C₂₆H₁₉O₁₂N₅S₂Br₂) = 815

MS: m/z 838, 21%, [M-2H+Na]⁻; m/z 816, 56%, [M-H]⁻; m/z 752, 31%, [M-H-SO₂]⁻; m/z 736, 72%, [M-H-HBr]⁻; m/z 672, 28%, [M-H-HBr-SO₂]⁻; m/z 644, 39%, [M-H-HBr-CHBr]⁻; m/z 624, 38%, [M-H+Na-BrCH₂(Br)CHCO]⁻; m/z 602, 100%, [M-BrCH₂(Br)CHCO]⁻; m/z 366.5, 16%, [M-2H-HBr]²⁻; m/z 300.5, 11%, [M-H-BrCH₂(Br)CHCO]²⁻.

The mass spectrum of this compound is more complex due to the presence of two sulfonic acid groups and two bromine atoms. The presence of more bromine atoms in a molecule usually causes

the consequent losses of HBr or Br⁻, which can lead to decreased relative abundance or absence of deprotonated molecule in the spectrum, as in the case of the sample studied. The special soft tuning parameters (i.e. the compound stability value 50%) were set to reduce the molecular ion decomposition, hence the deprotonated molecule [M-H]⁻ has 56%. Other fragment ions are related to the bromine-containing part of the molecule (m/z 736, 624 and 602) and confirm the presence of -COCH(Br)CH₂(Br) functionality. Two sulfonic acid groups in a molecule are identified by means of characteristic doubly charged ions, as described in previous works [48,49].

Application of prepared dyes

All prepared Dyes I – XII were applied to wool. The dyeing of wool was carried out by a combination of reactive and mordant dyeing. The wool was first dyed under acid conditions (adsorption of dye on the fibre, formation of electrostatic bonds). Following this mordanting with a metal salt took place (formation of metal complex dye) and then in the new bath the coloured samples were treated with NaHCO₃ (at pH 7-8) (fixation of dye to the fibre by covalent bonds, Figure 1) and finally washed. Results of the dyeing and fastness properties are summarised in Tables 4 – 6.

The wool was also dyed with Mordant Black 9 (Diamant Schwarz PV, sample from Bayer BRD) and Mordant Black 11 (Alizarine Chrome Black PT, sample from Spolek pro chemickou a hutní výrobu, Czech Republic) for the comparison of fastness properties. The application procedure was classical mordant dyeing, that is, acid dyeing of the wool sample with the mordant black dye followed by oxidation and metallisation with dichromate (K₂Cr₂O₇). The obtained results are shown in Table 7.

Table 4: Light fastness of dyed wool samples (4% coloration, Xe-test ISO 105-B02)

Dye	Unmet.	Mordant with FeCl ₃	Mordant with CrF ₃	Mordant with FeCl ₂
I	4	6-7	6	6
II	2	3-4	4	3-4
III	3-4	3-4	3-4	4
IV	4	4	4	4
V	3-4	3-4	3-4	4
VI	2	6-7	6	4-5
VII	2	6-7	6	3-4
VIII	3	3-4	4	4-5
IX	4	3	2	3-4
X	3	6	6-7	6-7
XI	3-4	6	6	4-5
XII	3-4	6	6	6

Table 5: Wash fastness of dyed wool samples (60 °C) (4% coloration, ISO 105 C03)

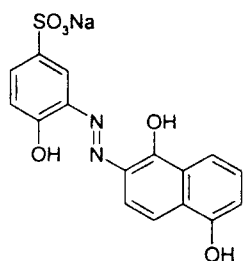
Dye	Unmet.	Mordant with FeCl ₃	Mordant with CrF ₃	Mordant with FeCl ₂
I	4 (R)a, 1-2b, 1-2c	4, 3, 3	4-5, 4, 4	4-5, 4, 3-4
II	2-3, 4, 3-4	4 (R), 4, 3-4	4-5, 4-5, 4	3-4(Y), 4Y, 4
III	4(Y), 4-5, 2-3	4-5 (Y), 4-5, 3-4	4-5, 4-5, 4	4,3-4,3(R)
IV	4-5, 5, 4	4-5, 5, 4	4-5, 5, 5	4-5,5,4
V	4-5, 4-5, 4-5	4-5, 4, 4	4-5, 4-5, 4-5	4-5,4-5,4-5
VI	4-5(Y), 5, 4-5	4-5(Y), 4-5, 4	4-5(R), 4-5, 4-5	4-5(R), 4-5,4-5
VII	4-5(Y), 5, 4-5	4-5, 4-5, 4	4-5(R), 4-5, 4-5	4R,4-5,4-5
VIII	4(R), 4, 2-3	4-5(R), 5, 2-3	4-5, 5, 4	4R,4,3R
IX	3(Y), 1, 3-4	3(Y), 1, 3-4	4-5, 2-3, 4-5	1(Y),2-3,2- 3
X	3(B), 4, 3-4	4(R), 5, 4	4(B), 5, 4	3Y,4-5,4
XI	4, 3-4, 1-2	4-5, 4-5, 4	4-5, 4-5, 3-4	3-4Y,4,4-5
XII	4, 3-4, 1-2	4-5, 4-5, 4	4-5, 4-5, 3-4	4-5, 4, 4

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

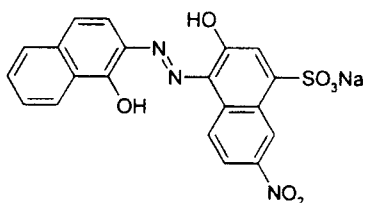
Table 6: Wash fastness of dyed wool samples (potting) (4% coloration, ISO 105 E09)

Dye	Unmet.	Mordant with FeCl ₃	Mordant with CrF ₃	Mordant with FeCl ₂
I	4-5(3R)a, 1b, 3c	4-5, 3, 4	4-5, 3-4, 4-5	4-5, 3-4, 4
II	3-4, 2-3, 4-5	4-5, 3, 4-5	4-5, 3-4, 4-5	3,4,4-5
III	4(Y), 2-3, 3-4	4(Y), 2-3, 4	4-5, 5, 4-5	4Y,3,4
IV	3, 2-3, 4	4, 2-3, 4	4-5, 4-5, 4-5	4-5,3-4,4-5
V	4, 3, 4-5	4-5, 4, 4-5	4-5, 4(R), 4-5	4-5Y,3-4,4
VI	3, 3-4, 5	4-5, 4, 4-5	4-5(R), 5, 5	4(R), 3,4
VII	3, 3-4, 5	4-5, 4, 4-5	4-5(R), 5, 5	3-4,4-5,4-5
VIII	2-3, 3, 4	4-5(Y), 4, 4-5	4-5(R), 4-5, 4-5	4,3,4
IX	2-3(Y), 3, 2-3	2-3(Y), 3, 2-3	4-5, 4-5, 4	2-3(Y),1,3-4
X	4, 2, 3-4	4, 3-4, 4	4(3B), 5, 5	4,3,4
XI	4, 1, 3-4	4-5, 1-2, 4-5	4, 2-3, 4	4,2-3,4-5
XII	4, 1, 3-4	4-5, 1-2, 4- 5	4, 2-3, 4	4, 2-3, 4

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



CI Mordant Black 9



CI Mordant Black 11

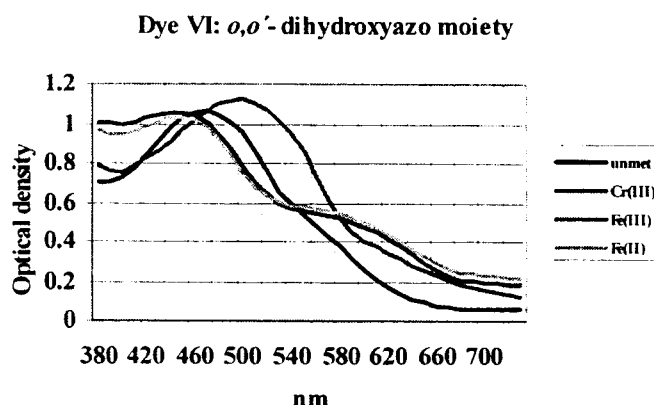
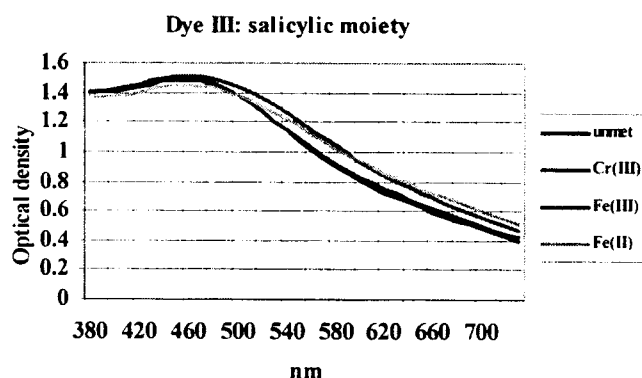
Table 7: Fastness properties of commercial samples (wool, 4% coloration, Cr-factor = 0.25)

Dye	Fastness data		
	Potting	Wash test 60°C	Xe-test
Mordant Black 9	4-5, 5, 5	4-5, 5, 5	7 – 8
Mordant Black 11	4-5, 5, 5	4-5, 5, 5	7 – 8

Reflection spectra

Optical density (reflection) spectra of dyed wool samples were recorded in the visible region (380 to 740 nm). The representative spectra of Dyes III and VI are shown in Figure 8.

Figure 8: Optical density spectra



From the spectra above it can be concluded, firstly, that complexation on the wool fibre with either Fe(II) or Fe(III) salt leads to the same result. This implies the idea, that due to the reductive properties of wool and oxidative properties of air oxygen a red/ox equilibrium is formed.

Secondly, complexation of mordant dyes with the *o,o'*-dihydroxyazo moiety by Cr(III) salt (medially

metallised) gives a complex with one or two absorption bands in the visible region of the spectra bathochromically shifted in comparison with the unmetallised dye. The origin of the bathochromic shift is usually explained by the ionisation of oxygen and nitrogen atoms in the complex (ionisation of the dye chromophore) [43-46]. Complexation with iron ions gives unfortunately two different absorption bands, one shifted bathochromically and one shifted hypsochromically. The origin of this "yellow band" is not explained in any literature, and its presence means that all iron complex dyes are in fact browns.

Thirdly, the complexation of mordant dyes with a salicylic group in the molecule moiety (terminally metallised) does not change the colour (or the light fastness) significantly.

CONCLUSION

A set of reactive mordant azo dyes (I – XII) has been prepared, where the mordant dyes contained the *o,o'*-dihydroxyazo moiety as a tridentate chelating ligand or the salicylic moiety as a bidentate ligand.

The reactive group incorporated in the dye molecule was a derivative of either the vinyl sulfonyl group or the 2-bromoacryloamidyl group.

Dyes I – XII were applied to wool and the coloured samples treated with Cr(III), Fe(III) or Fe(II) salts in the mordant dyebath under reactive dyeing conditions. The dyed samples were colorimetrically tested and wet fastness and light fastness were determined.

Dyes III – VII and X – XII had good wet fastness independent of the type of reactive group. Complexation with the metal ion increased the wet fastness slightly.

Dyes I, II, IV, VI – VIII and X – XII with the *o,o'*-dihydroxyazo moiety as tridentate chelating ligand showed good light fastness ($X_e \approx 6-7$) after mordanting with a metal salt, and the light fastness of the chromium complexes was comparable with that of the iron complexes. In contrast, mordanting of dyes III, V, and IX containing the salicylic moiety did not change the light fastness of the coloured samples significantly ($X_e \approx 4$).

Finally, the prepared dyes I – XII are not competitive with current commercial black mordant dyes such as Mordant Black 9 and Mordant Black 11. Nevertheless, syntheses of their reactive derivatives and their properties will be the aim of our continuing research.

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