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Studies on the Addition of Reactive Compounds to the Dyebath of Non-reactive Dyes: Part I. Improvement of the Colour Strength of Fabrics Dyed with Direct Dyes

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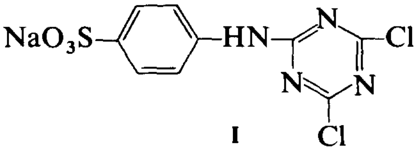
ABSTRACT

*Addition of the reactive compound 2,4-dichloro-6-(4-sulphoanilino)-*s-*triazine to dyebath solutions of several direct dyes under specified conditions generally leads to an increase in colour strength of dyed fabrics even after several washings. This increment depends, however, on the structure of dyestuff used.*

Direct Blue 2 (C.I. 22590) seems to be most suited for this procedure. Factors affecting the colour strength of the latter dye under different conditions were investigated.

1 INTRODUCTION

Although 2,4,6-trichloro-*s*-triazine (cyanuric chloride), and other reactive compounds, or their derivatives, have been used extensively for the preparation of fibre-reactive dyes,[1] no previous attempts seem to have been undertaken to study the effect of adding simple water-soluble reactive compounds to dyebaths of non-reactive dyes. In the present paper we are reporting on the results of adding 2,4-dichloro-6-(4-sulphoanilino)-*s*-triazine (I) to the dyebath of some direct dyes with an objective of improving colour strength and wet-fastness properties if possible.



I

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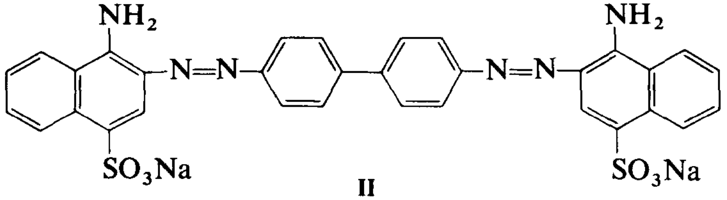
The direct dyes used (**II**–**IX**) contain amino, hydroxy or imino groups or combinations of these as follows.

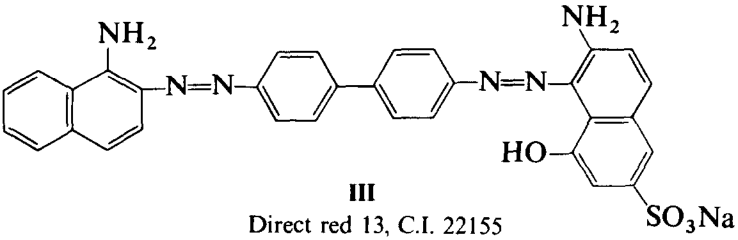
Dyestuff containing amino groups:



II

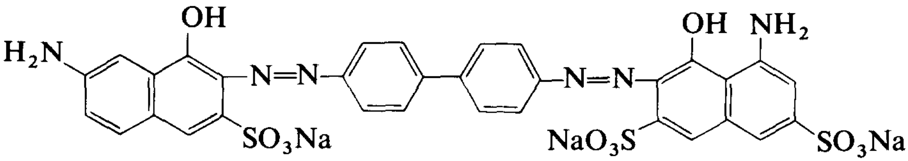
Direct red 28, C.I. 22120

Dyestuffs containing amino and hydroxy groups:



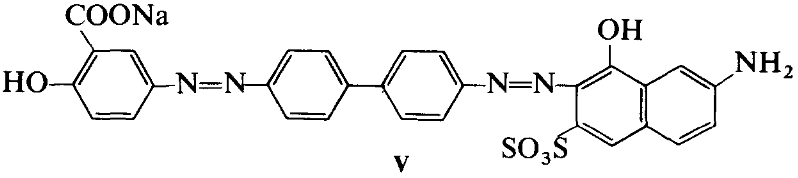
III

Direct red 13, C.I. 22155



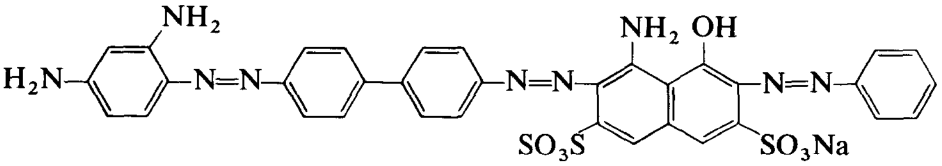
IV

Direct blue 2, C.I. 22590



V

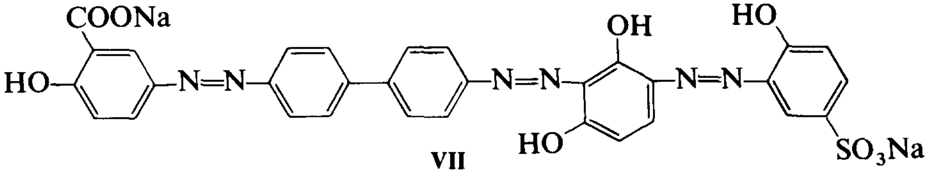
Direct brown 95, C.I. 30145



VI

Direct black 38, C.I. 30235

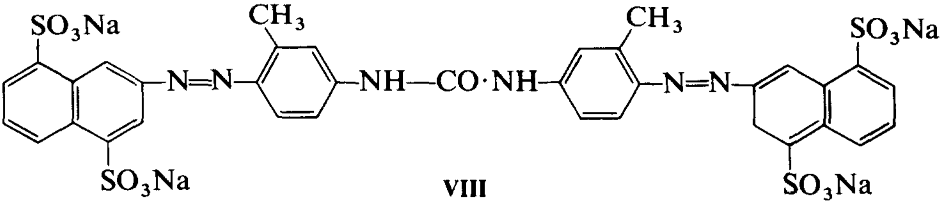
Dyestuff containing hydroxy groups:



VII

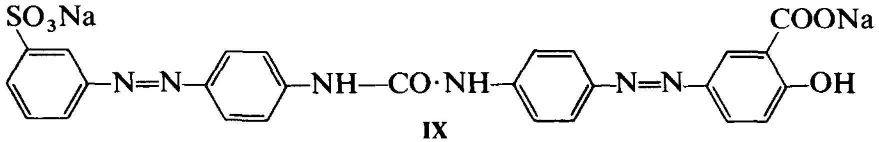
Direct brown 2, C.I. 22311

Dyestuffs containing imino groups:



VIII

Direct yellow 50, C.I. 29025



IX

Direct yellow 44, C.I. 29000

It is known that the stepwise replacement of halogen is clearly exhibited by cyanuric chloride.[2] Substituents such as amino and substituted amino powerfully deactivate the residual chlorine atoms after the first has been replaced by them, and other groups such as alkoxy or aryloxy cause a lower degree of deactivation.

With dyes containing amino groups, very little difficulty occurs in realizing the stepwise replacement of chlorine, and it is known that replacement of the first chlorine in (for example) compound **I** takes place at *c.* 40–50°C, whilst the second chlorine is substituted above 80°C.

Based on these considerations, compound **I** was added to solutions of dyes **II**–**IX**, to effect substitution of one chlorine atom (if possible) by a dye residue, then the conditions of the bath were adjusted to promote reaction of the second chlorine atom with the celluosic fibre.

The colour strength of fabrics dried, soaped and treated with a 50% aqueous solution of DMF was evaluated using the Kubelka–Munk equation.[3] Colour strength values after treatment with DMF were taken as an indicator of the reaction of the dye formed in solution with the fibre.

Other fastness properties were evaluated using standard procedures.

2 EXPERIMENTAL

2.1 Materials

2.1.1 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 litre^{-1} sodium carbonate and 3 g litre^{-1} soap at the boil for 4 h, then thoroughly washed and air-dried.

*2.1.2 Dyestuffs **II–IX***

Commercial direct dyes were used; these were kindly supplied by Ciba–Geigy Co.

*2.1.3 2,4-Dichloro-6-(4-sulphanilino)-*s*-triazine (**I**)*

Compound **I** was prepared according to the procedure of Fierz-David *et al.*[4]

2.2 Methods of application

2.2.1 General exhaustion method

Weights of the reactive compound **I** corresponding to different molar ratios relative to the weights of dyes in solution were added, liquor ratio 1:100, at 50°C, and allowed to stand for 30 min at pH 5·5–9. The fabric was then entered into the dye bath and left for 15–60 min. The temperature was then gradually raised to 90°C and the pH adjusted to 11 and dyeing was continued for another 15–60 min. Finally the fabric was rinsed and air-dried.

2.2.2 Pad–dry–cure method

The padding liquor was prepared by adding the different weights of reactive compound **I** to the dye solution at 50°C and pH 7·5 and allowed to stand for 30 min, then the pH of the solution was raised to 11. The fabric was then padded with this solution and dried at 55°C for 7 min, then baked at 160°C for 3 min.

2.2.3 Pad-batch method

The padding liquor was prepared as described above, then the padded fabric was rolled in polyethylene foil and allowed to stand for 2, 4 or 6 h at 90°C. The fabric was then air-dried.

The dyed fabrics from the above three methods were than washed with non-ionic detergent (3 g litre^{-1} at 60°C and/or 90°C for 30 min), then extracted with 50% DMF at 90°C for 15 min.

2.3 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. The K/S values were calculated from the reflectance measurements using the Kubelka–Munk equation.[3]

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

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

Evaluation of washing, rubbing, perspiration and light fastness were performed according to the standard methods.[5]

3 RESULTS AND DISCUSSION

Preliminary experiments using Direct Blue 2 (**IV**) and the reactive compound **I** indicated that maximum colour strength after boiling with DMF was obtained when the exhaustion method was applied. Therefore, for purposes

TABLE 1
Colour Strength of Fabric Dyed with Dyestuffs **II–IX** in Absence and Presence of Reactive Compound **I**[a]

Dyestuff	*Colour strength (K/S)*					
	Before wash A	*Before wash B*	*After wash at 90°C A*	*After wash at 90°C B*	*After DMF A*	*After DMF B*
II	12·53	17·53	9·83	15·14	2·64	4·31
III	11·84	14·64	9·23	11·84	4·31	5·62
IV	5·50	10·40	4·60	9·80	1·20	7·00
V	6·39	7·23	3·86	4·93	0·55	1·48
VI	14·17	16·87	10·93	11·22	1·53	3·26
VII	10·93	9·23	10·39	9·02	1·99	1·03
VIII	10·65	12·52	5·89	6·84	1·15	1·25
IX	8·83	12·53	6·50	8·46	1·18	3·56

[a] 4% shades of dyes **II–IX** were used: A, in absence of compound **I**; B, with compound **I** (molar ratio **I** to dye = 4:1).

TABLE 2

Fastness Properties of Fabric Dyed with Dyestuffs **II–IX** (4%) in Absence and Presence of Reactive Compound **I**[a]

Dyestuff	*Washing fastness*																		*Rubbing*				*Perspiration*		*Lightfastness*	
	At 40°C						*At 75°C*						*At 90°C*						*Dry*		*Wet*					
	Alt.		*Stc.*^{c}		*St.*^{w}		*Alt.*		*St.*^{c}		*St.*^{w}		*Alt.*		*St.*^{c}		*St.*^{w}									
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
II	3	3	2	2	2–3	2–3	3	3–4	1–2	1–2	2	2	3	3–4	1–2	1–2	2	2	3	3	2–3	2–3	3	3	5	5
III	3	3–4	2	2	3	3	3	3	2	2	2	2	3	3	1	1	1	1	3	3	2–3	2–3	4	4	6	6
IV	3–4	4	2–3	2	4	4	3	3–4	2	2	2	2	2–3	3–4	1	2	1	2	3–4	3	3	3	3	3–4	3	3
V	4	4	3	3	3	3–4	3	3–4	2	2	2	2	2–3	3–4	2	2	2	2	3	3	2	2	4	4	4–5	4–5
VI	4	4	2	2	4	3	3	3–4	2	2	2	2	3	3	2	2	2	2	3	3	2–3	2–3	3–4	4	3	3
VII	4	4	2–3	2–3	3–4	4	3–4	3–4	2	2	2	2	3	3	2	2	2	2	3–4	3–4	3	3	3–4	4	4	4
VIII	4	4	3–4	2–3	4	4	3	3	2	2	2	2	3	3	2	2	2	2	4	4	3	3	5	4	6	6
IX	4	4	3	3	4	4	3–4	4	2–3	2–3	3	3	3	3	2–3	2–3	3	3	4–5	4–5	3	3–4	4	5	6	6

[a] A and B as in Table 1; Alt., alteration; St.^{c}, staining on cotton; St.^{w}, staining on wool.

of comparison between the different dyes (**II**–**IX**) used in the present study, the same procedure was applied for all of them. The results of colour strength and fastness properties obtained are given in Tables 1 and 2.

A consideration of the data in Table 1 indicates the following:

(a) Addition of the reactive compound **I** results in most cases in an increase of colour strength values before and after washing. These increments differ, however, from one dyestuff to another.
(b) Increments in K/S values after washing at 90°C are especially pronounced in the case of dyestuffs **II**, **III**, **IV** and **IX**. In the case of dyes **V**, **VI** and **VIII** the increments are marginal. Dyestuff **VII** even shows a slight decrease.
(c) K/S values after DMF treatment are relatively high for dyestuffs **II**, **III**, **IV**, **VI** and **IX**. All of these dyes, except **IX**, contain two or more amino groups. These relatively high values would indicate the partial formation of covalent bonds between the reactive dye formed in solution and the fibre.

Data in Table 2 show that the wet-fastness properties were either unaltered or slightly improved.

From the above data it was also evident that, among all the dyes used, dyestuff **IV** seemed to be most suited for application by the above procedure since it gives high K/S values after DMF treatment. Therefore the different factors which affect its fixation were studied.

TABLE 3

Effect of Molar Concentration of Reactive Compound **I** on the Colour Strength of Fabric[a]

Molar ratio of compound **I**	*Colour strength* (K/S)				
	Before wash	*After wash at 60°C*	*After wash at 90°C*	*After DMF for fabrics washed at 60°C*	*After DMF for fabrics washed at 90°C*
—	5·5	4·6	4·0	1·2	1·1
1	8·5	8·3	8·3	4·7	4·5
2	8·5	8·3	8·3	5·3	5·0
3	8·5	8·3	8·3	6·0	5·8
4	10·2	9·8	9·4	7·0	7·0
6	10·4	9·8	9·4	7·2	7·2
8	10·4	9·8	9·6	7·2	7·2

[a] Dye concentration 4% and the general exhaustion method were used.

TABLE 4

Effect of Increasing Molar Ratios[a] of Reactive Compound **I** on the Colour Strength at Different Dye Concentrations

Concentration of dye (%)	*Colour strength (K/S)*																			
	Before wash				*After wash at 60°C*				*After wash at 90°C*				*After DMF for fabric washed at 60°C*				*After DMF for fabric washed at 90°C*			
	a	*b*	*c*	*d*	*a*	*b*	*c*	*d*	*a*	*b*	*c*	*d*	*a*	*b*	*c*	*d*	*a*	*b*	*c*	*d*
1	2·9	4·7	4·9	5·2	2·6	5·5	4·8	5·0	2·5	4·1	4·5	4·7	0·8	2·2	2·2	2·2	0·8	2·3	2·6	2·6
2	3·9	6·9	6·9	7·2	3·5	6·1	6·6	7·1	3·3	5·8	6·1	7·0	0·9	3·3	3·8	3·8	0·9	3·2	3·7	4·1
3	5·1	9·1	9·1	9·1	3·8	8·6	8·6	8·8	3·4	8·3	8·3	8·5	1·1	6·1	6·4	6·6	1·1	6·0	6·5	6·7
4	5·5	10·2	10·4	10·4	4·6	9·8	9·8	9·8	4·0	9·4	9·4	9·6	1·2	7·0	7·2	7·2	1·1	7·0	7·2	7·2
5	5·5	10·9	10·9	11·0	4·7	10·7	10·7	10·7	4·5	10·2	10·3	10·3	1·3	7·8	7·9	7·9	1·2	7·7	7·9	7·9

[a] Molar ratios of compound **I**: a, 0; b, 4; c, 6; d, 8.

TABLE 5

Effect of Time on the Colour Strength of Dyed Fabric Using the General Exhaustion Method[a]

Time (min) at 50 or 90°C	*Colour strength (K/S)*				
	Before wash	*After wash at 60°C*	*After wash at 90°C*	*AfterDMF for fabrics washed at 60°C*	*After DMF for fabrics washed at 90°C*
15	9·9	9·0	8·8	4·1	4·1
30	9·9	9·8	9·1	4·7	4·7
45	10·2	9·9	9·4	5·6	5·6
60	10·2	9·9	9·4	6·1	6·1

[a] A molar ratio of compound **I** to dyestuff **IV** of 4:1 was used.

3.1 Effect of increasing molar concentration of compound I

When increasing quantities of **I** were added to a solution of **IV**, the colour strength values increased until a molar ratio of 4:1 was reached; then the increment started to be marginal (Table 3).

Similar results were also obtained when increasing molar ratios of **I** were added to dye-bath solutions containing different concentrations of dyestuff **IV**.

3.2 Effect of time

When the cotton fabrics were left in the dyeing bath for different periods of time (15–60 min) at 50°C or 90°C, it was observed that increase of time was accompanied with enhancement in colour strength up to 30 min, then the increment started to be marginal. This holds true for samples before and after washing. However, after extraction with DMF the improvement in colour strength continued to increase up to 60 min.

3.3 Effect of addition of Na_2SO_4

The effect of addition of Na_2SO_4 on the colour strength is shown in Table 6. In contrast to the usual effect of Na_2SO_4 in increasing exhaustion, it was observed here that by addition of 5 g the salt causes a drop in colour strength. Further increase of the electrolyte from 5 to 20 g litre^{-1} has no more effect on colour strength. The decrease in colour strength may be due to the increases repulsion effect between the negatively charged -SO_3^- and

TABLE 6

Effect of Sodium Sulphate Concentration on the Colour Strength of Fabrics using the General Exhaustion Method[a]

Concn of Na_2SO_4 (g litre^{-1})	*Colour strength (K/S)*				
	Before wash	*After wash at 60°C*	*After wash at 90°C*	*After DMF for fabrics washed at 60°C*	*After DMF for fabrics washed at 90°C*
—	10·4	9·8	9·4	7·1	7·1
5	6·2	6·0	6·0	4·6	4·6
10	6·2	6·0	6·0	4·6	4·6
15	6·2	6·0	6·0	4·6	4·6
20	6·2	6·0	6·0	4·6	4·6

[a] A molar ratio of 4:1 of compound **I** to dyestuff **IV** was used.

TABLE 7

Effect of Different pH Values on the Colour Strength of Fabrics[a]

pH	*Colour strength (K/S)*		
	Before wash	*After wash at 90°C*	*After DMF*
5·5	10·2	9·5	6·0
6·5	10·2	9·5	6·5
7·5	10·2	9·5	7·0
9·0	10·2	9·5	6·5

[a] A dye concentration of 4% was used.

TABLE 8

Effect of Different Methods of Application (Exhaustion, Pad–Dry–Cure and Pad-Batch Method) on the Colour Strength of Fabrics[a]

Method of application	*Colour strength (K/S)*		
	Before wash	*After wash at 90°C*	*After DMF*
General exhaustion method	10·20	9·50	7·00
Pad-batch for 2 h	7·36	6·97	3·06
Pad-batch for 4 h	6·84	6·28	2·97
Pad-batch for 6 h	6·28	4·48	2·13
Pad–dry–cure method	5·21	3·00	1·80

[a] A molar ratio of compound **I** to dyestuff **IV** of 4:1 was used.

negatively charged SO_4^{2-} anions on the one hand and cellulose anions on the other, leading to lower adosrption and/or reaction of the dye with cellulose.

3.4 Effect of pH values

The effect of changing pH (5·5–9) on the colour strength is shown in Table 7. Colour strengths before and after wash are not effected by increasing the pH values. However, the highest colour strength values after DMF treatment are obtained at pH 7·5. These results indicate that compound **I** or its reaction product with dyestuff **IV** seems to be most stable at this pH value.

3.5 Effect of dyeing procedure

Colour strength values when different dyeing procedures (Sections 2.2.1, 2.2.2, 2.2.3) were used. These values, as shown in Table 8, indicate that the exhaustion method gives the highest values, followed by the pad-batch method, whereas the pad–dry–cure method gives the lowest values.

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