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Epoxy Reactive Dyes for Wool and Wool/polyester Blends

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ABSTRACT

Disperse azo dyes with two reactive epoxy groups were synthesised using N,N-*diglycidylaniline as the coupling component. Dyeing conditions, wet-fastness and light-fastness on wool and wool/polyester blends were studied.* © *1998 Elsevier Science Ltd*

Keywords: reactive dyes, epoxy, disperse, wool.

INTRODUCTION

Water-soluble reactive dyes based on 3-chloro-2-hydroxypropyl (I) or 2,3-epoxypropyl (II) functional groups (Fig. 1) have been known since 1957, when Ciba claimed them for the dyeing of cellulose [1]. In 1959, ICI patented disperse reactive dyes (not containing a sulfonic group) based on the reactive group (I) for the dyeing of synthetic polyamides [2]. Generally, reactive dyes containing functional groups I and II, except for the Procinyl dyes (Fig. 2), are not suitable, due to synthetic and application difficulties for the coloration of cellulose.

The reactive residues I and II can be introduced into dyestuffs in several ways. The main synthetic route is based on the preparation of a chromophore containing a strongly nucleophilic amino group, which when treated with epichlorohydrin (approx. 20 h, 25°C, pH 6–7) forms a reactive 3-chloro-2-hydroxypropylamino group or an *N,N*-bis(3-chloro-2-hydroxypropyl)-amino group. Such dyes served as a precursors for the synthesis of epoxy reactive dyes by the action of alkalis, i.e. under the conditions of application to cellulose (Fig. 3).

$R^1 = -CH_2-CH(OH)-CH_2Cl$

$R = -CH_2-CH(-O-)CH_2$

(I) (II)

Fig. 1. 3-Chloro-2-hydroxypropyl (R^1) and 2,3-epoxypropyl (R) functional groups.

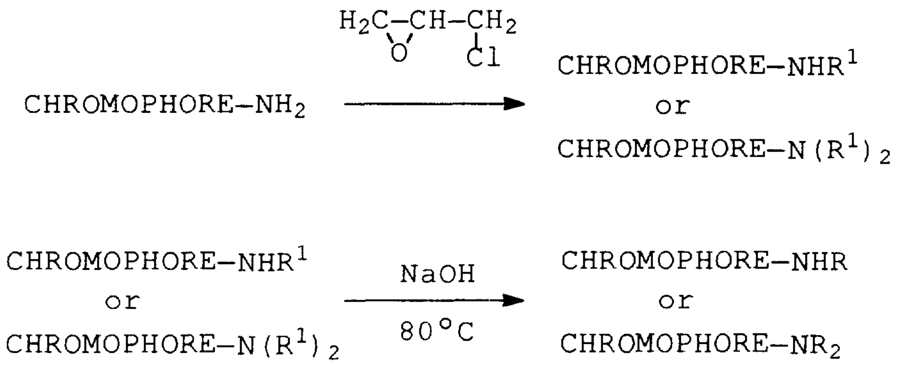
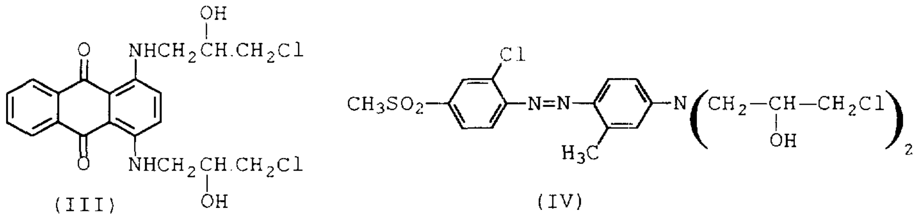


Fig. 2. Preparation scheme of reactive dyes with functional groups R^1 ($CH_2CH(OH)CH_2Cl$) and R (CH_2CHOCH_2).



(III) (IV)

Fig. 3. Reactive blue (III) and scarlet (IV).

Although water-soluble cellulose-reactive dyes of this type give dyeings with very good wet-fastness properties after padding and fixation in steam or dry heat in the presence of alkali, their activity is insufficient for exhaustion processes. Moreover, at the time of introduction, it was not easy to find brilliant and lightfast structures. On the other hand, disperse reactive dyes for polyamide fibres, such as the reactive blue dye III and the reactive red dye IV (Fig. 2) have achieved technical importance, because the reactivity this group with respect to the more nucleophilic amino group is optimized [3].

Recently, a trend to restrict Cr^{3+} and Co^{3+} complex dyes has been observed and therefore a demand for new, wet-stable dyes grows in the wool-textile industry. One possibility to resolve this problem is in the application of reactive dyes in which the epoxy reactive group is one of the most appropriate substituents.

Since alkali conditions cannot be used for the dyeing of animal fibres an epoxy reactive dye is more suitable than its precursor containing the functional group I. The epoxy group II reacts with the amino group of the substrate by a nucleophilic addition mechanism, and the reaction time depends on the application temperature.

The preparation of an epoxy reactive dye from a 'parent' dye (having an amino group in the molecule) does not lead to a pure dyestuff: reaction of the amino group with epichlorohydrin and dehydrochlorination with NaOH leads to a mixture of 2,3-epoxypropyl, 2-hydroxy-3-chloropropyl, and related amino derivatives. The ratio of these derivatives is similar to that of derivatives contained in crude *N,N*-diglycidylaniline [4]. It is thus impossible to purify such a dye mixture economically.

The synthesis of pure *N,N*-diglycilaniline (*N,N*-bis(2,3-epoxypropyl)aniline, a precursor for tetrafunctional epoxy resins) has been developed. Compound V can be prepared from aniline as outlined in Fig. 3. After the purification procedure (distillation), compound V is obtained in very pure form, for use as the secondary component in the preparation of azo dyes.

This paper deals with the synthesis of epoxy reactive dyes and their application properties with respect to wool and wool/polyester blends.

EXPERIMENTAL

Diazotation

4-Nitroaniline 4- and 3-aminobenzoic acid 4-aminobenzene sulfonic acid (2-chloro-4-nitroaniline, the *n*-propylester of 4-amino-benzoic acid and 4,4'-diaminodibenzosulfonamide were diazotised (resp. tetrazotised) by conventional methods, i.e. in dilute hydrochloric acid at 0–5°C with addition of aqueous $NaNO_2$ (5 mol l^{-1}).

Diazotation of 3-amino-6-nitrobenzoisothiazole [5]

3-Amino-6-nitrobenzoisothiazole (0.05 mol, 9.75 g) was added at ambient temperature and under intensive stirring to nitrosyl sulphuric acid (3.45 g of $NaNO_2$ in 32 ml of concentrated H_2SO_4). The suspension was stirred 3 h and the liquor then used for the coupling reaction.

General procedure for the coupling reaction

N,N-Diglycidylaniline (0.05 mol, 12.25 g, 84% purity) was dissolved in the mixture of 50 ml of water and 30 ml of ethanol. The solution was maintained at 0–5°C (external cooling with ice and acetone) and under vigorous stirring a solution of the diazonium compound (0.05 mol) was gradually added. The pH was adjusted to approx. 6–7 by addition of sodium acetate. When the coupling reaction was completed, the precipitated dyestuff was filtered, washed with water and dried at approx. 40°C. The purity of the dye was determined by HPLC (Table 1).

Application procedures (dyeing)

All dyeings of the wool were carried out from distilled water with a liquor ratio 20:1 and 1% mass concentration of a disperse dye (related to the mass of fabrics) using a laboratory Linitest dyeing machine (Hanau, BRD). The dye was dispersed by grinding of the dye with Slovasol 915 (oxyethylated nonylphenol, $n = 15$) in a mass ratio 1:1. The dyeing cycle was 30 min from 30 to 100°C, 30 min at 100°C, addition of alkali ($NaHCO_3$ or NH_4OH, resulting pH 7–8), 30 min at 100°C, cooling to 50°C. After this procedure the fabrics were removed, rinsed thoroughly with cold water, and washed 20 min at 70°C in a wash bath containing 1.5 g l^{-1} of sodium dodecylsulfate, 1 ml l^{-1} of 26% NH_4OH and 1 g l^{-1} of $NaHCO_3$. After this alkaline after treatment the fabrics were rinsed with cold water and air-dried at room temperature.

All dyeings of the wool/polyester mixtures (45/55%) were carried out from distilled water with carrier Spolapren XN (naphtalene-biphenyl type) with a concentration of 2 g l^{-1} in the dyebath, liquor ratio 20:1, 2% concentration of a 'dispersed' dye (related to the mass of fabrics), and using a laboratory dyeing machine Linitest (Hanau, BRD). The dye was dispersed by grinding of a dye with Slovasol 915 (oxyethylated nonylphenol, $n = 15$) in a mass ratio 1:1. The dyeing cycle was 30 min from 30 to 100°C, 60 min at 100°C, and cooling to 40°C. After this procedure the fabrics were removed, rinsed thoroughly with cold water, and washed 20 min at 70°C in a wash bath containing 1.5 g l^{-1} of sodium dodecylsulfate and 0.5 g l^{-1} of $NaHCO_3$. After this alkaline aftertreatment the fabrics were rinsed with cold water and air-dried at room temperature.

TABLE 1
HPLC Conditions

Column	Watrex 250×4 mm, Nucleosil 120-5 C18
Mobile phase	Acetonitrile/water: 90/10 Gradient pump spectra series P200
Flow	1 ml min^{-1}: 20 μl
Detector	W/VIS spectrum (210–780 nm) Spectra system UV 3000HR
Equipment	Thermo separation products

The absorption spectra of acetone solutions of the dyes and measurements of the exhaustion of the dye from the dyebath were carried out using HP 8453 diode array absorption spectrometer (Hewlett Packard).

Fastness tests

The wash fastness at 40 and 60°C was tested according to the procedure ISO 105-Al0S/C01,C02(1994). Potting was tested according to the procedure ISO 105/E09(1989). Light fastness were evaluated on a Xenotest 450 (Hanau, BRD) according to the procedure ISO 105:B02 (method 2).

RESULTS AND DISCUSSION

Synthesis of the dyes

The epoxy reactive dyes listed in Table 2 were prepared by diazotation of the aromatic amine and subsequent coupling of the diazonium compound with *N*,*N*-diglycidylaniline (V).

HPLC analysis confirmed that the prepared dyes **1**–**10** (purity higher than 95%) were slightly contaminated with other dyes due to impurities in the precursor *N*,*N*-diglycidylaniline [4]. (HPLC conditions are summarized in Table 1).

Physical properties of the prepared dyes **1–10** are summarized in Table 3.

The structure of dye **1** was confirmed by elemental analysis (Table 4) and NMR spectroscopy. The ability of the reactive groups II in dye 1 to react with an aliphatic amino group was tested by reaction with cyclohexylamine (Fig. 4). The product **11** was checked by HPLC and elemental analysis (Table 4). To ensure completion of the reaction within 30–60 min, a higher temperature (at least 80°C) was necessary.

Application of the dyes

Dyes **1**–**7** are disperse reactive dyes, whereas dyes **8**–**10** are water-soluble. The water-soluble dyes **8**–**10** were prepared in order to compare the dyeing conditions and wet-stability of the coloured substrates.

Dyes **1**–**10** reacted with substrates containing amino groups within 30–60 min (typical duration of dyeing procedures) at temperatures higher than 80°C. Furthermore, at this temperature the disperse dyes **1**–**7** are (due to the *N*,*N*-diglycidylamino group) partially soluble in water. Higher reaction temperature allows for diffusion of reactive disperse dyes into the fibre, and subsequent fixing reaction of the functional group. All the disperse reactive

TABLE 2
List of Prepared Dyestuffs ($R = \mathrm{CH_2CHOCH_2}$) Together with Reaction Yields with Respect to Primary Aromatic Amine

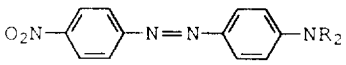
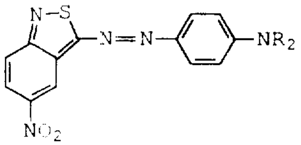
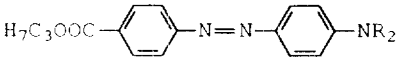
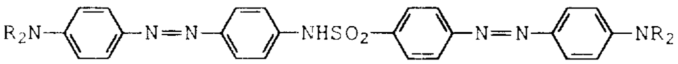
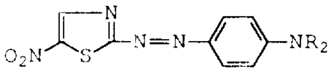
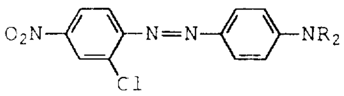
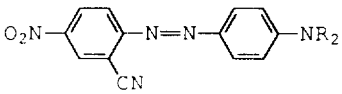
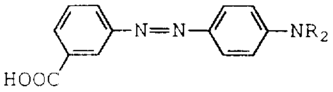
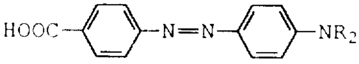
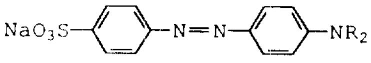
No.	*Yield (%)*	*Formula*
1	91	
2	54	
3	88	
4	82	
5	19	
6	81	
7	83	
8	67	
9	75	
10	90	

TABLE 3
Melting Points and Absorption Maxima (Measured in Acetone, *Measured in Water) of Dyes **1–10**

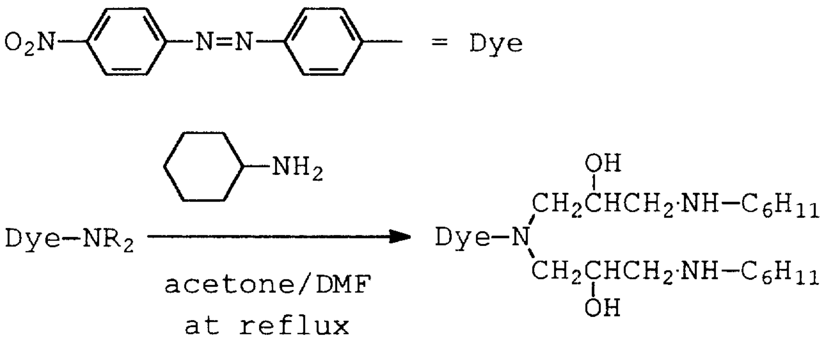
Dyestuff no.	*Color on wool*	*m.p. (°C)*	λ_{max} *(nm)*	ε ($l\ mol^{-1}\ cm^{-1}$)
1	Scarlet	121–122	460	30,561
2	Blue	131–133	575	26,680
3	Yellow	74–75	429	27,897
4	Yellow	>360	426	26,902
5	Blue	117–118	559	26,587
6	Red	102–103	485	30,043
7	Red	127–128	507	33,864
8	Yellow	107–108	412	21,536
9	Orange	158–159	431	23,448
10	Orange	>360	431*	12,480*

TABLE 4
Elemental Analyses of Dyes **1** and **11**

Dye	*Formula*	*Required (%)*			*Found (%)*		
		C	*H*	*N*	*C*	*H*	*N*
1	$C_{18}H_{18}N_4O_4$	60.95	5.08	15.80	61.33	5.13	16.22
11	$C_{30}H_{44}N_6O_4$	65.13	7.96	15.20	65.45	8.17	13.66

dyes **1**–**7** gave uniform dyeing of wool usually with a high rate of dye exhaustion from the dyebath due to the low hydrolysis rate of the epoxy groups. The high wash fastness is relatable to the fixation on the wool by at least two reactive groups. Results of the dyeings are summarized in Table 5.

Four dyes, viz., **2**, **6**, **7** and **8** were promising from the point of view of exhaustion and wet fastness. They were used for the coloration of the wool/polyester blends. The dyeings were uniform and their fastnesses are summarized in Table 6.



(11)

Fig. 4. Reaction of dye (1) with cyclohexylamine.

TABLE 5
Dyeing of Wool with Dyes **1–10** and Fastness Properties (1% Coloration, 1:20 Liquor Ratio)

Dye no.	*Exhaustion from dyebath (%)*	*Wash fastness 40°C*	*Wash fastness 60°C*	*Potting ISO 105/E09*
1	92.5	4–5[a]	4	4
		4–5[b]	2–3	3
		4–5[c]	4	4
2	86.5	4–5	4	4
		4–5	4	4
		4–5	4–5	4–5
3	25.0	4–5	4	4
		4–5	4–5	3
		4–5	4–5	4
4	72.5	4–5	4–5	4–5
		4–5	4–5	3–4
		4–5	4–5	4–5
5	95.0		Degradation of the dye	
6	70.0	4–5	4	4
		4–5	3	3
		4–5	4	4
7	80.0	4–5	4	4
		4–5	3	3
		4–5	4	4
8	73.9	4–5	4–5	4
		4–5	4–5	3
		4–5	4–5	4
9	68.9	4–5	4–5	4–5
		4–5	4–5	2–3
		4–5	4–5	4–5
10	63.7	4–5	4–5	4
		4–5	4–5	3
		4–5	4–5	4

[a] Colour change.
[b] Staining on wool.
[c] Staining on cotton.

The uniformity of the dyeings shows that polyester fibres (when covalent fixation of these dyes cannot be expected) can be conveniently dyed by these dyes in the same way as usual disperse dyes (containing some combination of ethyl, hydroxyethyl or cyanoethyl substituents on the amino group). Furthermore, a good combination of dyes and dyeing conditions was found, giving uniform and wet-stable dyeings by a one-step dyeing process.

Samples of wool dyed with dyes **2**, **4**, **6**, **7** and **8** were exposed to the standard light fastness test and the results are shown in Table 7.

TABLE 6
Dyeing of Mixtures Wool/Polyester (45/55%) with Epoxy Reactive Dyes and Fastness Properties (2% Coloration, 1:20 Liquor Ratio, $T = 100°C$)

Dye no.	*Wash fastness 40°C*	*Wash fastness 60°C*
2	4–5[a] 4–5[b] 4–5[c]	4 4 4–5
6	4–5 4 4–5	4–5 2–3 4
7	4–5 4–5 4–5	4–5 2–3 4–5
8	4–5 4–5 4–5	4–5 4–5 4–5

[a] Colour change.
[b] Staining on wool.
[c] Staining on polyester.

TABLE 7
Light Fastness of Expoxy Reactive Dyes (Wool)

Dye no.	*Light fastness*
2	2
4	3–4
6	3
7	3–4
8	4–5

In comparison with other classes of dyes used for dyeing of wool, the light fastness of the dyes reported here are low, and this will be further investigated in future researches.

CONCLUSIONS

We have prepared epoxy reactive dyes based on *N*,*N*-diglycidylaniline as coupling component. The synthetic procedure, starting from pure components, gave very bright dyes. The dyeings of wool and wool/polyester showed high wash fastness. Light fastness of the dyes needs to be improved in order for such products to have practical application.

ACKNOWLEDGEMENT

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