



A Novel Carboxy-dye Reactive System of Potential Applicability to Wool and Nylon Fibres. Part 1. Studies with Model Amines

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ABSTRACT

Dyes containing carboxylic acid groups have the potential to be reacted with the amino groups of wool and nylon fibres by prior activation with ethyl chloroformate (forming a mixed anhydride). The scope of this reaction has been examined in solution using a range of carboxy dyes with cyclohexylamine or lysine as model amine substrates. The expected amides are formed in good yields, and have been isolated and characterised. A preliminary study of the reactive dyeing of wool and nylon-6.6 indicates that dyeings with high wet fastness can be achieved with this system.

1 INTRODUCTION

Reactive dye systems containing carboxylic acid groups were first developed by Burlington Industries Inc.¹ in 1978 when it was claimed that they could be

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applied to cellulosic fibres successfully at pH 4–6 in the presence of cyanamide, under curing conditions. This reaction was later confirmed and studied for other di-imides.^{2,3}

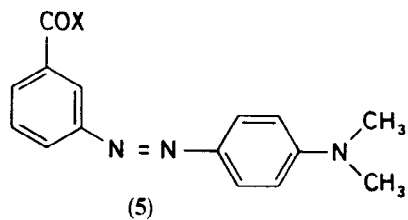
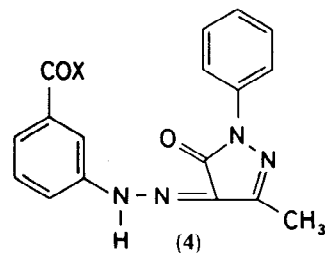
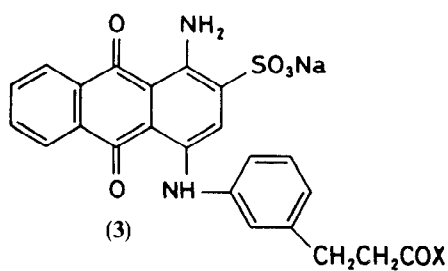
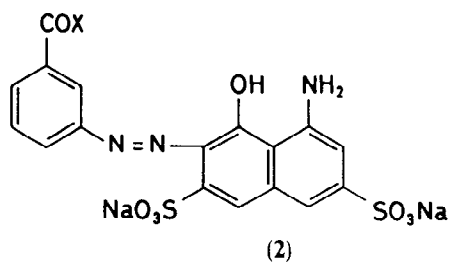
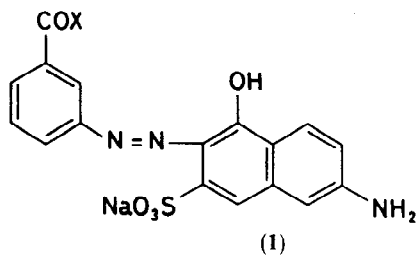
Theoretically these dyes should also react with fibres containing amino groups, such as wool and nylon, with the formation of an amide link. Model experiments⁴ indicate that the cysteine, lysine, histidine, and *N*-terminal residues of wool are the main sites of reaction with reactive dyes.

Previous workers, investigating the fixation of carboxylic acid dyes on wool using dicyclohexylcarbodi-imide (DCCI) as the activating reagent, found difficulty in obtaining acceptable fixation levels due to competing dyebath hydrolysis. In one case hydrolysis was avoided by the use of organic solvents when applying carboxylic acid dyes in the presence of DCCI by exhaustion.⁵ In another case the proportion of water mixed with an organic solvent was progressively lowered and padding/thermofixation was used instead of exhaustion. Both procedures resulted in higher fixation yields.⁶ Di-imides other than DCCI were also tested. The methods used in these two cases would however face many practical problems for commercial application to wool, particularly concerning use of solvent, padding efficiency and thermofixation effect on the wool.

We now report an investigation of another activating reagent which might permit the application of carboxylic dyes to wool and nylon by exhaustion from an aqueous dyebath. In order to establish the most suitable dyes and the optimum conditions for producing the amide link, trial condensation reactions were carried out with model amines representative of the reactive residues of nylon and wool (namely cyclohexylamine and lysine, respectively). The resultant amides were isolated and characterised and the efficiency of the reaction assessed. Preliminary results for the reactions of the dyes with wool and nylon-6.6 fibres are presented.

2 DISCUSSION

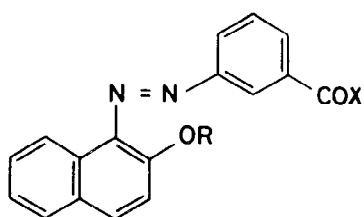
The carboxy dyes **1a–7a** were used in this study. The azo dyes were synthesised by diazotisation of *m*-aminobenzoic acid followed by coupling of the corresponding diazonium salt to the appropriate coupling components (H acid, J acid, β -naphthol, *N*-phenyl-2-methyl-5-pyrazolone and *N,N*-dimethylaniline). The anthraquinone **3a** was obtained by condensing *m*-aminophenylpropanoic acid with bromaminic acid, in aqueous solution in the presence of CuSO₄ and NaHCO₃. The blue dye **7a** was obtained by condensing *m*-aminobenzoic acid with quinizarin in the presence of zinc and boric acid.



(a) X = — OH

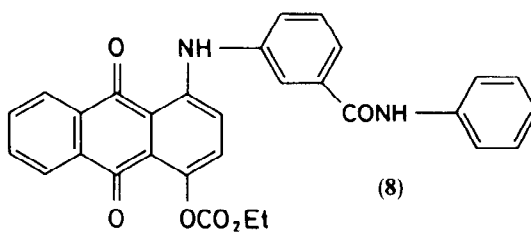
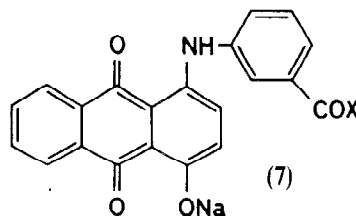
(b) X = — NH —

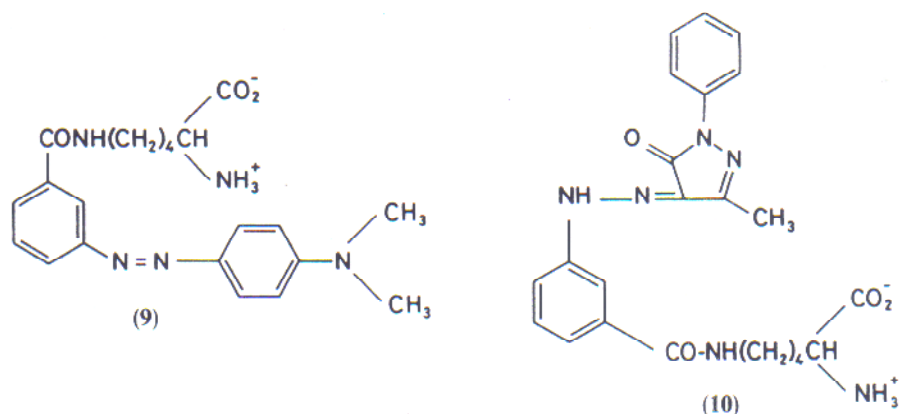
(c) X = — OEt



(6a) R = H, X = OH

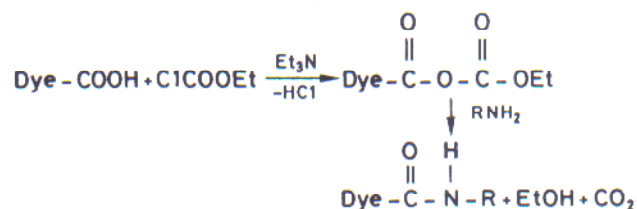
(6b) R = COOEt, X = — NH — Ph





The dyes were purified by salting out, crystallisation from dimethylformamide/acetone, or chromatography, and were obtained in yields ranging from 62 to 90%. They all gave acceptable elemental analyses. The carboxylic acid dyes were then reacted with cyclohexylamine and in the case of **4a** and **5a**, also with lysine, using an activating agent. These amines were chosen to simulate nylon and wool. The corresponding amides **1b–7b** and **8–10** were isolated and identified.

In the first instance dicyclohexylcarbodi-imide was used as the activating reagent for the carboxylic group prior to reaction with the amine. It was found that it was very difficult to obtain pure amides due to contamination of the products with dicyclohexylurea. A mixed anhydride method was then examined, using ethyl chloroformate as the activating reagent.⁷ The dye was dissolved in dimethylformamide (DMF) and was reacted with ethyl chloroformate and triethylamine at low temperature (-5 to -10°C) to form the mixed anhydride (Scheme 1). The amine was then added and the reaction continued at room temperature. In this case, the by-products from the reaction did not cause problems in the isolation of the resultant amides. (The liberated HCl is neutralised with triethylamine and the other products are CO_2 and ethanol.) The amides **1b–7b** and **8** were obtained in yields ranging from 31% to 100% (Table 1) and were characterised after



Scheme 1

TABLE 1
Reaction of Carboxy Dyes with Cyclohexylamine using Ethyl Chloroformate as Activating Agent

Product	Number of equivalents of ClCO_2Et	Yield (%)	Method of purification
1b	3.5	50	Preparative plate, silica. Solvent: <i>n</i> -butanol, <i>n</i> -propanol, ethyl acetate, water (2:4:1:3).
2b	3.5	50	P. plate, cellulose, same solvent.
3b	2.0	100	P. plate, cellulose, same solvent.
4b	1.05	74	Column chromatography, silica, CHCl_3 .
5b	3.0	42	Column chromatography, silica, CHCl_3 .
5c	3.0	17	Column chromatography, silica, CHCl_3 .
6b	3.0	31	Column chromatography, silica, CHCl_3 .
7b	2.1	32	Preparative plate, silica, ether.
8		36	Preparative plate, silica, ether.

purification by chromatography. In the reaction with **5a**, the ethyl ester **5c** was produced in addition to the amide **5b**.

The amides **6** and **8** were carbonates, as shown by IR and NMR spectroscopy. Compound **8** was obtained simultaneously with the amide **7b**. All the amides (**1-6**, **8**) and the ester (**5c**) gave acceptable analytical data and showed the expected carbonyl absorption in the IR (Table 2a).

It was also possible to obtain melting points and $^1\text{H-NMR}$ data (Table 2b) for the products **4-8**.

To examine an amine model more closely resembling the structure of wool, the amino acid lysine was used. Lysine was first reacted with the Cu(II) ion, which complexed the α -amino and carboxylic groups.⁵ The ϵ -amino group of the protected amino-acid was then allowed to react with the activated dyes⁷ and finally the copper was removed⁹ by using ethylenediamine tetra-acetic acid (EDTA), thus giving the amides **9** and **10** (Scheme 2), which were characterised by IR and elemental analysis.

3 A PRELIMINARY STUDY OF THE REACTIVE DYEING OF WOOL AND NYLON

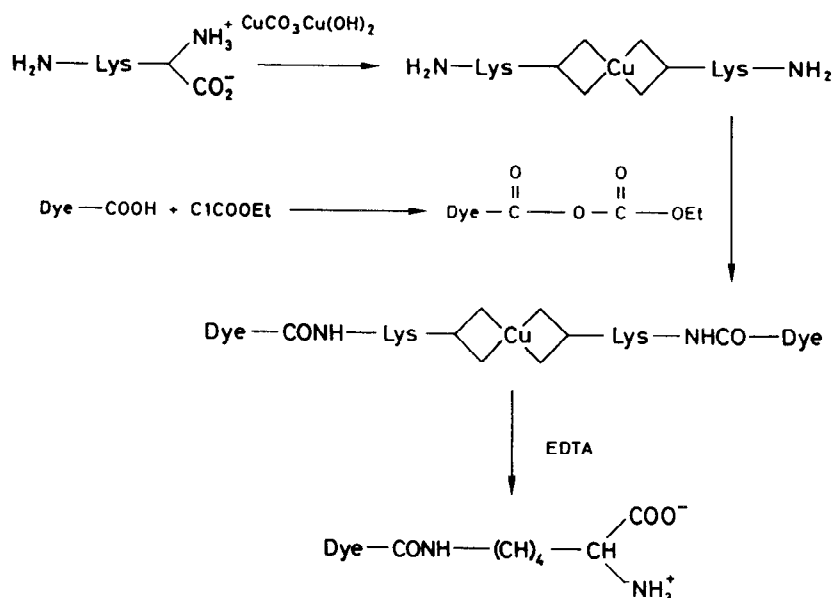
Having succeeded so far with the model compounds, it was decided to use this method of activation of carboxylic groups as a means of reactive dyeing wool and nylon-6.6. The carboxy dyes **4a-6a** and **7** were treated with ethyl chloroformate as described and in their activated form were used to dye wool and nylon.

TABLE 2
(a) Characterisation Data for *N*-Cyclohexylamide Dyes 1b–7b, 8 and Ester 5c

Compound	Elemental analysis (%)		Infrared (C=O) absorption (ν cm^{-1})
	Theory	Found	
1b	C(56.32), H(4.69), N(11.42) $\text{C}_{23}\text{H}_{23}\text{N}_4\text{O}_5\text{SNa}$	C(55.7), H(5.15), N(11.05)	1 635
2b	C(41.6), H(4.52), N(8.43) $\text{C}_{23}\text{H}_{23}\text{ClN}_4\text{O}_8\text{S}_2\text{Na}_2, 2\text{H}_2\text{O}$	C(41.5), H(4.1), N(8.43)	1 635
3b	C(56.68), H(5.37), N(6.84) $\text{C}_{29}\text{H}_{28}\text{N}_3\text{O}_6\text{SNa}_2, 2.5\text{H}_2\text{O}$	C(56.7), H(5.4), N(6.3)	1 640
4b	C(68.48), H(6.2), N(17.36) $\text{C}_{23}\text{H}_{25}\text{N}_5\text{O}_2$	C(67.8), H(6.35), N(16.45)	1 632
5b	C(72.0), H(7.42), N(16.0) $\text{C}_{21}\text{H}_{26}\text{N}_4\text{O}$	C(71.8), H(7.55), N(15.75)	1 630
5c	C(68.68), H(6.39), N(14.14) $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_2$	C(67.55), H(6.30), N(13.75)	1 723
6b	C(70.11), H(6.07), N(9.44) $\text{C}_{26}\text{H}_{27}\text{N}_3\text{O}_4$	C(69.35), H(6.15), N(9.3)	1 755 1 630
7b	C(70.12), H(4.97), N(6.06) $\text{C}_{27}\text{H}_{23}\text{N}_2\text{O}_4\text{Na}$	C(69.35), H(5.40), N(5.80)	1 620
8	C(70.30), H(5.47), N(5.47) $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_6$	C(69.65), H(5.60), N(5.55)	1 625 1 670 1 755

(b) NMR Data for Dyes 4b–7b, 5c and 8

Compound	$^1\text{H-NMR}$
4b	δ (60 MHz, CdCl_2) 0.5–2 (11H, m, cyclohexylamine), 2.3 (3H, s, CH_3), 6.4–8.15 (10H, m, Ar–H)
5b	δ (60 MHz, CDCl_3) 0.75–2.20 (11H, m, cyclohexylamine), 3.0 (6H, s, NMe_2), 6.1 (1H, broad s, NH), 6.75 (2H, d, $J = 8$ Hz, $2 \times \text{H}$ <i>ortho</i> to NMe_2), 7.15–8.14 (6H, m, 2,4,5,6-H and $2 \times \text{H}$ <i>meta</i> to NMe_2)
5c	δ (60 MHz, CDCl_3) 1.35 (3H, t, $J = 7$ Hz, OCH_2CH_3) 3.02 (6H, s, NMe_2), 4.35 (2H, q, $J = 7$ Hz, OCH_2CH_3), 6.67 (2H, d, $J = 8$ Hz, $2 \times \text{H}$ <i>ortho</i> to NMe_2), 7.15–8.15 (6H, m, 4,5,6-H and $2 \times \text{H}$ <i>meta</i> to NMe_2), 8.43 (1H, t, $J = 1.5$ Hz, 2-H)
6b	δ (60 MHz, d_6 -DMF) 0.90–2.20 (11H, m, cyclohexylamine), 1.38 (3H, t, $J = 7$ Hz, OCH_2CH_3), 4.33 (2H, q, $J = 7$ Hz, OCH_2CH_3), 6.20–7.10 (1H, broad s, NH), 7.45–8.90 (10H, m, Ar–H)
7b	δ (60 MHz, CDCl_3) 1.0–2.20 (11H, m, cyclohexylamine), 5.8–6.1 (1H, broad s, NH), 6.9–8.4 (11H, m, NH and Ar–H)
8	δ (60 MHz, CDCl_3) 1.0–2.2 (14H, m, cyclohexylamine and OCH_2CH_3), 3.8–4.2 (1H, broad s, NH), 4.2–4.7 (2H, q, $J = 7$ Hz, OCH_2CH_3), 7.1–8.5 (11H, m, NH and Ar–H)



Scheme 2

The dyes were activated in DMF as described, for 20 min, and the triethylamine hydrochloride was then filtered off. The DMF solution was added to water (150 ml) with stirring and, after adding the fibre, the mixture was boiled for 30 min. The fibre was removed, washed, boiled for 15 min with soap and water and then submitted to the ISO 105 CO3 test. The results of the test for the four dyes are shown in Table 3, and it can be seen that fastness properties are far superior to those expected for conventional acid dyeing with the carboxy dyes, indicating significant fixation of the chromophore to the fibre.

TABLE 3
Wash Fastness of Reactive Fibres Dyed with Carboxy Dyes 4a-7a

Carboxy dye	Colour	Change in shade	
		Wool	Nylon-6.6
		With activation	With activation
4a	Yellow	4	4-5
5a	Yellow	4	4-5
6a	Orange	3-4	4-5
7a	Blue	3	4

4 EXPERIMENTAL

4.1 General procedure for the reaction of dyes with cyclohexylamine

The dye was dissolved in dimethylformamide (DMF), the temperature was maintained at -5 to -10°C (external cooling with ice in methanol), and triethylamine and then ethyl chloroformate in equimolar amounts were added. The cold mixture was stirred until most of the dye had reacted (monitored by TLC) (typically about 15 min). Cyclohexylamine was added and the mixture was stirred at room temperature overnight. Triethylamine hydrochloride was filtered off and the solution was evaporated to dryness under reduced pressure. The resulting mixture was then purified by column or preparative thin-layer chromatography on silica or cellulose.

4.2 Procedure for the reaction with lysine

4.2.1 Preparation of lysine-copper complex

To a solution of DL-lysine monohydrochloride (1.8 g, 10 mmol) in water (100 ml), cupric carbonate (basic, 3 g) was added slowly. After boiling for 2 h, the undissolved cupric carbonate was removed from the hot mixture by filtration and washed with hot water (10 ml). The filtrate and washings were combined and treated with acetone until a precipitate formed. The liquor was allowed to stand for 3 h, filtered, and the residue dried, giving the complex as a blue powder (2.1 g, 60%).

4.2.2 Synthesis of the amide dye-lysine **9**

The dye (0.5 g, 1.9 mmol) was dissolved in a mixture of dimethylformamide (100 ml) and triethylamine (0.77 ml, 5.6 mmol), and to this was added ethyl chloroformate (0.53 g, 4.9 mmol) maintaining a temperature of -5 to -10°C . After stirring for 20 min, a solution of the lysine-copper complex (0.33 g, 1.9 mmol) in water (3 ml) was added. The mixture was stirred at room temperature overnight and the yellow product (0.8 g, 52%) was filtered off and dried.

Removal of copper. The solid **9** (0.8 g) was dissolved in 2M-HCl (45 ml), and an aqueous solution of ethylenediamine tetra-acetic acid (0.1M, 20 ml) was added. The mixture was stirred for 1 h and an aqueous solution of NaOH (2M) was added. The resultant precipitate was filtered off, washed with water and ethanol, and dried. The product was dissolved in 2M-HCl and reprecipitated with 2M-NaOH. It was filtered off, washed with water and ethanol and dried to give the amide **9** as a yellow solid (0.18 g, 25%), m.p. $208-210^{\circ}\text{C}$; ν_{max} (KBr disc) 3300, 1638, 1600 cm^{-1} . Found: C, 60.9; H, 6.7; N, 16.65. $\text{C}_{21}\text{H}_{27}\text{N}_5\text{O}_3 \cdot \text{H}_2\text{O}$ requires C, 60.72; H, 6.99; N, 16.87%.

4.2.3 Synthesis of the amide dye-lysine **10**

The dye (0.6 g, 1.7 mmol) was dissolved in a mixture of DMF (150 ml) and triethylamine (0.28 ml, 2.0 mmol) and to this was added ethyl chloroformate (0.2 ml, 2.0 mmol) while keeping the mixture at a temperature of -5°C . After stirring for 10 min, a solution of the lysine-copper complex (0.3 g, 0.85 mmol) in cold water (40 ml) was added. The mixture was stirred at room temperature overnight and the yellow solid was filtered off, washed with water and ethanol, and dried.

Removal of copper. The crude solid was dissolved in 0.1 M-EDTA (50 ml) when a yellow product precipitated on cooling. This was filtered off and washed with water and ethanol and dried (0.48 g, 62%). Part of the solid (0.2 g) was dissolved in DMF with a few drops of 6 M-HCl. A 4 M solution of NaOH was added until a precipitate formed. The yellow solid was filtered off, washed with water and ethanol and dried to give the amide **10** (0.18 g, scaled up yield 56%) m.p. $223-224^{\circ}\text{C}$; ν_{max} (KBr disc) 3400, 1638 cm^{-1} . Found: C, 59.35; H, 5.7; N, 18.1%. $\text{C}_{23}\text{H}_{26}\text{N}_6\text{O}_4 \cdot \text{H}_2\text{O}$ requires C, 58.97; H, 5.98; N, 17.94%.

5 CONCLUSIONS

It has been shown that carboxylic acid dyes can be reactively dyed on wool and nylon-6.6 using ethyl chloroformate as activating agent. Reaction of the dyes with the model amines cyclohexylamine and lysine confirms that amide formation can occur via reaction with the free amino groups in the polymers, thus giving covalent linkage of the dye to the polymer. These bonds would be sufficiently strong to withstand the alkaline conditions used in the ISO 105 CO3 test, as indeed was the case.

Dyes with no sulphonic acid groups gave the best results, which suggests that the preferred carboxy dyes would not have too great an affinity for wool and nylon-6.6, which would imply that better levelness and less uneven dyeings could be achieved.

The low pH necessary for fixation is also an advantage since it means that there is less wool damage.

It is noteworthy that the dyes containing sulphonic groups (i.e. **1a-3a**) did not fix on wool and nylon-6.6, even though they formed amides with cyclohexylamine. The possibility of extending this reactive system to the practical reactive dyeing of polyamide fibres is the subject of further study, and will be reported in a future publication.