

# Copper Salts in the Post-metallization of Non-genotoxic Direct Dyes

Jin-Seok Bae\* and Harold S. Freeman

Department of Textile Engineering, Chemistry, and Science,  
North Carolina State University, Raleigh, NC 27695-8301, USA

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**Abstract:** Copper (II) salts are used as metallizing agents in the synthesis of new non-genotoxic direct dyes for cotton. Specifically, cotton fabric is dyed with non-genotoxic disazo direct dyes and then treated with copper salts. The complexes are characterized by neutron activation analysis, absorption spectrometry and standard Salmonella mammalian mutagenicity assay, and the after-treated fabrics are evaluated for lightfastness and washfastness. Direct dyes possessing *ortho*-propoxy and *ortho*'-hydroxy substituted systems formed the corresponding nonmutagenic 1:2 dye:metal complex and undergo significant improvement in lightfastness following metallization.

**Keywords:** Metallization, Direct dyes, Neutron activation, Lightfastness, Mutagenicity

## Introduction

It has long been known that after-treatment with salts of metals, such as chromium, aluminum, iron, etc., can give not only varied shades, but can also improve the light and washfastness properties of many direct dyes[1-13]. Probably, in all cases, the dye is in a position to form a chelate with the metal ion, forming a large molecular complex, which might be less soluble in water (which is responsible for improved washfastness properties). Also, the newly formed complex may be more stable photolytically than the original dye. Thus there is an increase in the lightfastness of dyes with certain specific structures when complexing occurs.

Many attempts[1-13] have been made in the past to improve the lightfastness properties of direct dyes on textile materials by after-treatment methods. Among the various after-treatments mentioned in the literature, treatment with metallic salts and particularly with copper sulfate is of commercial importance.

Metallization of dyes originally occurred during the mordanting process to help fix the dye to the substrate.

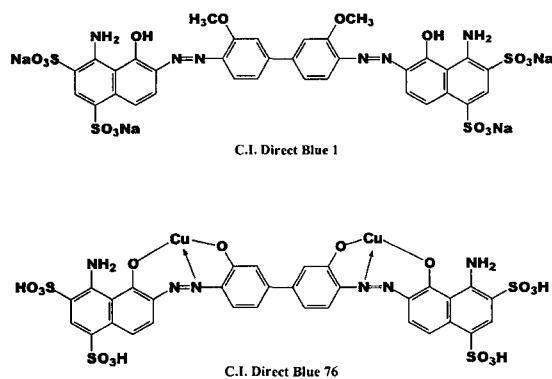


Figure 1. Structures of C.I. Direct Blue 1 and 76.

Premetallized dyes are now used widely in various outlets to improve the properties of dyes, particularly its lightfastness. However, this is at the expense of brightness since metallized azo dyes are duller than nonmetallized dyes.

A major application for copper complexes is in the prior metallization or after-treatment of direct dyes containing at least one *ortho*, *ortho*'-dihydroxyazo or *ortho*-methoxy-*ortho*'-hydroxyazo chromophoric system[5-13]. The best-known example is C.I. Direct Blue 76, a greenish blue copper complex derived from C.I. Direct Blue 1 by metallization with cuprammonium sulfate in the presence of an alkanolamine (Figure 1).

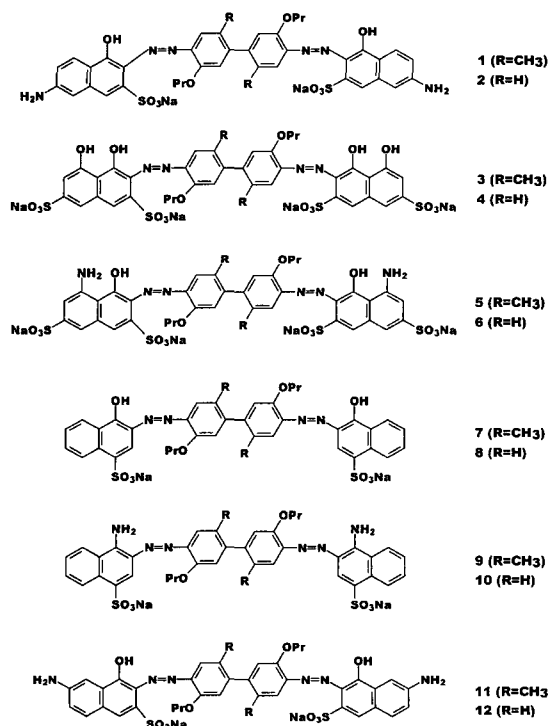
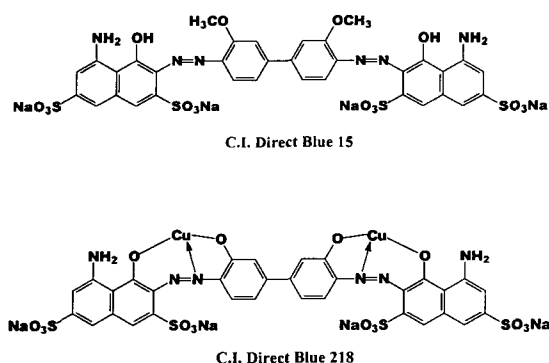


Figure 2. Structures of Direct dyes from Non-Genotoxic Diamines.

\*Corresponding author: jbae@unity.ncsu.edu



**Figure 3.** Structures of C.I. Direct Blue 15 and 218.

A series of new direct dyes (Figure 2) from non-genotoxic diamines were synthesized and evaluated as potential alternatives to certain benzidine-based dyes in the previous research[14]. Results from fastness testing indicated that the new dyes had comparable colors and intensities to structurally related commercial dyes but had low lightfastness. Bearing in mind that after-treatment with  $\text{Cu}^{2+}$  ions can improve the light and washfastness properties of metallizable direct dyes, we examined the suitability of dyes **1-12** for Cu-complex formation. Though it is well known that the treatment of dyes such as C.I. Direct Blue 15 with  $\text{CuSO}_4$  gives simultaneous cleavage of the methyl groups and Cu-complex formation (Figure 3)[15], it has not been shown that the propyl groups of the present dyes can be removed in the same way.

In the present study, the metallization of dyes **1-12** was undertaken. The effectiveness of the metallization reactions was judged with the aid of atomic absorption, neutron activation, and spectroscopic analyses. However, the low water solubility of the copper complexes posed potential application problems. Since the unmetallized precursors possessed higher solubility, it seemed to us that applying them to cotton prior to metallization followed by treatment with copper (II) sulfate would be a viable alternative to exhausting than in their premetallized form. This approach worked well, giving dyeings with colors and technical properties comparable to premetallized copper complexes.

## Experimental

### General

All of the chemicals used in this work were obtained from Aldrich Chemical Co., Milwaukee, WI. The mercerized cotton fabric was obtained from Test Fabrics, Inc. and the style number was 400M. The apparatus used to dye the cotton fabric was an Ahiba Texomat dyeing machine. Washfastness and lightfastness were measured by using an Atlas Launder-ometer and Atlas 3SUN Hi 35 high irradiance Xenon Weather-ometer, respectively.

Absorption spectra were recorded on a Varian Cary 3 UV-Visible spectrophotometer and thin layer chromatography (TLC) was conducted using Whatman 250  $\mu\text{m}$  silica gel

60A plates. The apparatus used for atomic absorption was Perkin Elmer AAnalyst 300 and for neutron activation analysis was Pulstar pneumatic terminus. Color values such as L,  $a^*$ ,  $b^*$  and K/S were measured for dyed fabric before and after copper treatment by using Data Color International Spectrophotometer and Color Tools QC (ver. 1.2.4) software for color quality control.

### Synthesis of Cu-complexed Dyes

First, cuprammonium sulfate  $[\text{Cu}(\text{NH}_3)_4\text{SO}_4]$  was prepared by dissolving  $\text{CuSO}_4$  (3.9 g, 0.5 mol) in  $\text{NH}_4\text{OH}$  (13 ml) and precipitated by adding ethanol (10 ml)[16] and then dye ligands were prepared as described previously[14].

The unmetallized dyes (0.2-0.25 g, 2-2.3 mmol) were dissolved in water (20 ml) at  $60^\circ\text{C}$  and then cuprammonium sulfate (0.1-0.15 g, 4-4.6 mmol) was added. Piperidine (0.01 g) was added and the reaction was stirred at reflux for 15 h. The progress of the reactions was followed by TLC ( $\text{BuOH}:\text{EtOH}:\text{NH}_4\text{OH}:\text{pyridine}/4:1:3:2.2$  or  $\text{BuOH}:\text{EtOH}:\text{NH}_4\text{OH}:\text{H}_2\text{O}/3:1:0.5:1.5$ ), and the dyes were isolated by adding  $\text{NaCl}$  to effect precipitation. The precipitated dyes were collected by filtration and dried.

### Post-metallization of Direct Dyes

A 1 % dyeing (owf) was carried out at pH 7 using a 60:1 liquor ratio. In this regard, the mercerized cotton fabric (5 g) was wet out with hot water and added to the dyebath consisting of dye (0.05 g) and water (270 ml) at  $60^\circ\text{C}$ . The temperature was raised to  $95^\circ\text{C}$  and maintained for 30 min.  $\text{Na}_2\text{SO}_4$  solution (10 %, 15 ml) was added to the dyebath and dyeing was continued for 30 min. The dyebath temperature was cooled to  $80^\circ\text{C}$  ( $180^\circ\text{F}$ ). A solution of the  $\text{CuSO}_4$  (0.015 g, 15 ml) (2 mol/mol dye) was added and the bath was boiled for 45 min. The dyed fabric was removed, rinsed with cold water, and air-dried.

### Washfastness Determination

The washfastness of dyed fabric was evaluated using AATCC test method 61-1996 No. 2A[17]. The dried fabric was evaluated for color change and staining of adjacent undyed multifiber fabric. The rating scale was 1 (poor) to 5 (excellent).

### Lightfastness Determination

The lightfastness of dyed fabric was evaluated using AATCC test method 16-1998 option E[17]. The fabric was evaluated for color change using a scale of 1 (poor) to 5 (excellent).

### Mutagenicity Test

The assay employed was based upon those developed by Ames and co-workers[18]. For this assay, the introduced rat liver used in the S9 mix was prepared using male Sprague-Dawley rats. Two strains of *Salmonella typhimurium* were used: TA 98 and TA 100. In this method, a compound was judged to be mutagenic if the number of revertant colonies was twice the background count (i.e., number of colonies at

the 0- $\mu\text{g}$  dose).

## Result and Discussion

### Synthesis

Direct dyes 1-12 were dissolved in water and cuprammonium sulfate and piperidine were added. The reaction mixture was

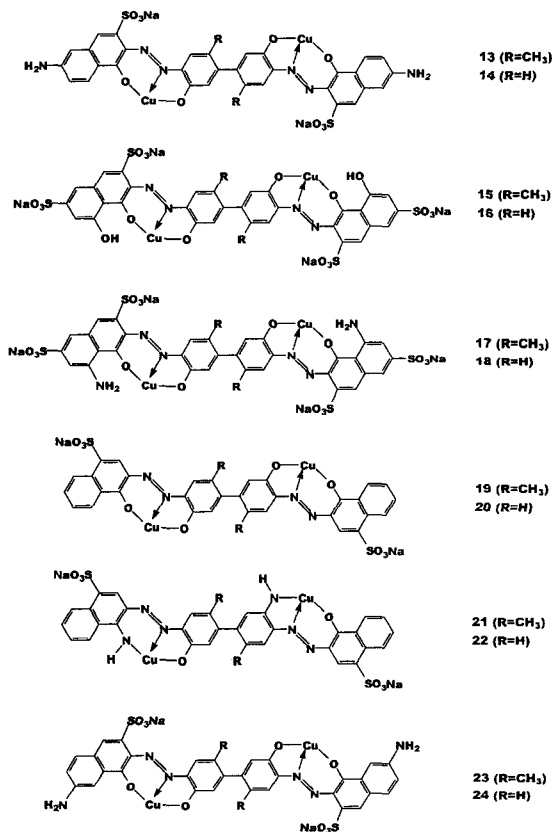
**Table 1.** Yield,  $R_f$  and  $\lambda_{\text{max}}$  of copper-complex dyes

Dye	Yield (%)	$R_f$	$\lambda_{\text{max}}$ (nm)
13	82	0.23 <sup>a)</sup>	522
14	77	0.24 <sup>a)</sup>	516
15	85	0.23 <sup>b)</sup>	568
16	75	0.22 <sup>b)</sup>	568
17	71	0.21 <sup>b)</sup>	577
18	69	0.25 <sup>b)</sup>	568
19	72	0.19 <sup>a)</sup>	510
20	79	0.26 <sup>b)</sup>	588
21 <sup>c)</sup>	n/a	n/a	n/a
22 <sup>c)</sup>	n/a	n/a	n/a
23	82	0.20 <sup>a)</sup>	553
24	74	0.19 <sup>a)</sup>	547

<sup>a)</sup>BuOH:EtOH:NH<sub>4</sub>OH:H<sub>2</sub>O/3:1:0.5:1.5.

<sup>b)</sup>BuOH:EtOH:NH<sub>4</sub>OH:pyridine/4:1:3:2.2.

<sup>c)</sup>dye degradation occurred.



**Figure 4.** Structures of target copper-complexed dyes.

stirred at reflux for 15 h. The dyes were isolated by adding NaCl to effect precipitation, filtration and drying. The yield,  $R_f$  and  $\lambda_{\text{max}}$  of copper-complex dyes are shown in Table 1 and target structures are shown in Figure 4.

### Atomic Absorption and Neutron Activation Analysis

To confirm the Cu levels in the dyes obtained, atomic absorption analysis was attempted. However, due to the very low solubility of the Cu<sup>2+</sup> complexes, atomic absorption analysis gave useful data only for dye 24. In the case of dye 24, the measured amount of copper (15.2 ppm) was very close to the calculated amount (14.8 ppm). Also, neutron activation analysis was employed to investigate the Cu levels in the dyes obtained. For dyes 13, 14, 15, 19, and 24, the measured Cu levels were similar to calculated values. Dye 21 and 22, in which an *ortho*-propoxy group in combination with an *ortho*-amino group exists, showed very low Cu levels, indicating that Cu-complex formation did not occur. For dyes 16, 18, 20, and 23, the measured Cu levels were close to one half of the calculated values. It seems that only one Cu<sup>2+</sup> ion was incorporated into these dye structures. This may have happened because the resultant 1:1 complexes precipitated before the second Cu ion could react. Three of the four dyes have R = H, which suggests that linearity plays a role in the crystallization process. The results of neutron activation analysis are shown in Table 2.

### Post-metallization

The low water solubility of the copper complexes posed dye application problems. Since the unmetallized precursors possessed higher solubility, it seemed better to apply them directly to cotton prior to metallization and treat the dyed fabric with CuSO<sub>4</sub>, as an alternative to exhausting the dyes in their premetallized form. This approach worked well, giving dyeings with colors and technical properties comparable to the premetallized complexes (13-24).

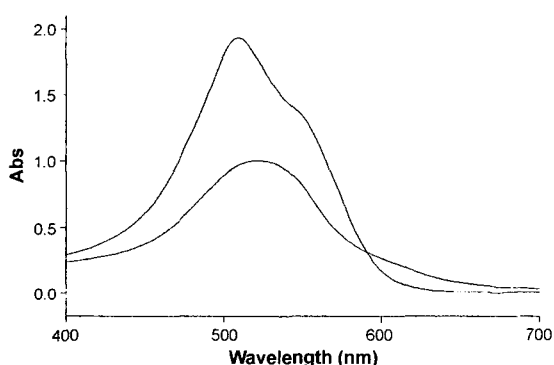
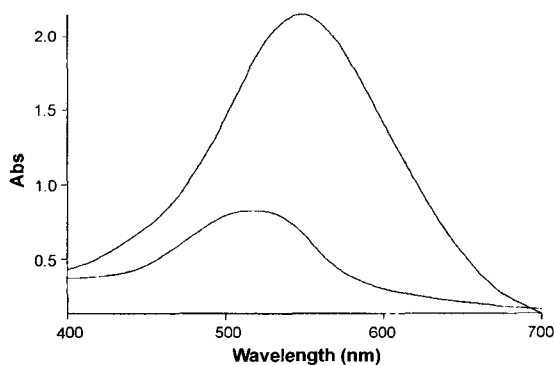
For cotton dyed with dyes 1-12, treatment with solutions of CuSO<sub>4</sub> produced a noticeable color change, as indicated in Table 3. Also, the actual representative UV-Visible absorption spectra are shown in Figures 5 and 6. The more

**Table 2.** Summary of data from neutron activation analysis

Dye	Measured value (%)	Calculated value (%)
13	11.04	13.94
14	12.29	14.88
15	10.44	11.37
16	7.21	11.66
17	1.16	11.39
18	6.41	11.68
19	11.29	14.41
20	9.01	14.89
21	0.53	14.49
22	0.24	14.96
23	7.69	13.94
24	14.05	14.38

**Table 3.** Color generated on cotton before and after Cu<sup>2+</sup> treatments

Dye	Initial color	Cu <sup>2+</sup> treatment
1	Purple	Pale Violet
2	Violet	Deep Violet
3	Sky Blue	Pale Gray
4	Mid Blue	Sky Blue
5	Steel Blue	Pale Blue
6	Bright Blue	Mid Blue
7	Pale Purple	Pinkish Red
8	Royal Blue	Bright Blue
9	Orange	Pink
10	Red	Violet
11	Pale Violet	Reddish Gray
12	Navy Blue	Bluish Gray

**Figure 5.** Absorption spectra of dyes 1 (upper) and 13 (lower).**Figure 6.** Absorption spectra of dyes 2 (upper) and 14 (lower).

intense absorptions correspond to unmetallized dyes 1-12 in each case. Overall, the absorption spectra of metallized dyes showed hypsochromic shifts compared with unmetallized dyes. The exception was dye 13, which is derived from 2,2'-dimethyl-5,5'-dipropoxybenzidine and J-acid. The absorption spectra of dyes 21 and 22 could not be obtained because of dye degradation.

#### *L\**, *a\**, *b\** Values for Cotton before and after Cu<sup>2+</sup> Treatments

In general, the lightness/darkness value, *L\**, increased

**Table 4.** *L\**, *a\**, *b\** values for cotton dyed with 1-12 before and after Cu<sup>2+</sup> treatments

Dye	<i>L*</i>	<i>a*</i>	<i>b*</i>
1	36.12	33.41	-13.54
13	41.53	20.10	-8.88
2	27.86	12.40	-19.27
14	31.38	16.29	-17.93
3	61.34	2.85	-20.41
15	75.62	7.41	-5.70
4	45.99	-4.60	-25.39
16	63.89	-5.55	-15.35
5	59.03	0.74	-20.22
17	77.17	0.21	-5.58
6	42.99	-3.18	-31.89
18	62.90	-6.37	-15.49
7	52.50	27.45	-14.48
19	56.17	30.17	0.80
8	33.50	8.52	-31.06
20	40.07	5.75	-23.25
9	63.43	28.25	24.95
21	74.14	16.79	-0.38
10	35.80	40.36	9.61
22	34.05	13.57	-19.26
11	43.31	8.30	-11.31
23	56.62	8.55	-3.84
12	30.53	-0.60	-16.29
24	36.16	3.10	-7.99

following the CuSO<sub>4</sub> treatment of fabrics dyed with 1-12. Cotton fabrics dyed with 1-8 and 11-12 became lighter following metallization with Cu<sup>2+</sup>, and possessed yellower character than the corresponding untreated dyed fabrics. Fabrics dyed with naphthionic acid based dyes 9-10 had greener and bluer shades after Cu<sup>2+</sup> treatment than the corresponding untreated dyed fabrics. While the fabrics dyed with 9-10 had a bluer character after Cu<sup>2+</sup> treatment, others had a yellower character after Cu<sup>2+</sup> treatment. Fabrics dyed with 1, 3, 5, 7, 9, and 11, in which 5,5'-dipropoxybenzidine (R=H) was used, had greener character (lower *a\** values) before and after Cu<sup>2+</sup> treatment. Fabrics dyed with 2, 4, 6, 8, 10, and 12, in which 2,2'-dimethyl-5,5'-dipropoxybenzidine (R=CH<sub>3</sub>) was used, had redder shades (higher *a\** values) before and after Cu<sup>2+</sup> treatment. The *L\**, *a\**, *b\** color values for the untreated dyed fabric and the corresponding Cu<sup>2+</sup> treated cotton fabrics are reported in Table 4.

#### *K/S Determination for Dyed Fabrics before and after Cu<sup>2+</sup> Treatments*

Absorption spectra were recorded to give K/S values for dyed cotton before and after treatment with Cu<sup>2+</sup>. Table 5

**Table 5.** Absorption spectral data for dyeings generated on cotton

Dye	Before Cu <sup>2+</sup> treatment		After Cu <sup>2+</sup> treatment	
	$\lambda_{\max}$ (nm)	K/S	$\lambda_{\max}$ (nm)	K/S
1	550	8.201	530	4.541
2	565	10.141	540	8.682
3	595	1.083	550	0.315
4	605	3.620	610	1.021
5	602	1.613	580	0.298
6	615	6.050	610	1.210
7	560	2.425	510	2.276
8	580	8.202	575	5.024
9	495	2.016	520	0.476
10	520	10.329	560	6.897
11	578	3.127	550	1.398
12	603	9.260	580	5.548

contains the wavelengths of maximum absorption and K/S values identified for the direct dyes and their metal complexes. There was a hypsochromic shift following metallization of dyes **1-8** and **11-12** with Cu<sup>2+</sup>, but the spectra of naphthionic acid based dyes **9** and **10** underwent a bathochromic shift following Cu<sup>2+</sup> treatment. The former dyes possess *ortho*-propoxy, *ortho'*-hydroxy groups as ligands around the azo bonds, while the latter dyes, **9** and **10**, have *ortho*-propoxy, *ortho'*-amino groups as ligands.

The absorption spectra for fabrics dyed with **1-12** and Cu<sup>2+</sup> treated are almost the same as those arising from solutions of dyes **13-24**. When using solutions of **13-24**, only the dye derived from 2,2'-dimethyl-5,5'-dipropoxybenzidine and J-acid (cf. **13**) showed a bathochromic shift. Interestingly, fabrics dyed with naphthionic acid based dyes **9** and **10** also underwent a bathochromic shift following Cu<sup>2+</sup> treatment. While the absorption spectra of dyes **21** and **22** could not be obtained in solution, absorption spectra could be recorded

**Table 6.** Lightfastness and washfastness ratings before and after post-metallization with Cu<sup>2+</sup>

Dye	Lightfastness (color change)		Washfastness (color change)	
	Before treatment	After Cu <sup>2+</sup> treatment	Before treatment	After Cu <sup>2+</sup> treatment
1	2	3	1-2	1
2	3	4	3-4	2-3
3	2	3	1	1-2
4	2	2-3	2	2
5	1-2	2	1	1-2
6	2-3	2-3	1-2	1-2
7	1	2-3	1	2
8	2-3	4	2-3	1-2
9	1	1	1	1
10	2	1	3	2
11	2	3-4	1	1-2
12	3-4	4-5	3-4	2

on the fabric. This suggests that the complexes are much less stable in solution.

### Fastness Properties

Table 6 shows the lightfastness and washfastness ratings for unmetallized dyes **1-12** on cotton, before and after CuSO<sub>4</sub> treatments. As expected, Cu<sup>2+</sup> treatment gave an improvement in lightfastness. This is especially true for dyes **2**, **8**, **11**, and **12** which showed excellent lightfastness following post-metallization. Improvements of lightfastness were less satisfactory with dyes **9** and **10**, in which an *ortho*-propoxy group was combined with an *ortho'*-amino group. This observation is consistent with the results from neutron activation studies which showed very low levels of Cu in the corresponding pre-metallized dyes.

Following Cu<sup>2+</sup> treatment, lightfastness (color change) was generally better when R=H (**2**, **6**, **8**, **12**) and washfastness was also better when R=H (**2**, **4**, **10**, **12**), since the structures of those dyes are more linear than dyes **1**, **3**, **5**, **7**, **9**, **11**, which are based on 2,2'-dimethyl-5,5'-dipropoxybenzidine (R=CH<sub>3</sub>) was used. In terms of couplers used, dye lightfastness and washfastness were generally better when J-acid (cf. **1**, **2**), NW-acid (cf. **7**, **8**) and  $\gamma$ -acid (cf. **11**, **12**) were used, while naphthionic acid (cf. **9**, **10**) gave dyes with the poorest fastness properties after Cu<sup>2+</sup> treatment.

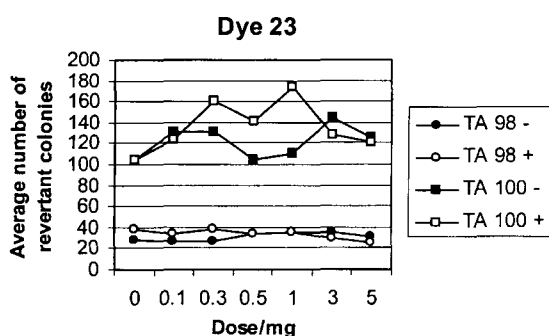
Cu<sup>2+</sup> treatments did not give a significant improvement in the washfastness (change in the color) of any dyes. However, ratings for staining on cotton and wool were better after Cu<sup>2+</sup> treatment than before Cu<sup>2+</sup> treatment. Also, as would be anticipated, staining on cotton was lower when the less linear dyes **1**, **3**, **5**, **7**, **9**, and **11** were used after Cu<sup>2+</sup> treatment. Data for staining on cotton and wool before and after Cu<sup>2+</sup> treatments are summarized in Table 7.

### Mutagenicity Test

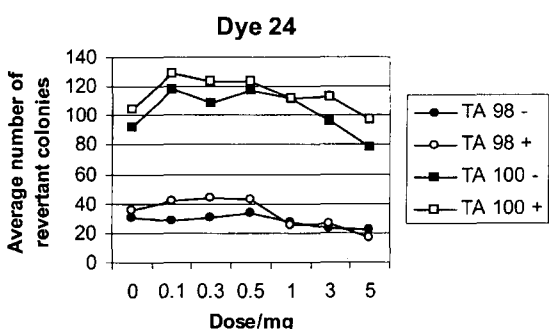
The dyes were evaluated in the standard Salmonella mammalian mutagenicity assay. Figures 7 and 8 show the

**Table 7.** Washfastness ratings for dyeings generated on cotton

Dye	Before Cu <sup>2+</sup> treatment		After Cu <sup>2+</sup> treatment	
	Staining on cotton	Staining on wool	Staining on cotton	Staining on wool
1	2	3	3	4-5
2	2	5	2	5
3	5	5	5	5
4	3	5	4-5	5
5	4	5	5	5
6	2-3	5	4	5
7	3	3	3	4-5
8	2	5	4	5
9	3-4	4	4-5	5
10	2	4	3	5
11	3	5	4-5	5
12	2	5	3-4	5



**Figure 7.** Dose response of Dye 23 using standard mutagenicity assay with bacteria strains TA98 and TA100 with (+) and without (-) S9 rat liver enzyme metabolic activation. DMSO = base count.



**Figure 8.** Dose response of Dye 24 using standard mutagenicity assay with bacteria strains TA98 and TA100 with (+) and without (-) S9 rat liver enzyme metabolic activation. DMSO = base count.

representative (23, 24) dose response curve for each of the dyes tested. The background count is established for a control test in which no dye is present. A mutagenic response is recorded if the number of revertant colonies counted is at least twice the background count. As can be seen from Figures 7 and 8, all clearly established the dyes as nonmutagenic with and without S9 activation for TA98 and TA100. This data showed that copper complexes of new direct dyes were also nonmutagenic in the standard Ames test as well as unmetallized direct dyes.

### Conclusion

The results of this investigation demonstrate that it is possible to prepare nonmutagenic copper complexes of the new disazo direct dyes, confirming that an *ortho*-proproxy group can be cleaved by  $\text{CuSO}_4$  en route to metal-complex formation. Although the low water solubility of the  $\text{Cu}^{2+}$  complexes prevents their direct application to cotton, post-metallization of the direct dyes on cotton is effective, giving dyeings with colors and properties comparable to premetallized Cu complexes, especially for the lightfastness.

The effects of post-metallization on fabric color can be quantified by measuring  $L$ ,  $a$ ,  $b$  values and recording  $\lambda_{\text{max}}$  in K/S spectra. As expected, post-metallization also improves lightfastness but unexpectedly there is little change in washfastness.

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