Dyes and Pigments, Vol. 38, Nos 1–3, pp. 19–39, 1998
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Printed in Great Britain
PII: S0143-7208(98)00002-3
0143-7208/98 $19.00+0.00

Effects of Histidine on the Fading of Cu-complex Azo Dyes on Cellulose and a Testing Method for Color Fastness to Light and Perspiration

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(Received 25 November 1997; accepted 7 January 1998)

ABSTRACT

When no histidine was present on cellulose, Cu-complex azo dyes showed a small fading on exposure, irrespective of whether they were wet or dry, although the abstraction of copper atoms slightly promoted the fading. The color changes of the dyes by immersing in aqueous histidine and/or EDTA were much larger than those by exposure. When histidine was present on the fabrics, the histidine had a large effect on the fading, especially in the case of wet fabrics, giving large color change. In some cases, color changes by exposure were larger than those observed by the immersion. However, the large color changes after exposure were found to be considerable, due to the yellowing of cotton fabrics by histidine, when histidine was singly used. The yellowing increased with an increase in the concentration of histidine and in the pH-values of aqueous histidine, and decreased by drying the fabrics before exposure. © *1998 Elsevier Science Ltd. All rights reserved*

Keywords: Histidine, reactive dye, Cu-complex azo dye, fading, cellulose, yellowing.

INTRODUCTION

The broad application of reactive dyes to cellulose fabrics has not always resulted in success. The defects of reactive dyes have often been realised after

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heavy duty wear of fabrics dyed with reactive dyeings, e.g. the imperfect stability of the dye–fibre bond, giving lower wet fastness of deep dyeings, and the poor color fastness to light and water, to chlorinated water, and to light and perspiration [1–3]. As a result, a testing method for the color fastness to light and perspiration was established (JIS L 0888) in the Japanese Industrial Standards [4] in 1978 in order to reproduce such consumer problems. The testing method, however, has some limitations and the method cannot reproduce the same behavior as in consumer use [1–3, 5]. Although some amendments of artificial perspiration in the methods have been proposed [6–9], no modification of the JIS method has yet been made.

We have previously investigated the photofading of reactive dyes, including Cu-complex azo dyes, on cellulose and found extraordinary effects of histidine on the fading of the Cu-complex dyes on cellulose, compared with the effects of the other substrates on reactive dyeings [10–13]. Substrates such as histidine and lactate on cellulose have been shown to promote the photoreduction of dyes on irradiation [14–19].

In order to discriminate the effect of histidine on the color changes by the immersion in aqueous histidine alone, and the compound effects of light and histidine on the fading of the immersed fabrics, we made the spectral measurements of cellophane dyed with Cu-complex azo dyes without irradiation after immersing in aqueous histidine, and have so far revealed the occurrence of the following phenomena [20–23]:

1. On immersing dyed and undyed cellulose in aqueous histidine, histidine adsorbed on cellulose depending on pH. The maximum adsorption occurred at pH 6.
2. Histidine coordinated to the copper atom of Cu-complex azo dyes on cellulose, an additional adsorption, and whilst abstracting the copper atom, slowly in many cases, in one special case (Blue-2Cu) it did so rapidly and in another case (Blue-Cu) did not abstract at all.
3. The color variations as a result of the coordination of histidine to and/or the abstraction of the copper atom in the dyes on cellulose proceeded more slowly than the adsorption on cellulose did.
4. The rates of the color variations, or of the coordination followed by the abstraction, were dependent upon the concentration and the pH of the immersing solution; the rates and the extent of color changes depended on the chemical structure of the dyes examined. The color changes of the immersed samples were promoted by temperature, when the samples were wet.
5. The absorption spectra of the dyed cellophane, after the coordination and/or the abstraction, changed with the pH of re-immersing buffer solution or with drying, due to the pH change in cellulose.

In a previous paper [13], the fading of a monochlorotriazinyl (MCT) Cu-complex azo dye and a vinylsulfonyl (VS) dye on cellulose, after immersing the dyed fabrics in an aqueous histidine, was examined as a function of the time of exposure. On immersing the dyed fabrics in an aqueous histidine, reactive Cu-complex azo dyes on cellulose underwent considerable color changes, during which the copper atoms of the dyes are abstracted and/or ligand exchange occurs, to generate free hydroxyl groups. The hydroxyl group, and especially carboxyl group, dissociate depending on the pH on cellulose, giving large color changes. After immersing in aqueous histidine, not only Cu-complex dyes whose copper atoms have been abstracted or coordinated by histidine, but also some amount of histidine adsorbed without coordination, exist on cotton fabrics depending upon the conditions of immersion of the cotton fabrics, unless the fabrics are washed after immersion, in addition to the original dyes. The fading of all the dye species on fabrics are usually accelerated by the substrate on the fabrics, showing a complex fading behavior.

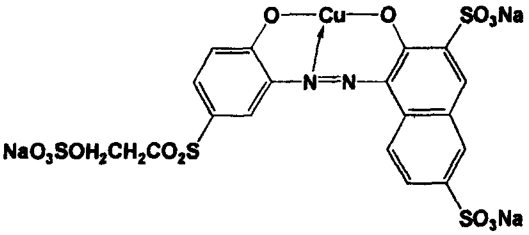
In this paper, abnormal features of the color changes of reactive Cu-complex azo dyes on cellulose by histidine are summarized. The fading of cotton fabrics dyed with some types of Cu-complex azo dyes, which are previously immersed in aqueous histidine, is further investigated. The effects of histidine on the fading are examined on immersing, and after immersing and washing. In order to compare the fading behavior of Cu-complex azo dyes with that of dyes other than Cu-complex ones, the fading behavior of a typical reactive azo dye, C.I. Reactive Red 194, was also examined by the same procedures. On the basis of the present and previous results [12, 15, 16], the specific behavior in the color changes of these fabrics by the irradiation is discussed, and some comments on the testing methods for color fastness to light and perspiration are made.

EXPERIMENTAL

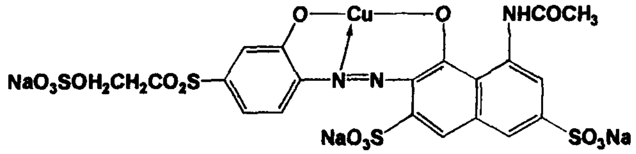
Dyes used

Three VS reactive dye, supplied by DyStar Japan Ltd, and a hetero-bifunctional reactive dye, supplied by Sumitomo Chemical Co. Ltd, were used. The chemical structures of the dyes used and their abbreviations shown in parentheses are as follows:

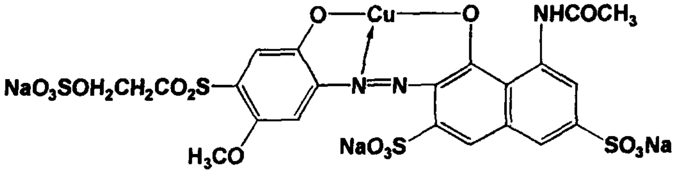
1. C.I. Reactive Red 23, C.I. 16202 (Red 23)



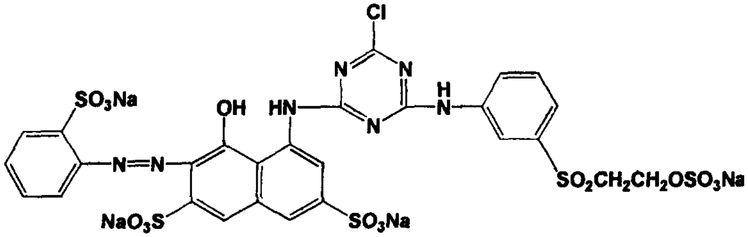
2. A VS 1:1 Cu-complex azo dye (Blue-Cu)



3. C.I. Reactive Violet 5, C.I. 18907 (Violet 5)



4. C.I. Reactive Red 194, C.I. 18214 (Red 194)



Dyeing of fabrics and spectroscopic measurements

Cotton fabrics were dyed by the exhaustion dyeing without alkaline addition for 30 min and then by fixation dyeing with sodium carbonate for 90 min under the conditions: liquor ratio, 30:1; temp., 50°C; dyes, 1.0% o.w.f.; Na_2SO_4, 50 g dm^{-3}; Na_2CO_3, 20 g dm^{-3}. Chemicals used were of reagent grade and were used as received. Absorption spectra were measured by a Ubest V-560 spectrophotometer (Jasco Corp.). The reflection spectra of dry fabrics were measured by the same spectrophotometer equipped with an apparatus for reflection and the color differences between the original samples as dyed and the treated ones were calculated from the spectra by a computer program equipped.

Pretreatment of fabrics and exposure

Dyed cotton fabrics were immersed in various aqueous histidine solutions for 4 h at room temperature. The pHs of aqueous histidine base of 0.020 and 0.040 mol dm^{-3} were 7.56 and 7.70, respectively, without addition of phosphate buffer, and adjusted with hydrochloric acid to 5.50. The pHs of the solution changed after the addition of phosphate buffer. Sodium chloride (0.050 mol dm^{-3}) was added to the solution. Ethylene diamine tetraacetic acid (EDTA) of 0.050 mol dm^{-3}, whose pH was adjusted with 2.0 M sodium hydroxide to 12.0, was used to abstract copper atoms of the dyes on cotton fabrics by immersing for 6 h.

According to B method of JIS L 0888 method [4], the pretreated, initially wet and dried fabrics were exposed to a carbon arc by a fadeometer for a prescribed time.

RESULTS AND DISCUSSION

Color variation of Cu-complex azo dyes on cotton fabrics on immersing in aqueous histidine

Color differences between the original and Cu-abstracted dyes on the immersed fabrics before exposure are listed as the chromaticity values and by ΔE^*_{ab} by the pretreatment in Tables 1 and 2. The values of L^* for the original dye treated by various aqueous histidine were almost similar to those for the untreated original dye, but the values of a^* and b^* for the immersed fabrics were considerably changed from those for the original dyed fabrics. The nearly constant values of L^* imply no decrease in the concentration of the dyes on cellulose, while the variations of a^* and b^* show color change. These results obtained for dyed fabrics were consistent with those obtained for the dyed films mentioned below and in the Introduction [20–23].

By treatment with EDTA and/or histidine, C.I. Reactive Red 23 showed large changes in the values of a^* and small ones in those of b^* in many cases (cf. Table 1). Exceptionally large variations in the values of a^* and b^* were observed by treatment with EDTA and then by that with histidine at

TABLE 1

Color Variations of C.I. Reactive Red 23 on Cotton Fabrics by Various Pretreatment for 4 h for Original Dyes and for 0.5 h for Cu-abstracted Dyes and by Exposure for 8 h (cf. Fig. 1)

Dye	*Pretreatment*	*After pretreatment*				*Conditions of exposure*	*After exposure for 8 h*				*Total color difference* ΔE^*_{ab}
		L^*	a^*	b^*	ΔE^*_{ab}		L^*	a^*	b^*	ΔE^*_{ab}	
Original	No	62.94	37.87	−4.57	—	Dry	64.10	37.88	−4.51	1.16	1.16
						Initially wet	63.94	37.38	−4.30	1.15	1.15
	Histidine, pH 5.50	64.29	36.85	−5.32	1.85	Dry	63.28	35.92	−5.35	1.37	2.13
						Initially wet	65.06	32.42	−3.08	5.02	6.03
	Histidine, pH 5.50, wash	63.38	37.06	−4.32	0.96	Initially wet	64.23	36.21	−4.65	1.18	2.03
	Histidine, pH 7.56	63.05	32.50	−7.53	6.13	Dry	64.55	32.13	−6.51	1.85	6.27
						Initially wet	64.33	25.80	−1.82	8.90	12.46
	Histidine, pH 7.5, buffer[a]					Initially wet	63.91	27.29	−4.80	6.94	10.63
	Histidine, pH 7.6, wash	62.74	34.80	−5.10	3.12	Initially wet	64.63	36.78	−4.73	2.76	2.02
Cu-abstracted	No	62.06	26.65	−7.17	11.55	Dry	65.23	27.41	−5.56	3.64	10.75
						Initially wet	64.93	25.53	−7.19	3.08	12.77
	Histidine, pH 5.50	62.52	26.26	−7.17	11.90	Dry	64.90	26.54	−5.48	2.93	11.53
						Initially wet	66.85	23.47	−0.80	8.19	15.39
	Histidine, pH 7.56	61.00	23.51	−11.89	16.23	Dry	64.51	21.78	−10.99	4.02	17.39
						Initially wet	66.06	16.46	−2.69	12.65	21.72
	Histidine, pH 7.5, buffer[a]					Initially wet	65.33	20.76	−5.75	8.64	17.32

[a] 0.02 M phosphate buffer (0.01 M NaH_2PO_4 + 0.01 M Na_2HPO_4).

TABLE 2

Color Variations of Blue-Cu on Cotton Fabrics by Various Pretreatment for 4 h for Original Dyes and for 0.5 h for Cu-abstracted Dyes and by Exposure for 8 h (cf. Fig. 2).

Dye	*Pretreatment*	*After pretreatment*				*Conditions of exposure*	*After exposure for 8 h*				*Total color difference* ΔE^*_{ab}
		L^*	a^*	b^*	ΔE^*_{ab}		L^*	a^*	b^*	ΔE^*_{ab}	
Original	No	51.11	5.74	−26.01	—	Dry	52.47	5.93	−26.69	1.53	1.53
						Initially wet	52.77	5.80	−26.42	1.71	1.71
	Histidine, pH 5.50	52.44	13.48	−25.40	7.88	Dry	53.00	12.94	−23.91	1.68	7.73
						Initially wet	54.99	9.24	−19.56	7.65	8.30
	Histidine, pH 5.50, wash	51.78	12.64	−25.27	6.97	Initially wet	51.55	10.90	−25.27	1.76	5.23
	Histidine, pH 7.56	52.58	15.69	−24.25	10.21	Dry	54.50	13.97	−21.76	3.58	9.86
						Initially wet	57.17	6.40	−9.50	18.03	17.60
	Histidine, pH 7.5, buffer[a]					Initially wet	59.30	6.04	−10.98	17.94	17.12
	Histidine, pH 7.6, wash	51.66	15.72	−24.90	10.06	Initially wet	52.82	11.82	−24.57	4.08	6.48
Cu-abstracted	No	51.93	18.71	−24.51	13.08	Dry	53.56	16.63	−23.36	2.88	11.47
						Initially wet	52.45	16.39	−23.16	2.73	11.11
	Histidine, pH 5.50	53.20	19.39	−23.43	14.05	Dry	54.42	16.87	−22.27	3.03	12.20
						Initially wet	55.25	14.63	−18.22	7.35	12.52
	Histidine, pH 7.56	53.23	18.31	−23.34	13.02	Dry	55.12	15.26	−20.79	4.40	11.57
						Initially wet	57.42	8.78	−10.26	16.72	17.24
	Histidine, pH 7.5, buffer[a]					Initially wet	58.66	7.41	−11.09	17.15	16.80

[a] 0.02 M phosphate buffer (0.01 M NaH_2PO_4 + 0.01 M Na_2HPO_4).

pH 7.56. No completion of the reaction between C.I. Reactive Red 23 on cotton fabrics and histidine for 4 h seemed to be attained at pH 5.50 and 7.56, although higher completion was obtained at pH 7.56. The color differences between washed and non-washed samples immersed previously may be due to the pH differences between them, and to the coordination of histidine to the copper atom of dyes on the unwashed fabrics.

In the case of Blue-Cu, rough completion in the reaction between the dye and histidine on cotton fabrics at pH 7.56 occurred, but completely at pH 5.50 as shown in Table 2. On immersing in aqueous histidine, Blue-Cu on the fabrics showed a large change in color [20, 22, 23]. Thus, the treatment of Blue-Cu on cellulose with aqueous EDTA and/or histidine resulted in a large increase in the values of a^* and little change in those of b^*. When histidine on cellulose was washed off before exposure, a mixture of original and ligand-exchanged dyes showed a larger rate of fading than that of the original dye. Histidine could not abstract all the copper atoms in Blue-Cu, but *o*-oxo ligands of the dye were substituted by histidine ligand to give free *o*-hydroxyl groups [20]. Since this *o*-hydroxyl group has a value of pK_a around neutral, the ligand exchange results in an appreciable change in color [20].

Fading of Cu-complex azo dyes and the dyes whose Cu atoms were abstracted

In order to elucidate the differences in the fading behavior between the original and Cu-abstracted dyes, the fading of Cu-complex azo dyes whose copper atoms were abstracted by dipping in aqueous EDTA at pH 12 for 6 h, as well as of the original dye, was examined as shown in Fig. 1 for C.I. Reactive Red 23 and in Fig. 2 for Blue-Cu. On exposure within 8 h, a small fading of the original and Cu-abstracted species for C.I. Reactive Red 23 and Blue-Cu occurred on dry and wet fabrics on which no histidine existed. When the chromaticity values of the original dry fabrics were used as reference, the values of ΔE^*_{ab} for dyes whose copper atoms were partially or completely abstracted on dry and wet fabrics were decreased with the time of exposure (cf. Tables 1 and 2). However, such abstraction of the copper atom from both these dyes slightly increased the rate of fading. Initial wetting of fabrics had little effect on the fading of both the dyes. Fading of a mixture of the original and Cu-abstracted dyes on cellulose, obtained by washing the dyed fabrics immersed previously in aqueous histidine at pH 5.50 and 7.56, confirms this fact.

Effect of histidine on exposure of Cu-complex dyes and Cu-abstracted dyes

As reported in previous papers [10–15], substrate adsorbed had pronounced effects on the fading of dyes on cellulose, to give reductive fading. Since

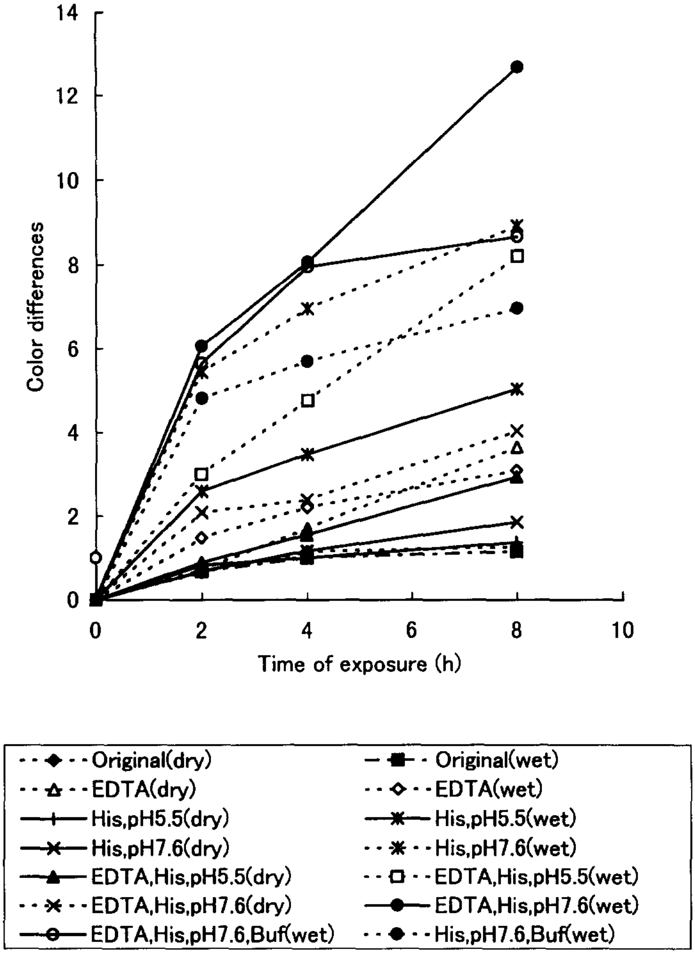


Fig. 1. Fading of the original and Cu-abstracted dyes for C.I. Reactive Red 23 on cotton fabrics and fabrics previously immersed in aqueous histidine (0.02 mol dm^{-3}) at pH 5.50 and 7.56, on exposure to carbon arc (cf. Table 1).

histidine shows considerable adsorption on cellulose and had a significant influences on the color of Cu-complex azo dyes due to the coordination and/or the abstraction before exposure, the influences of histidine on the dyes after exposure have been recognized to be anomalous among substrates such as lactic acid, glucose, aspartic acid, panthothenic acid, if the chromaticity values of the original fabrics were used as the reference for estimating the color differences after the exposure.

In order to analyze the effects of histidine on Cu-complex dyes, the effects on the fading of the Cu-abstracted species for both the dyes were examined. Since color variations of Cu-abstracted dyes may also occur due to the

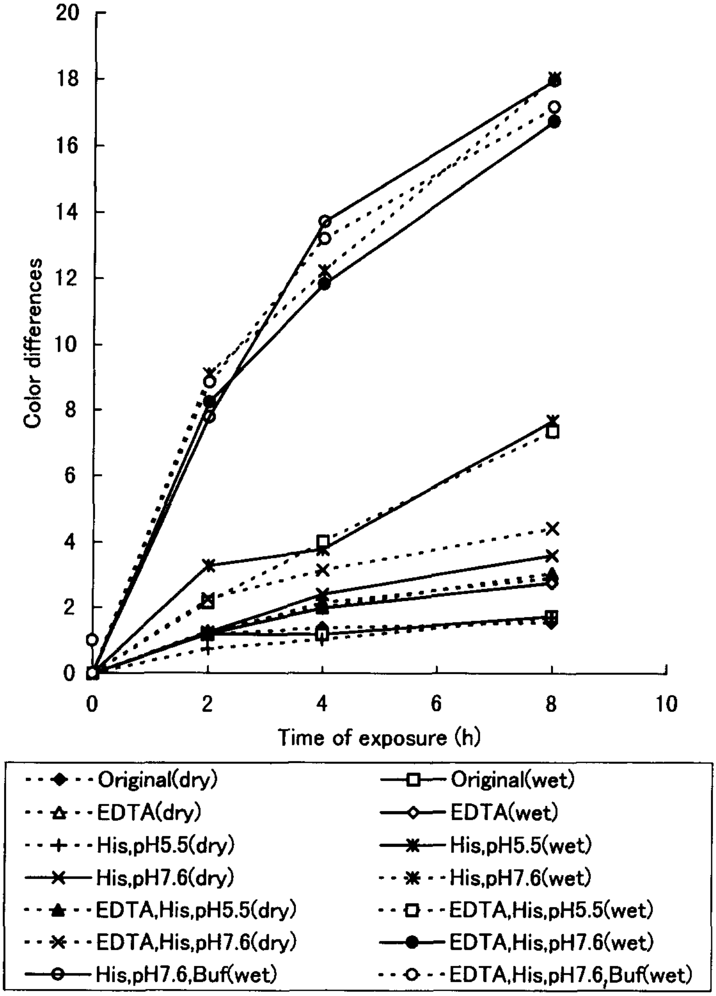


Fig. 2. Fading of the original and Cu-abstracted dyes for Blue-Cu on cotton fabrics and fabrics previously immersed in aqueous histidine (0.02 mol dm^{-3}) at pH 5.50 and 7.56, on exposure to carbon arc (cf. Table 2).

dissociation of hydroxyl groups by change of pH on cellulose [20–23], the variations need be analyzed by dividing them into the contributions from the dissociation and the fading. In the case of original Cu-complex dyes, the contribution of the abstraction of copper atoms, which occurs also during exposure of wet fabrics, may be further added to the color variations.

The results of the exposure of the original and Cu-abstracted species for both the dyes on cotton fabrics previously immersed in aqueous histidine (0.02 mol dm^{-3}) at pH 5.5 and 7.6 are also shown in Figs 1 and 2 and in Tables 1 and 2, and are compared with the results on the fabrics on which no histidine exists, in order to evaluate the effects of histidine and humidity on their fading.

In general, histidine had a small promotion effect on the fading of the two dyes on dry fabrics, although the abstraction of copper atoms promoted the rate of fading. On the other hand, in cases of initially wet fabrics immersed in aqueous histidine, considerable promotion effects by histidine on the fading were observed, and the abstraction of copper atoms proceeded further by heat during the exposure, as mentioned above. Compared with the fading on the corresponding dry fabrics, initial wetting and an increase in the pH of aqueous histidine accelerated profoundly the fading of both the dyes on the immersed cotton fabrics (cf. next section).

Analyzing the differences in the chromaticity values between unexposed and exposed fabrics dyed with both the dyes, the exposure produced further complex changes in the values of a^* and b^*, besides, an increase in those of L^* by fading. Thus, the exposure of both the dyes on immersed fabrics brought about further decrease in the values of a^*, and an increase in those of b^*, with a few exceptions. The exposure of the original dyes on initially wet cotton fabrics immersed previously in aqueous histidine resulted in an increase in the values of b^*, beyond the original color reverse on the immersion (cf. Tables 1 and 2). Especially, the variations of b^* for the original and Cu-abstracted species of both the dyes on initially wet fabrics were very large at pH 7.56, implying the exceptional behavior of histidine at pH 7.56 on initially wet fabrics, although the original dyings of C.I. Reactive Red 23 showed smaller variations of b^* compared with the other cases. But, in the case of Blue-Cu, since the wavelength of the maximum absorption shifted by the abstraction of copper atoms, it was difficult to estimate precisely the degree of fading by changes in reflectance at a definite wavelength.

As was reported previously [23], the incomplete abstraction of and/or coordination to the copper atoms by histidine are thermally promoted during irradiation. This effect may contribute to the increase in the values of b^* for C.I. Reactive Red 23, although the contribution to Blue-Cu, which has higher rates in the coordination, may be smaller.

An increase in the values of b^* implies yellowing of the irradiated fabrics: this is discussed in the next section.

Yellowing of cotton fabrics immersed in aqueous histidine by exposure

In order to confirm whether or not this behavior is due to a decrease in reflection at the short wavelengths in the visible region by the yellowing of histidine itself by exposure, washing of exposed fabrics and a blank test of undyed fabrics immersed previously in aqueous histidine were made. The chromaticity values of a blank test immersed in aqueous histidine at different

TABLE 3

Chromaticity Values for Cotton Fabrics Immersed in Aqueous Histidine (0.020 M and 0.040 M + 0.05 M NaCl) at Different pHs for 4 h by Irradiation for 8 h to Carbon Arc

Concentration of histidine	*pH*	*Conditions of exposure*	*Chromaticity values after exposure*			
			L^*	a^*	b^*	ΔE^*_{ab}
—	—	Original sample	91.01	−0.18	−0.02	—
0.020 M	5.50	Dry	91.16	0.35	−0.15	0.57
		Initially wet	90.27	0.37	1.75	2.00
	7.56	Dry	91.26	0.32	−0.01	0.56
		Initially wet	89.15	0.26	4.32	4.74
0.040 M	5.50	Dry	91.24	0.33	0.03	0.56
		Initially wet	89.42	0.59	3.75	4.16
	7.74	Dry	91.31	0.22	0.09	0.51
		Initially wet	87.74	0.33	7.37	8.10
(+ 0.01 M buffer[a])	7.58		90.18	−0.06	2.88	3.02
(+ 0.05 M buffer[a])	7.41	Initially wet	89.97	−0.09	1.75	2.05

[a] Equimolar (Na_2HPO_4 and NaH_2PO_4) phosphate buffer.

pHs are shown in Table 3. Yellowing by exposure increased with an increase in the pH of aqueous histidine and in the time of exposure. Simple washing of irradiated fabrics did not erase the yellowing. Drying of fabrics before exposure resulted in smaller yellowing than in the case of initially wet fabrics. The results of this study indicate that yellowing by histidine itself has a large effect on an increase in the values of b^* on exposure. But when histidine is used with the addition of phosphate buffer, the buffer clearly diminishes the yellowing in the blank test (cf. Table 3). The effects of phosphate buffer were examined for C.I. Reactive Red 23 and Blue-Cu on initially wet fabrics under the conditions of pH 7.5 and 0.02 M phosphate buffer. As shown in Figs 1 and 2 and in Tables 1 and 2, a small or little suppression effect of yellowing was observed by the addition of phosphate buffer.

Addition of substrate other than histidine, however, seems also to have a suppression effect of yellowing. Thus, little yellowing is observed in the practical testing methods for the color fastness to light and perspiration, except for anthraquinone and phthalocyanine dyes, which showed color variation by photo-reduction on exposure [24].

Effect of histidine concentration on fading

In order to further examine the color variations by immersion and exposure, cotton fabrics dyed with Blue-Cu were immersed in aqueous histidine base of different concentrations and exposed under various conditions. The results are shown in Fig. 3. The color variations on immersion increased with an

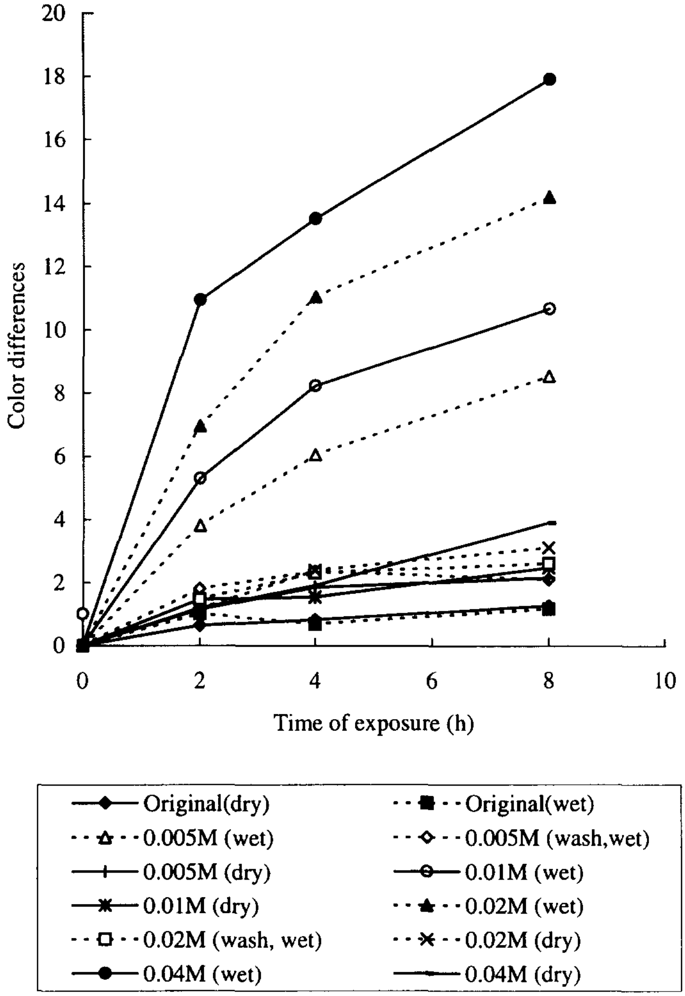


Fig. 3. Effect of the concentration of histidine on the fading of Blue-Cu on cotton fabrics previously immersed in aqueous histidine of different concentration at pH 7.56, on exposure to carbon arc (cf. Table 4).

increase in the concentration of histidine, as listed in Table 4. Moreover, even if the effect of yellowing of cotton fabrics by histidine is taken into consideration, the fading of Blue-Cu on wet fabrics was promoted with an increase in the concentration of aqueous histidine, although the real promotion of fading was smaller than the apparent one. Thus, the anomalous effect of histidine on the fading of Cu-complex azo dyes may disappear, resulting in a small promotion effect of histidine on the fading of dyes on cellulose. The apparent large promotion effects by histidine are regarded as being due mainly to the yellowing of cotton fabrics during fading.

TABLE 4

Color Variations of Blue-Cu on Cotton Fabrics Immersed in Aqueous histidine of Different Concentrations at pH 7.56 and by Exposure for 8 h (cf. Fig. 3)

Concentration of histidine	*Pretreatment*	*After pretreatment*				*Conditions of exposure*	*After exposure for 8 h*				*Total color difference*
		L^*	a^*	b^*	ΔE^*_{ab}		L^*	a^*	b^*	ΔE^*_{ab}	ΔE^*_{ab}
0	No	55.03	5.73	−26.36	—	Dry	55.62	5.54	−25.28	1.25	1.25
0.005 M	As immersed	55.27	10.78	−24.64	5.17	Dry	56.32	9.44	−23.63	2.13	4.78
						Initially wet	58.08	6.10	−18.14	8.50	8.78
	Washing	54.37	11.07	−25.37	5.47	Initially wet	56.04	8.83	−24.46	2.08	3.77
0.010 M	As immersed	55.53	11.80	−24.22	6.48	Dry	56.99	10.71	−22.92	2.45	6.37
						Initially wet	55.29	6.51	−15.03	10.62	11.36
	Washing	54.92	13.05	−25.11	7.44	Initially wet	56.32	9.32	−23.74	4.21	4.63
0.020 M	As immersed	55.76	13.12	−22.59	8.34	Dry	57.99	12.09	−20.88	3.09	8.91
						Initially wet	60.30	7.24	−10.47	14.15	16.81
	Washing	55.20	14.87	−24.77	9.29	Initially wet	55.44	12.48	−23.79	2.59	7.24
0.040 M	As immersed	54.40	15.73	−23.48	10.43	Dry	56.78	13.24	−20.35	3.88	9.78
						Initially wet	60.97	6.33	−4.61	17.84	22.55
	Washing	55.11	16.18	−24.28	10.67	Initially wet	56.26	14.22	−21.62	3.50	9.80

The fading of the dye on dry fabrics immersed previously was accelerated a little, compared with the fading of original dyed fabrics. In absence of histidine, little promotion effect was observed for the immersed fabrics, if histidine on fabrics was washed off before exposure.

Analyses of color variation for Cu-complex azo dyes by exposure

The original C.I. Reactive Violet 5 on cotton fabrics had high lightfastness even though the fabrics were wet as in the case of C.I. Reactive Red 23, Blue-Cu and Blue-2Cu [13] when no histidine was present on the fabrics, as shown in Fig. 4. This dye on the fabrics immersed in an aqueous histidine for 4 h showed relatively small color variation [20, 22, 23] as shown on the ordinate, which afterwards became less by washing with water. However, C.I. Reactive Violet 5, whose copper atoms were partially coordinated and/or abstracted by histidine, showed very large color variations and/or fading at initial time of exposure. Although the contributions by both the phenomena could not be distinguished, the coordination and/or abstraction by histidine may be thermally promoted at the initial time of exposure, in addition to the fading [23]. Besides these phenomena of the dye itself, there may exist yellowing of cotton fabrics by histidine, as mentioned previously (cf. Yellowing of cotton fabrics, above). When the fabrics were washed before exposure, the rate of fading on subsequent exposure decreased. In general, Cu-complex azo dyes show no anomalous fading behavior when no histidine exists on dyed fabrics, or when the interaction between histidine and the copper atoms is excluded.

Comparison between the effect of histidine on the fading for usual reactive azo dyes and that for Cu-complex azo dyes

In order to clarify the abnormal effect of histidine on the fading for Cu-complex azo dyes, the effect of histidine on the fading for a reactive azo dye, C.I. Reactive Red 194, was examined by the same procedures as those of Figs 1–3. The results of the concentration and pH effects of aqueous histidine on the fading are shown in Fig. 5. As in the case of Blue-Cu (cf. Figure 2), apparent promotion effects of histidine on the fading became larger with an increase in the concentration, pH, and humidity, giving the same tendency of yellowing. Since the contribution of yellowing cannot be fully deduced from the total fading, the real promotion effects of histidine on the fading of C.I. Reactive Red 194 may not be able to be quantitatively determined. But, histidine accelerates the reductive fading of azo dyes [14–19]. When histidine is used to examine the fading of reactive dyes on cotton fabrics, the effect of yellowing should be taken into consideration, and this factor is discussed below (cf. next section).

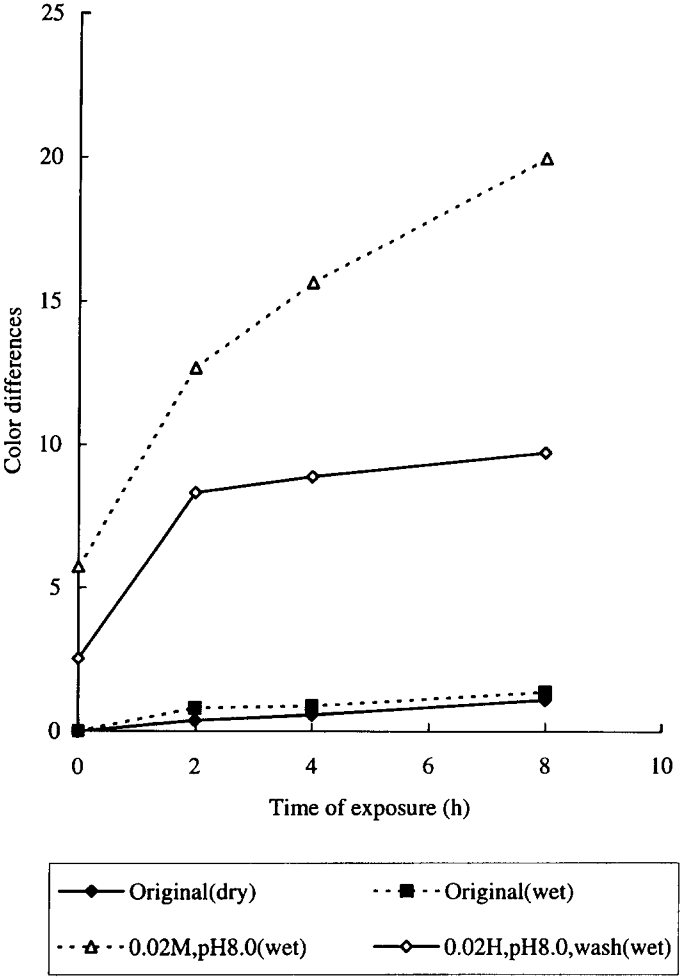


Fig. 4. Fading of C.I. Reactive Violet 5 on cotton fabrics and fabrics previously immersed in aqueous histidine (0.02 mol dm^{-3} + 0.05 M NaCl, pH adjusted to 8.00 with Na_3PO_4) for 4 h, on exposure to carbon arc. The color differences show the values of ΔE^*_{ab} between the exposed test sample and the original one.

Comments on the testing method for color fastness to light and perspiration

On exposure of dyed cotton fabrics dripped with sweat, in general, photo-oxidative fading may occur initially, followed by photo-reductive fading [15, 24–26]. The rates or magnitude of both the fadings depends on the potential properties of dye itself and such conditions of the fabrics as humidity, the amount and nature of the substrate, additional perspiration, rate of drying, etc. Various problems concerned with the fading and/or color

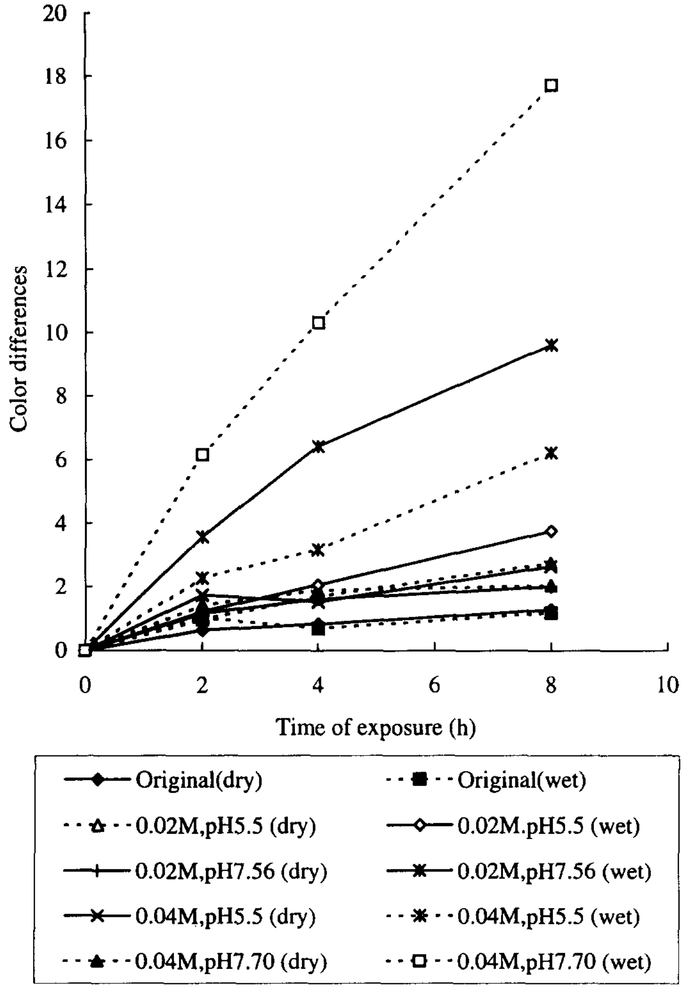


Fig. 5. Fading of C.I. Reactive Red 194 on cotton fabrics previously immersed in aqueous histidine of different concentration at pH 7.56, on exposure to carbon arc.

variations of reactive dyes have been investigated in a series of studies [10, 11, 14, 23, 25], the results of which may be summarized as follows:

Assessment of JIS L 0888 method [4]

In the establishment of testing methods for color fastness to light and perspiration, JIS adopted two kinds of artificial perspiration at pH 5.5 and 8.0 for the testing methods for the color fastness to perspiration, and introduced a glass vessel for the exposure to prevent the rapid evaporation of artificial sweat from initially wet dyed fabrics immersed in aqueous artificial perspiration, and to keep the fabrics under the conditions of RH 100%, although the same apparatus for exposure as that for the estimation of lightfastness was adopted as the alternative procedure. Originally, JIS seems to aim to imitate the exposure of sweated cloths and to obtain as similar a fading as possible to that experienced in consumer stages. The JIS L 0888 method can classify the photostability of dyes with low color fastness including Cu-complex azo dyes, but with high fastness on sweated fabrics [25].

Artificial perspiration
Some modifications have been proposed with respect to artificial perspiration [6–10] and to the methods of exposure. From an assessment of the testing methods including JIS methods and its modifications, only limited methods, or artificial perspiration, have been confirmed to be successful [25]. All the modified methods showed that the concentrations of substrate of the JIS methods were too low to classify the photostability to the compound effects of light and perspiration for dyes with high color fastness. Since the concentration of substrate can be arbitrarily adjusted, the optimal one may be determined depending upon the conditions of testing. But, there then remain problems on the pH of artificial perspiration, the use of histidine, and the abnormal effect of histidine on Cu-complex azo dyes which need to be resolved.

pH. Many methods use both acid and alkaline artificial perspiration, some of which were originally introduced to examine the color variation due to the interaction between Cu-complex azo dye and histidine. ATTS adopted 3.5 as the pH of acid perspiration and Mizuno used this pH. However, no dye was found which showed a larger fading by acid perspiration than that by an alkaline perspiration [25]. Moreover, the real pH effects on the fading behavior may be too complex to estimate by use of one-point measurement [19, 25].

Yellowing. When histidine is used as substrate under some particular conditions, yellowing of cotton fabrics seems to be inevitable. Since some histidine is contained in perspiration, it is essentially inherent in the exposure of sweated cotton fabrics. But when histidine is used as a mixture of phosphate buffer and other substrate as in ATTS methods, yellowing is almost suppressed. When histidine is used as base or hydrochloric acid salt on addition of neutral salts such as sodium chloride or sulfate, yellowing occurred. Substrate other than histidine thus plays a role of yellowing inhibitor for histidine in the mixture.

Substrate other than histidine. Lactic acid is also one of the main components of perspiration, although it is not easy to use because of relatively low stability, and the difficulty in precise adjusting of concentration, etc. It has no anomalous effects on the color change on Cu-complex azo dyes and gives lower yellowing of cotton. If no difference of Cu-complex dyes was apparent from other kinds of dyes, lactic acid may be best alternative for histidine, as proposed by the present authors [27].

Initial wetting and time of immersion. The JIS L 0888 method [4] uses a squeezing method with two glass rods as the dehydration method. The dehydration should be strictly controlled, such as centrifugation, since the fading may be proportional to the amounts of substrate on the fabrics. Moreover, if Cu-complex azo dyes are not excluded, there exist problems with respect to the time of immersion. The interaction of the dyes and histidine depends also upon the concentration and pH of the aqueous histidine. The color changes also change with the dyes themselves. Thus, Cu-complex azo dyes and histidine make the testing methods of color fastness to light and perspiration very complex. Before the establishment of testing methods, whether or not Cu-complex azo dyes and histidine are excluded, must therefore be decided.

The conditions of initial wetting, adopted initially in the JIS method, seem to result in initial oxidative fading, though not always, depending upon the degree of wetting and the properties of dye.

One-point measurement

Reactive dyes have diverse properties in their photo-reductivity and oxidizability [11–18], and among them Cu-complex azo dyes show color changes depending upon the concentration and pH of aqueous histidine and the time of immersion [20–23]. Depending on the environmental conditions, different properties are evident on exposure, to show oxidative and/or reductive fading [24–27]. Thus, one-point measurements adopted in the testing methods for color fastness to light, and to light and perspiration, cannot estimate the different properties precisely, although this is an essential problem to all the testing methods.

SUMMARY

Reactive Cu-complex azo dyes on cellulose have high light fastness even under wet conditions. But on immersing the dyed fabrics in an aqueous histidine, they undergo considerable color changes, during which the copper atoms of the dyes are abstracted and/or the ligand exchange occurs, to give free hydroxyl groups. After immersion in aqueous histidine, there exist not only Cu-complex azo dyes whose copper atoms are abstracted and/or coordinated by histidine on cellulose fabrics unless the fabrics are washed, but

also some amount of histidine and the original dyes, depending upon the conditions of immersion of the cotton fabrics. The fading of all the species of the Cu-complex azo dyes on fabrics by exposure is accelerated by substrate on the fabrics, to show anomalous fading behavior and/or color variations, especially when the fabrics are wet initially. Yellowing of fabrics contributes considerably to the total color variation, if phosphate buffer and substrate other than histidine were not added to the aqueous histidine.

ACKNOWLEDGEMENTS

The authors thank Sumitomo Chemical Co. Ltd and DyStar Japan Ltd for their cooperation in the preparation of the present study. This work was supported by a Grant-in-Aid for Scientific Research (B) by the Minister of Education, Science and Culture, Japan, to whom our thanks are due.

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