Dyes and Pigments **19** (1992) 223–232

Addition of Reactive Compounds to the Dyebath of Non-Reactive Dyes
Part VI: Mechanism of Fixation of Direct Blue 2 by Cyanuric Chloride on Cotton and Precationized Cotton

B. M. Youssef, M. M. Kamel & M. Kamel

Textile Research Division, National Research Centre, Dokki, Cairo, Egypt

(Received 10 February 1992; accepted 27 March 1992)

ABSTRACT

A simple procedure for the formation and fixation of a reactive dye, having a high-affinity skeleton, within the interstices of cotton fibres is described. It involves dyeing cotton with Direct Blue 2, followed by treating the dyed fibre with cyanuric chloride and finally reacting the dichlorotriazinyl–dye, presumably formed in situ, *with the neighbouring cellulosic chains. Factors affecting dye fixation and the mechanisms involved are studied.*

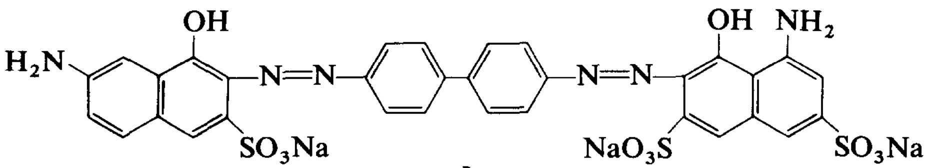
INTRODUCTION

This paper is a continuation of a series that commenced in 1991 (Refs 1–3 and Kamel *et al.*, unpublished work).

It has been previously reported[4] that, although it would be possible, in principle, to produce reactive dyes of increased affinity by using a direct-cotton-dye type of structure, this would not be a practical proposition because it would be unlikely that 100% of the dye would be fixed and the part that was not fixed (hydrolysed dye) would impair the wet-fastness properties of the reactive dye. For this reason, the tendency in the development of reactive dyes has always been to use dye structures of relatively low affinity so that removal of hydrolysed dye is facilitated. In addition, low-affinity dyes have high rates of diffusion and therefore very attractive levelling and penetration properties.

On the basis of these considerations, it appeared to us that it might be possible to avoid the above problems if the cotton was initially dyed with a direct dye possessing a suitable chemical structure, followed by its conversion, within the interstices of the fibre, into a reactive dye, and subsequent fixation of the latter onto the neighbouring cellulosic chains. From a practical point of view, the two latter steps, namely conversion into the reactive-dye form and its fixation, can be implemented in one aftertreatment process.

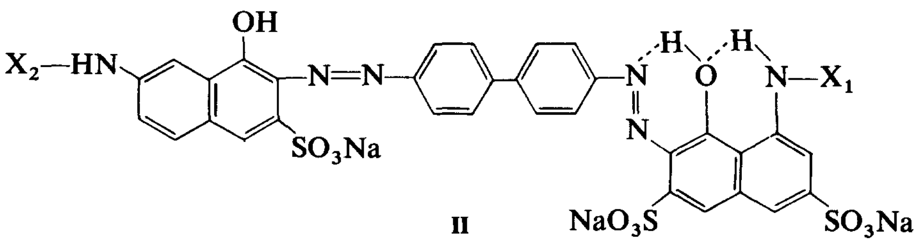
To study the feasibility of this idea, we selected Direct Blue 2 (**I**) as a model dye. The choice of this dye was based on previous results, which indicated that it reacts with cyanuric chloride and with 2,4-dichloro-6-(*p*-sulphoanilino)-triazine to give high degrees of reactive fixation on cotton.[1,2]



I

Direct Blue 2 [C.I. 22590]

The mechanism of fixation of this dye within cellulose can be visualized to proceed as follows: (*a*) **I**, which has two amino groups, would react with cyanuric chloride, under the experimental conditions described, to yield one of the three reactive-dye species **IIa**, **b** or **c**, or, more probably, mixtures of the three; (*b*) the reactive-dye species so formed would react, after alkaline treatment, with cellulose.



II

IIa: X_1 = –dichlorotriazinyl, X_2 = H
b: X_1 = H, X_2 = –dichlorotrizinyl
c; X_1 = X_2 = –dichlorotriazinyl.

The high degree of reactive fixation obtained would suggest the formation of species **IIa** or **IIc**, or both, in good yields. Both species, which contain the H–acid–dichlorotrizinyl moiety, would be expected to be highly reactive, like other similarly constituted dyes.[5,6]

Factors affecting reactive-dye fixation by this aftertreatment procedure were studied to determine the optimal conditions for its application.

Furthermore, it appeared that a pretreatment with a commercial cotton cationizing agent, e.g. Sandene 8425, might enhance colour strength, since, in addition to reactive fixation, any residual direct dye or hydrolysed reactive dye would be bound to this reagent. Accordingly, a series of experiments involving the use of this substance was also undertaken.

Colour strength was assessed before and after treatment with cyanuric chloride. Reactive-dye fixation was evaluated after boiling with 50% aqueous dimethylformamide. Washing fastness was evaluated at 90°C by using a standard procedure.[7]

EXPERIMENTAL

1. Materials

1.1 Cotton fabric

Cotton fabric, mill-scoured and bleached (140 g m^{-2}), was kindly supplied by El-Beida Dyers Co., Kafr El-Dawar, Egypt. The fabric was further treated with a solution containing 5 g $liter^{-1}$ sodium carbonate and 3 g $liter^{-1}$ soap at the boil for 4 h and was then thoroughly washed and air-dried.

1.2 Dyes and reagents

Commercial Direct Blue 2 (I) was used. This was supplied by Ismadye Co., Egypt. Sandene 8425 liquid,[8] which is an aliphatic polyamine for the cationization of cellulosic fibres, was used. This product was supplied by Sandoz.

1.3 Cationization of cotton

Cotton fabric was wetted into a neutral bath at 30°C (liquor ratio 20:1) for 5 min with stirring. Sandene 8425 liquid (4% w.o.f) was then added, and the bath was stirred for 10 min. The temperature was raised to 70°C over 25 min and sodium carbonate (2 g/liter) added to bring the pH to about 9·5–10. The treatment was undertaken for 20 min; the bath was then cooled and drained, and the fabric was rinsed and dried at 100°C for 3 min.

2. Methods of application

2.1 Dyeing of cotton and cationized cotton

Direct Blue 2 (0·25–4%) (w.o.f) was pasted with cold water. Sufficient boiling water was added with constant stirring to bring it into solution. Sodium chloride (10% w.o.f) was then added to the liquor. The cotton fabric or pre-cationized cotton fabric, or both, were introduced into the dyebath (liquor

TABLE 1
Effect of Varying Concentration of Cyanuric Chloride at a Constant Depth of Shade of Dye I (2%) on the Colour Strength and Washing Fastness of Dyed Cotton Fabric (A) and Cationized Cotton (B)

Percentage of cyanuric chloride in aftertreatment bath	*Colour strength (K/S)*			*% Fixation*			*Washing fastness at 90°C*		
	Before wash	*After wash*	*After DMF*	*a*	*b*	*c*	*Alt.*	*St.^{c}*	*St.^{w}*
			Dyed fabrics (A)						
0	10·13	4·66	0·932	46·00	9·20	20·00	4	1–2	2
1	9·44	5·90	4·48	62·50	47·45	75·93	4–5	3	4–5
2	9·44	6·63	4·99	70·23	52·86	75·26	4–5	3	4–5
3	9·44	7·36	5·70	77·96	60·38	77·44	4–5	3	4–5
4	9·44	7·65	5·89	81·03	62·39	77·99	4–5	3	4–5
8	9·44	7·65	5·89	81·03	62·39	77·99	4–5	4	4–5
			Dyed fabrics (B)						
0	14·17	11·48	7·80	81·01	55·04	67·94	4	1	2
1	14·17	11·64	10·39	82·14	73·32	89·26	4	2	4
2	15·14	12·53	11·52	82·76	76·08	91·93	4	2	4–5
3	15·14	12·53	11·52	82·76	76·08	91·93	4	2	4–5
4	15·14	12·53	11·52	82·76	76·08	91·93	4	2	4–5
8	15·14	12·53	11·52	82·76	76·08	91·93	4	2–3	4–5

Aftertreatment with cyanuric chloride for 1 h at room temperature and pH 6·5.
a = % fixation after soap with respect to before-soap value.
b = % fixation after DMF with respect to before-soap value.
c = % fixation after DMF with respect to after-soap value.
Alt. = alteration, St.^{c} = staining on cotton, St.^{w} = staining on wool.

ratio 1:50) at 40–50°C. The temperature of the bath was raised to boiling over a period of 30–40 min, after which dyeing was continued for 1 h.

2.2 Dye fixation with cyanuric chloride

The dyed fabrics were placed in a bath containing a suspension of cyanuric chloride in the presence of 1% surfactant (sodium lignin sulphonate). The pH, time and temperature of the aftertreatment were varied as described in the tables. The dyed fabrics were then placed in another bath containing 10% sodium carbonate and kept for 60 min at 40°C. They were washed with a non-ionic detergent (3 g/liter at 90°C for 30 min), and samples were finally extracted with 50% DMF at 90°C for 15 min.

3. Colour strength

The treated fabric samples were evaluated for colour strength, expressed as *K/S*, before and after washing and after extraction with 50% DMF, a

Perkin–Elmer Lambda 38 UV/VIS spectrophotometer being used. The K/S values were calculated from the reflectance measurements by using the Kubelka–Munk equation:[9]

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_0)^2}{2R_0}$$

where R = decimal fraction of the reflectance of the dyed fabric;
R_0 = decimal fraction of the reflectance of the undyed fabric;
K = absorption coefficient; and
S = scatting coefficient.

Evaluation of washing fastness for soaped samples was performed according to the standard method:[7]

$$\%\ \text{Fixation}\ a = \frac{K/S\ \text{after soap}}{K/S\ \text{before soap}} \times 100$$

$$\%\ \text{Fixation}\ b = \frac{K/S\ \text{after DMF}}{K/S\ \text{before soap}} \times 100$$

$$\%\ \text{Fixation}\ c = \frac{K/S\ \text{after DMF}}{K/S\ \text{after soap}} \times 100$$

(See Table 1 for the meaning of *a*, *b* and *c* in the above equations.)

RESULTS AND DISCUSSION

The present investigation has several objectives: (*a*) to study whether it would be possible to convert a dye with a high-affinity skeleton, located within the interstices of the fibres, into a reactive dye by aftertreatment with cyanuric chloride, and to determine to what extent this conversion could be effected; (*b*) to study the optimal conditions under which the conversion could be achieved; (*c*) to investigate the improvements (if any) in colour strength and washing-fastness properties after wet treatments.

Preliminary experiments showed that an aftertreatment of the dyeings of **I** with a suspension of cyanuric chloride in the presence of 1% surfactant, followed by fixation with sodium carbonate, gave higher colour-strength values than the untreated samples after washing. Accordingly, we proceeded to study the effect of different parameters on this process as follows.

(a) Effect of concentration of cyanuric chloride in the aftertreatment bath

The following observations can be made from the results in Table 1.

(i) The colour-strength values after soaping and dimethylformamide extraction usually increase with increase of concentration of cyanuric chloride up to a certain value and then tend to stabilize.

(ii) In all cases, cationized cotton samples give higher *K/S* values and percentage fixation than non-cationized ones under identical conditions.

(iii) The values for staining on cotton are somewhat better for non-cationized cotton treated with cyanuric chloride than for cationized cotton. The values for change in shade and staining on wool are, however, excellent in both cases. The lower values for staining on the cationized cotton can be attributed to the higher depth of shade obtained as compared with the non-cationized samples.

(iv) An increase in the concentration of cyanuric chloride to 8% causes an increase of one point in staining rating.

(b) Effect of depth of shade

A study of this parameter was undertaken by using fabrics dyed in different bath concentrations (to obtain different depth of shades) followed by an aftertreatment with the same concentration of cyanuric chloride (Table 2).

TABLE 2
Colour Strength and Washing Fastness at 90°C of Dyeings with Different Shade Depths and Aftertreatment with Cyanuric Chloride (2%)[a]

Percentage dyebath concentration	*Colour strength (K/S)*			*% Fixation*			*Washing fastness at 90°C*		
	Before wash	*After wash*	*After DMF*	*a*	*b*	*c*	*Alt.*	*St.*[c]	*St.*[w]
			Dyed fabrics (A)						
0·25	2·64	1·87	0·93	70·75	35·07	49·57	4	3	4–5
0·50	4·60	2·91	1·80	63·26	39·02	61·68	4	3	4–5
1·00	7·10	5·14	3·56	72·39	50·14	69·26	4	3	4–5
2·00	9·44	7·10	4·99	75·21	52·86	70·28	4–5	3	4–5
3·00	11·25	8·46	6·39	75·20	56·80	75·53	4–5	3	4–5
4·00	12·91	10·39	8·12	80·48	62·89	78·15	4–5	3	4–5
			Dyed fabrics (B)						
0·25	4·79	3·81	2·72	79·54	56·78	71·39	4	3	4–5
0·50	6·84	6·18	4·48	90·35	65·49	72·49	4	2–3	4–5
1·00	11·52	10·93	7·96	94·87	69·09	72·82	4	2	4–5
2·00	15·14	12·53	11·52	82·76	76·08	91·93	4	2	4–5
3·00	15·14	14·17	11·52	93·59	76·08	81·29	4	2	4
4·00	15·14	15·14	12·53	100·00	82·76	82·76	4	2	4

[a] See footnotes to Table 1 for explanation of symbols used.

TABLE 3
Effect of Temperature on the Colour Strength of the Dyed Non-Cationized (A) and Cationized Cotton (B)

Temperature (°C)	*Colour strength (K/S)*					
	A			*B*		
	Before wash	*After wash*	*After DMF*	*Before wash*	*After wash*	*After DMF*
10	9·02	5·70	2·54	14·64	11·22	9·23
20	10·39	5·98	3·68	15·14	12·91	9·66
30	10·39	7·10	4·99	14·64	13·72	11·52
40	9·23	6·73	4·00	14·64	12·91	11·22

2% of dye **I** and aftertreatment with 2% cyanuric chloride as in Table 1.

The *K/S* values shown in Table 2 indicate that, for both non-cationized and cationized cotton samples, these values increase progressively with an increase in colour depth. As expected, however, cationized cotton always gives higher *K/S* values than non-cationized. The staining on cotton is also better in the case of non-cationized cotton samples.

(c) Effect of temperature of the cyanuric chloride aftertreatment bath

This effect is demonstrated in Table 3.

The data in this table seem to indicate that a temperature of 30°C gives the highest results of reactive fixation in both non-cationized and cationized samples.

TABLE 4
Effect of pH on Colour Strength of Non-Cationized Cotton (A) and Cationized Cotton (B)

pH	*Colour strength (K/S)*					
	A			*B*		
	Before wash	*After wash*	*After DMF*	*Before wash*	*After wash*	*After DMF*
4	10·65	5·37	5·29	13·30	12·91	10·65
5	10·39	6·39	5·21	13·30	13·30	10·39
6	10·39	6·61	5·37	13·72	12·91	10·13
7	9·23	6·18	5·21	13·72	12·53	10·65
8	8·64	6·18	5·21	13·30	12·18	10·39

2% of dye **I** and aftertreatment with 2% cyanuric chloride as in Table 1.

TABLE 5
Effect of Reaction Time on Colour Strength of Non-Cationized Cotton (A) and Cationized Cotton (B)

Time (min)	*Colour strength (K/S)*					
	A			*B*		
	Before wash	*After wash*	*After DMF*	*Before wash*	*After wash*	*After DMF*
10	10·65	6·18	3·60	13·30	11·84	8·83
20	9·44	6·73	4·54	14·64	11·84	10·13
30	9·44	7·36	4·66	14·64	11·84	10·65
45	9·44	7·36	5·14	14·64	11·84	10·65
60	9·44	8·12	5·89	15·14	12·18	10·93

2% of dye **I** and aftertreatment with 2% cyanuric chloride as in Table 1.

(d) Effect of pH of the aftertreatment bath on reactive fixation

Table 4 indicates the extent of this effect.

As expected in the case of cotton, values near or at neutral give the best reactive-fixation values. However, the variation in colour-strength values between pH 4 and pH 8 seems to be minimal. On the other hand, acid pH values seem slightly to favour reactive fixation in the case of cationized cotton. This increase can, however, be explained by the increase in dye uptake, by ion–ion interaction, onto Sandene treated fabric.

(e) Time of aftertreatment with cyanuric chloride

An aftertreatment of 60 min with cyanuric chloride seemed to give optimal results in both cases, as can be seen from Table 5.

SUMMARY AND CONCLUSIONS

(i) A procedure is described that endeavours to avoid the problems known to be associated with the use of direct dyes in the preparation of reactive dyes, such as a low rate of diffusion and impaired wet-fastness properties, due to the high affinity of hydrolysed and unreacted dye. It involves dyeing cotton and precationized cotton with a direct-dye base, followed by an aftertreatment of the dyeings obtained with cyanuric chloride and finally with sodium carbonate. It was found that, although cyanuric chloride has very little affinity to cellulose, this reagent diffuses into the interstices of the fibres, to react with the direct-dye base located within.

(ii) The conversion and subsequent fixation of the direct-dye base on the fibre depend upon many factors, including: (*a*) the physical form of the cyanuric chloride suspensions, (*b*) the concentration of this reagent and the depth of shade of the dyeing, (*c*) the temperature and pH of the aftertreatment bath, and (*d*) the time of aftertreatment.

(iii) In the majority of cases, dyeings aftertreated with cyanuric chloride followed by alkali fixation give higher *K*/*S* values than those not subjected to this treatment.

(iv) Values of *K*/*S* on cationized cotton (Sandene 8425 liquid) are always higher than those on ordinary cotton under identical conditions. This is undoubtedly partly due to the cationic charge on the surface of cotton fibre imparted by this reagent.

(v) The wet-fastness properties of dyeings on ordinary and cationized cotton are greatly improved, especially when high concentrations of cyanuric chloride are used. The staining caused by the dyed samples treated with Sandene is always at least one rating point less than that for untreated cotton. This may be attributed to the higher concentration of the direct-dye base on the former samples, which is due to ion–ion interaction.

(vi) Treatment of dyeings of **I** on cotton with cyanuric chloride and sodium carbonate renders them more resistant (fast) to removal by the soaping process. Two types of dye species seem to cause this enhanced fastness, namely reactive and non-reactive (unreacted and/or hydrolysed reactive), as can be seen when comparing *K*/*S* values after washing with those after DMF.

(vii) In the case of cationized cotton, several mechanisms of dye interaction with the fibre may be suggested, namely: (*a*) the formation of covalent bonds between cellulose/Sandene and dye, (*b*) the formation of a chemical bond between the reactive dye formed and cellulose, and (*c*) ion–ion interaction of hydrolysed dye molecules on the cationic-positive centres.

In conclusion, it is possible to obtain dyeings of a direct dye with high affinity to cotton fibres and with improved wet-fastness properties by aftertreatment with cyanuric chloride and subsequent alkaline fixation.

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