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An Assessment of Testing Methods of Color Fastness to Light, Water and Perspiration, and Related Methods with Some Reactive Dyes

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ABSTRACT

Testing methods for the color fastness to light and perspiration, including JIS L 0888 and their improved ones, were applied to cotton dyeings using 14 reactive dyes, seven monochlorotriazinyl, three vinylsulfonyl, and four hetero-bifunctional dyes, to examine whether or not these methods could assess the potential properties of dyes. The fading behavior of these dyes on dry and wet fabrics was also examined. The effects of substrate, water, and the pH of aqueous artificial perspiration in which the test fabrics were immersed on the initial and subsequent fading for these dyes were analyzed in terms of their potential properties. On exposure, many dyes on cotton fabrics which are wet and contain some substrate undergo initially an oxidative fading from the surface, and subsequently a reductive fading depending upon their properties. JIS methods using the smallest amounts of substrate in these testing methods gave the highest rating of color change, while the Mizuno method with the largest amounts gave the lowest rating. The ATTS and LACT methods adequately classified the rating of these dyes, while the JIS and Mizuno methods did so insufficiently. Tests of the pH effect in the methods were fruitless, though very complex, if the Cu-complex azo dyes were excluded. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: colorfastness to light and water, colorfastness to light and perspiration, reactive dye, cotton fabrics, fading.

1 INTRODUCTION

On exposure of reactive dyes on cellulose in various aqueous solutions, the potential properties of the dyes can be elucidated [1–6]. On exposure of dry cotton fabrics, some of their properties are lost and others are manifested depending upon environmental conditions such as the content of oxygen in the atmosphere, substrate on the fabrics, surface dyeing, etc. In the presence of substrate, most reactive dyes on cellulose show reductive fading [1, 5]. Thus, in many cases, the environmental conditions of exposure seem to determine whether oxidative or reductive fading occurs, if the dyes on cellulose have potential properties to show both such mechanisms. In general, the dyes may show oxidative fading at the initial time of irradiation, and later they may have a tendency to show the reductive one.

Reactive copper-complex azo dyes, on the other hand, are excluded from dyes used in the present study, because histidine has an abnormal effect not only on the color change of the dyes on immersing the dyed fabrics, but also on their fading [7, 8]. Color changes of the dyes by histidine have been previously reported [7–11]. It was also found that neither Cu-complex azo dyes whose cotton dyeings were suitable for wear under conditions and which were likely to be sweaty, nor a testing method which could discriminate between suitable and unsuitable cotton dyeings of Cu-complex dyes for wear were evident [8].

In the present study, the fading behavior of monochlorotriazinyl, vinylsulfonyl and their bifunctional reactive dyes on cellulose is examined by practical testing methods for the color fastness to light and perspiration. The methods are the JIS (Japanese Industrial Standards) testing methods [12] and some testing methods [13–16] proposed to improve the JIS methods. The fading behavior on dry and wet cotton fabrics is also examined to clarify the effects of water and substrate on fading. The results of testing for colorfastness to light and perspiration, as well as to light and water, are analyzed to assess the testing methods in terms of the potential properties of dyes used.

2 EXPERIMENTAL

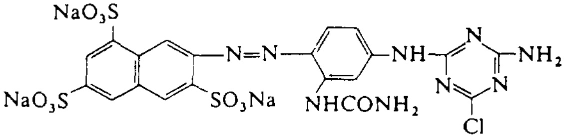
2.1 Materials

2.1.1 Dyes used

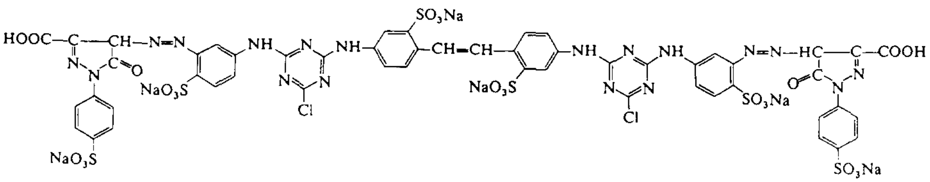
Seven monochlorotriazinyl (MCT), supplied by Nippon Kayaku Co. Ltd., three vinylsulfonyl (VS), supplied by Sumitomo Chemical Co. Ltd., and their four bifunctional reactive dyes, supplied by Sumitomo Chemical Co. Ltd. and DyStar Japan Ltd. (Red 227), were used. Their chemical structures are shown below or by CI Constitution Number if available. The abbreviations of dye names used in the present paper are shown in parentheses.

(a) MCT reactive dyes

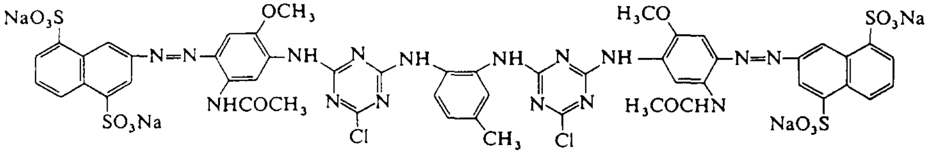
(1) A MCT azo dye (Yellow R)



(2) A MCT stilbene disazo dye (Yellow)

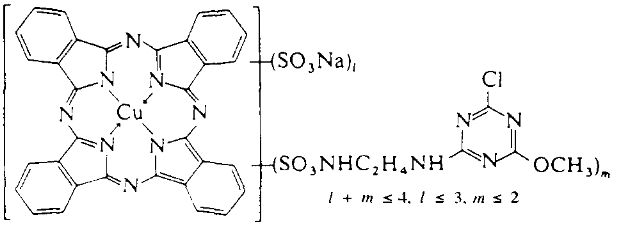


(3) A MCT disazo dye (Orange)

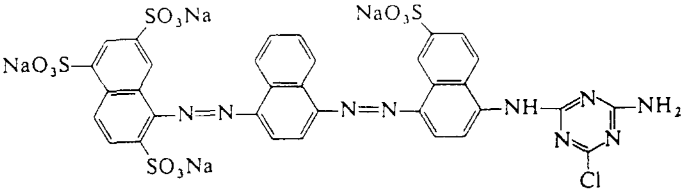


(4) Cl Reactive Red 4, CI 18105 (Red 4)

(5) A MCT Cu-phthalocyanine dye (Cu-Pc)

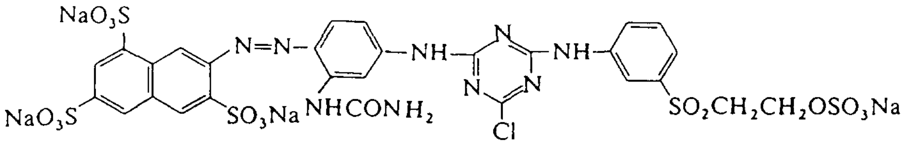


(6) CI Reactive Blue 2, CI 61211 (Blue 2)
(7) A MCT disazo dye (Brown)

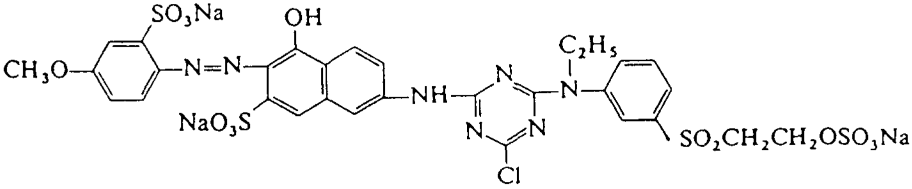


(b) VS dyes
(8) CI Reactive Red 22, CI 14824 (Red 22)
(9) CI Reactive Blue 19, CI 61200 (Blue 19)
(10) Cl Reactive Black 5, Cl 20505 (Black 5)

(c) Bifunctional reactive dyes
(11) CI Reactive Red 194, CI 18214 (Red 194)
(12) CI Reactive Red 227, CI 18215 (Red 227)
(13) A bifunctional monoazo yellow dye (Yellow BF)



(14) A bifunctional monoazo reddish yellow dye (Orange BF)



2.1.2 Dyeing methods

In order to obtain as even dyeing of cotton fabrics as possible with MCT dyes, exhaustion dyeing was carried out at 85°C with Yellow R, Yellow, Orange, and Brown for 2 h, and with the other three MCT dyes for 30 min under the following conditions: dye, 1.0% o.w.f.; Na_2SO_4, 50 g dm^{-3}; liquor ratio, 30 : 1. In the case of the VS and bifunctional dyes, exhaustion dyeing was done at 60°C for 30 min under the same conditions. After the equilibrium adsorption, sodium carbonate ($20\,g\,dm^{-3}$) was added to the dyebath to fix the adsorbed dye by maintaining the dyebath at the dyeing temperature for 1 h. After fixation, the dyed fabrics were washed thoroughly with boiling water to remove unfixed dyes.

2.2 Testing methods and measurements

The testing methods used are shown in Table 1. Irradiation of the test fabrics was made using a carbon-arc fadeometer by setting the sample on a sample holder in the glass vessel for JIS L 0888 [12]. In the case of exposure of the fully wet sample (EvWet in Table 1), this sample was always kept wet during the exposure by setting a wet gauze on the rear side of the exposing sample and the other edge of the gauze was dipped into water at the bottom of the glass vessel. In cases of wet samples (H_2O and the other testing methods except for LACT in Table 1), a specimen of dyed cotton was dipped in the aqueous solution and squeezed with two glass rods according to the methods specified in the table before the exposure.

Reflection spectra of dyed fabrics before and after exposure under various conditions were measured by a Ubest V-560 spectrophotometer (Jasco Corp.) equipped with a reflection measurement apparatus and the CIE tristimulus values were obtained by using CIE illuminant and observer conditions of D65/10° [17]. CIELAB values and the color difference values (ΔE^*_{ab}) were calculated by a computer program fitted to the spectrophotometer, and those of ΔE_F (change in color) and GS_c (gray scale rating for color change) were done according to ISO 105–A05 [18]. The values of ΔE_{cmc} (2:1) were calculated according to ISO 105–J03 [17].

3 RESULTS AND DISCUSSION

In a series of studies, [1–6, 16, 19–21], the properties of some MCT and VS dyes on cellulose have been investigated by means of spectral analysis after exposure under various conditions. The ISO and JIS testing methods [22, 23] for the color fastness to light examine the color variations of dyed fabrics by exposure, referring to the fading of the blue scale. In the present study, by applying several testing methods for color fastness to light, fastness to light and water, and fastness to light and perspiration of these dyes, including four mixed-bifunctional ones on cotton fabrics, the relationships between color variations and the time of exposure were determined and analyzed in terms of their potential properties. Discussions in this paper are on the assumption that the hydrazone form is the species which is preferentially photo-oxidized

TABLE 1

Testing Methods for Fastness to Light and Perspiration (cf. Tables 2 and 3, and Figs 2–8)

Testing method	*JIS L 0888 method [12]*		*ATTS method [13, 14]*		*Mizuno method [15]*	*Lactate method [16]*	*Water method*
Abbreviation	JIS(5.5)	JIS(8)	ATTS(3.5)	ATTS(8)	MZN	LACT	H_2O, EvWet[d]
Components in artificial perspiration (Conc. g dm^{-3})	His·HCl(0.5), NaCl(5) $NaH_2PO_4 \cdot 2H_2O$ (2.2)	$Na_2HPO_4 \cdot 12H_2O$ (5)	His·HCl(0.5), 85% Lac(5), Asp(0.5), Pan(5), Glu(5), NaCl(5), $Na_2HPO_4 \cdot 12H_2O$(5)		His·HCl(5),NaCl(5) 85%Lac(5), $Na_2HPO_4 \cdot 12H_2O$(5)	85% Lac(24), NaCl(5)	Distilled water
pH adjusting	NaOH (N/10)	NaOH (N/10)	CH_3COOH	NaOH	CH_3COOH	NaOH	–
pH	5.5	8.0	3.5	8.0	3.5	6.0	6.0
Time of immersion	30 min		30 min		30 min	24 h	30 min
Dehydration method	Squeezing[b]		Squeezing[b]		Squeezing[c]	Centifugation	Squeezing[b]
Exposure[a] until (Rating)	A method (3)		A method (3)		B method (4)	A method (3)	A method (3)

His = L-histidine, Lac = lactic acid, Asp = DL-aspartic acid, Pan = sodium D-panthotenate, Glu = glucose.

[a] Exposure by JIS L 0888 method until the rating of the Blue Scale shown in this table is faded to standard.

[b] Squeezing with two glass rods according to JIS L 0888 method.

[c] Squeezing with two glass rods, whose pick up is 100–150%.

[d] Initially wet (H_2O) and 'ever-wet' (EvWet) samples (see text) are exposed by use of the A method.

and the azo form is the species which is photo-reduced, although this assumption may result in some problems as yet unresolved.

3.1 Fading on dry fabrics (lightfastness)

The fading behavior of 14 dyes on dry cotton fabrics is shown in Fig. 1 and is summarized in Table 2. All the dyes underwent a two step fading behavior, [20, 21], viz, an initial fading and a smaller subsequent one except for Yellow. Since most dyes do undergo initial oxidative fading on cotton due to the large surface area, in order to possess high light fastness, the ease with which they are photo-oxidized and undergo subsequently reductive fading, which is suppressed or inhibited by oxygen, needs to be controlled.

CI Reactive Red 22, which has high photosensitivity, showed rather low light stability under conditions which promoted oxidative fading. Yellow is a pyrazolinyl azo dye which can undergo oxidative fading since it may exist predominantly as the hydrazone form [24, 25]. Among the MCT dyes examined so far [20, 21], CI Reactive Red 4 has an ease with which it is not only photo-oxidized but also photo-reduced. Then, on exposure in air, this dye undergoes a large initial fading, followed subsequently by an O_2-suppressive reductive fading. Cu-Pc has a similar property to that of CI Reactive

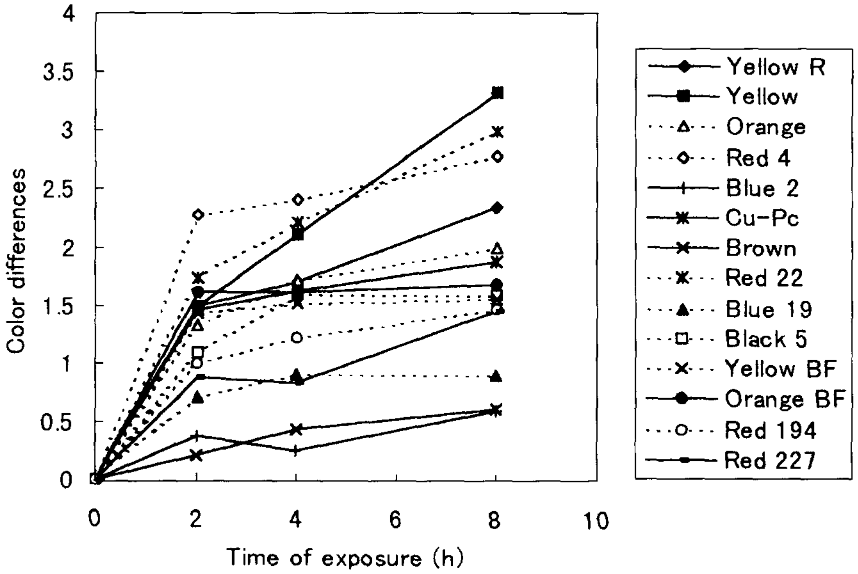


Fig. 1. Relationships between ΔE^*_{ab} and the time of exposure for reactive dyes on dry cotton fabrics on exposure to a carbon-arc fadeometer.†

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†For Figs 1–8 c.f. Section 2.1.1 for the abbreviation of dyes in captions (CI numbers).

TABLE 2

Values of ΔE^*_{ab} for the Fading of Reactive Dyes on 'Ever-Wet' and Dry Cotton Fabrics and Comparison between them (cf. Figs 1 and 2)

Dye	*On dry fabrics* *init.*[a]	*sub.*[b]	*On ever wet fabrics* *init.*[a]	*sub*[b]	*Ratio of initial fading*[c]	*Ratio of subsequent fading*[d]
CI Reactive Red 22	1.7	1.3	4.4	>7.1	2.6	>5
Orange BF	1.6	0.1	1.7	5.8	1.1	>30
Yellow	1.4	2.0	1.5	2.6	1.1	1.3
CI Reactive Black 5	1.1	0.5	1.6	1.8	1.5	3.6
Brown	0.3	0.3	0.4	0.7	1.3	2.3
CI Reactive Blue 2	0.4	0.2	1.2	0.2	3.0	1.0
CI Reactive Blue 19	0.7	0.2	0.7	0.6	1.0	3.0
CI Reactive Red 4	2.3	0.5	4.4	0.2	1.9	0.4
Yellow R	1.5	0.9	2.1	0.7	1.4	0.8
Cu-Pc	1.5	0.5	2.1	0.1	1.4	0.2
Orange	1.3	0.7	2.4	0.1	1.8	0.1
Yellow BF	1.4	0.2	1.1	0.2	0.8	1.0
CI Reactive Red 194	1.0	0.5	0.5	0.9	0.5	1.8
CI Reactive Red 227	0.9	0.6	0.8	0.7	0.9	1.1

[a] Values of ΔE^*_{ab} at 2 h (time of exposure).

[b] Values of ΔE^*_{ab} between 2 and 8 h (time of exposure).

[c] Ratio of ΔE^*_{ab} at 2 h (time of exposure) on dry and 'ever-wet' fabrics.

[d] Ratio of ΔE^*_{ab} between 2 and 8 h (time of exposure) on dry and 'ever-wet' fabrics.

Red 4, although Cu-Pc has higher photo-stability. The photo-reductive fading of Cu-Pc is suppressed by oxygen on exposure in air and then showed some initial fading and slow subsequent reductive fading suppressed by oxygen. Although the magnitudes of initial fading were different with the dyes studied, the four bifunctional dyes examined showed a similar two step fading behavior.

For dyes with high lightfastness, like most dyes examined in the present study, the rates of subsequent fading decide eventual lightfastness rating, although the magnitude of the initial fading must be as small as possible. Thus, a long time of exposure is required to determine the final rating of the lightfastness. Although the fading on dry cotton fabrics is not more complicated than that on wet or sweaty fabrics (as noted below) the fading behavior on dry fabrics is also not simple, i.e. a two step behavior in many cases, and an initially oxidative and subsequently reductive fading behavior is observed [20, 21].

From the fading behavior illustrated in Fig. 1, the magnitudes of total fading for dyes with high light stability on dry cotton fabrics are in the following order:

$$\begin{aligned}&\text{Brown} \approx \text{Blue 2} < \text{Blue 19} < \text{Red 194} \approx \text{Red 227} \leq \text{Yellow BF}\\&\approx \text{Black 5} \approx \text{Orange BF} < \text{Cu-Pc} < \text{Orange} < \text{Yellow R}\end{aligned} \tag{1}$$

The light stability of the other dyes may be regarded as poor.

3.2 Colorfastness to light and water

In general, the lightfastness of reactive dyes on cotton fabrics is lowered by water adsorbed by the cellulose [26, 27]. Besides the promotion of oxygen supply, water may also have an effect on the azo-hydrazone tautomerism [28–31] and the degree of such influences varies with different dyes. AATCC has established the testing methods for the colorfastness to light and water, [32, 33], in which wetting and radiation of test dyed fabrics are repeated.

In the present study, the fading behavior of dyes on wet cotton fabrics was examined. The results are shown in Fig. 2 and summarized in Table 2. Exposure on initially wet and gradually drying dyed fabrics gave almost similar results to those on 'ever wet' fabrics except for CI Reactive Red 22 and CI Reactive Black 5 (cf. H_2O in Table 3), where the gray scale ratings for both of these dyes were estimated by the same method as used in the testing method for colorfastness to light and perspiration (cf. Table 1). Only the results on 'ever wet' fabrics are further discussed.

Compared with the fading on dry cotton fabrics, the fading of several dyes on wet fabrics was promoted by water, while that of other dyes was suppressed, as listed in Table 2. Acceleration effects were observed for eight of the dyes used, while suppression effects by water were apparent for Yellow BF, CI Reactive Red 194, CI Reactive Red 227, Yellow R, Orange, and CI

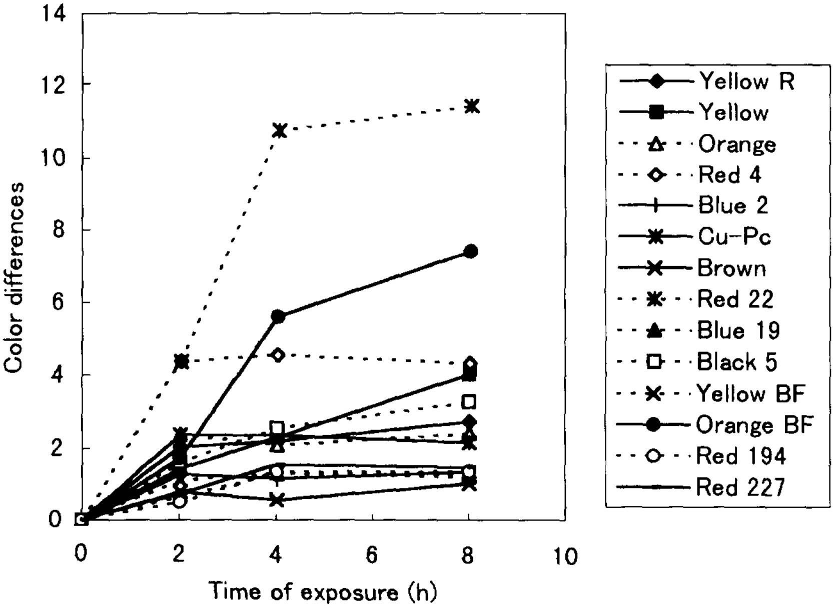

Fig. 2. Relationships between ΔE^*_{ab} and the time of exposure for reactive dyes on 'ever-wet' cotton fabrics on exposure to a carbon-arc fadeometer.

TABLE 3

Values of ΔE^*_{ab},[a] ΔE_{cmc} (2:1),[a] ΔE_F[b] and GS_c (gray scale rating for color change)[b] for Monochlorotriazinyl, Vinylsulfonyl, and their Bifunctional Reactive Dyes Estimated by Some Testing Methods for Colorfastness to Light and Perspiration, and Chromaticity Values (L^*) of Test Fabrics (cf. Table 1)

Testing method		*JIS(5.5)*	*JIS(8)*	*ATTS(3.5)*	*ATTS(8)*	*LACT*	*MZN*	H_2O	*EvWet*
Time of exposure		*8 h*	*8 h*	*8 h*	*8 h*	*8 h*	*16 h*	*8 h*	
Yellow R	ΔE^*_{ab}	3.23	3.17	4.63	6.48	4.61	9.47	3.28	2.81
$L^* = 81.00$	ΔE_{cmc}	1.27	1.24	1.81	2.52	1.79	3.69	1.28	1.21
	$\Delta E_F(GS_c)$	1.71(4)	1.63(4)	2.45(3.5)	3.48(3)	2.59(3.5)	5.20(2.5)	1.78(4)	1.63(4)
Yellow	ΔE^*_{ab}	3.58	5.70	4.62	11.32	3.95	11.98	4.59	4.11
$L^* = 84.84$	ΔE_{cmc}	1.32	2.09	1.71	4.16	1.45	4.50	1.68	1.50
	$\Delta E_F(GS_c)$	1.71(4)	2.71(3.5)	2.24(3.5)	5.63(2.5)	1.95(4)	6.06(2)	2.20(3.5)	1.84(4)
Orange	ΔE^*_{ab}	2.81	2.74	6.01	5.54	3.33	15.63	1.54	2.49
$L^* E_{cmc}$	1.15	1.03	2.15	2.00	1.29	5.55	0.63	1.12	
	$\Delta E_F(GS_c)$	1.39(4)	1.13(4.5)	2.68(3.5)	2.41(3.5)	1.70(4)	7.35(2)	0.72(4.5)	1.69(4)
Red 4[c]	ΔE^*_{ab}	5.35	7.38	8.88	15.91	11.01	13.74	4.98	4.40
$L^* = 61.12$	ΔE_{cmc}	2.29	3.07	3.73	6.58	4.63	5.68	2.15	1.99
	$\Delta E_F(GS_c)$	3.59(3)	4.93(2.5)	6.30(2)	11.69(1)	8.01(2)	9.54(1.5)	3.49(3)	3.71(3)
Blue 2[c]	ΔE^*_{ab}	1.44	1.58	3.89	4.35	3.01	8.18	1.66	1.43
$L^* = 63.26$	ΔE_{cmc}	0.91	0.83	2.16	2.41	1.58	4.60	0.74	0.65
	$\Delta E_F(GS_c)$	2.54(3.5)	1.45(4)	3.60(3)	4.00(3)	2.56(3.5)	8.47(1.5)	1.59(4)	1.44(4)
Cu-Pc	ΔE^*_{ab}	7.02	6.11	14.82	14.74	12.14	19.16	1.96	2.24
$L^* = 67.61$	ΔE_{cmc}	3.24	2.81	6.71	6.71	5.45	9.03	0.87	1.15
	$\Delta E_F(GS_c)$	5.64(2.5)	5.35(2.5)	12.40(1)	12.84(1)	9.93(1.5)	19.68(1)	1.30(4)	2.53(3.5)
Brown	ΔE^*_{ab}	1.17	1.21	3.83	2.20	2.90	10.28	1.25	1.10
$L^* = 51.80$	ΔE_{cmc}	0.85	1.03	1.94	1.30	1.45	4.98	0.58	0.70
	$\Delta E_F(GS_c)$	1.61(4)	1.94(4)	3.50(3)	2.35(3.5)	2.63(3.5)	9.19(1.5)	0.98(4.5)	1.02(4.5)
Red 22[c]	ΔE^*_{ab}	4.39	6.67	7.88	13.77	12.74	11.61	4.80	11.53
$L^* = 61.58$	ΔE_{cmc}	1.85	2.77	3.28	5.72	5.39	4.83	2.01	4.85
	$\Delta E_F(GS_c)$	3.06(3)	4.47(2.5)	5.87(2)	10.14(1.5)	9.68(1.5)	8.26(1.5)	3.43(3)	9.35(1.5)
Blue 19[c]	ΔE^*_{ab}	2.52	2.05	5.67	6.50	4.39	12.34	1.07	1.28
$L^* = 53.88$	ΔE_{cmc}	1.30	0.95	2.75	2.97	2.01	5.98	0.54	0.57
	$\Delta E_F(GS_c)$	2.06(4)	1.03(4.5)	3.09(3)	3.89(3)	2.42(3.5)	8.09(2)	0.52(4.5)	1.28(4)
Black 5[c]	ΔE^*_{ab}	3.66	4.83	12.49	14.48	12.16	16.57	1.18	3.35
$L^* = 39.48$	ΔE_{cmc}	2.12	2.77	7.25	8.29	7.24	9.42	0.70	1.90
	$\Delta E_F(GS_c)$	4.19(2.5)	4.61(2.5)	15.17(1)	16.02(1)	16.09(1)	16.85(1)	1.36(4)	4.23(2.5)
YellowBF	ΔE^*_{ab}	2.51	1.39	3.93	4.00	2.75	8.68	1.22	1.35
$L^* = 77.31$	ΔE_{cmc}	0.93	0.72	1.41	1.45	0.99	3.12	0.79	0.53
	$\Delta E_F(GS_c)$	1.18(4.5)	0.85(4.5)	1.68(4)	2.11(3.5)	1.24(4.5)	3.87(3)	0.78(4.5)	1.13(4.5)
OrangeBF	ΔE^*_{ab}	3.76	4.47	4.93	9.80	4.34	8.64	6.91	7.49
$L^* = 57.40$	ΔE_{cmc}	1.64	1.78	1.97	3.92	1.79	3.40	2.77	3.19
	$\Delta E_F(GS_c)$	2.92(3.5)	2.68(3.5)	3.19(3)	6.05(2)	2.92(3.5)	5.33(2.5)	3.62(3)	5.01(2.5)
Red 194[c]	ΔE^*_{ab}	2.00	4.01	5.97	15.37	9.78	11.39	1.35	1.42
$L^* = 57.20$	ΔE_{cmc}	1.01	1.52	2.31	5.91	3.80	4.38	0.58	0.64
	$\Delta E_F(GS_c)$	1.50(4)	2.09(4)	3.44(3)	9.36(1.5)	6.13(2)	6.78(2)	1.33(4)	1.07(4.5)
Red 227[c]	ΔE^*_{ab}	1.88	3.82	5.87	15.24	8.87	11.37	1.21	1.55
$L^* = 56.96$	ΔE_{cmc}	0.88	1.47	2.26	5.93	3.44	4.44	0.47	0.65
	$\Delta E_F(GS_c)$	1.35(4)	2.06(4)	3.31(3)	9.59(1.5)	5.41(2.5)	7.20(2)	0.67(4.5)	1.29(4)

[a] Estimated by ISO 105-J03, 1995.

[b] Estimated by ISO 105-A05, 1996.

[c] CI reactive generic name.

Reactive Red 4. Despite the presence of water, the subsequent reductive fading of some dyes was suppressed by oxygen on wet cellulose fabrics.

Very large promotion effects were observed on the fading of CI Reactive Red 22 and Orange BF. Cl Reactive Red 22 on the front surface of wet fabrics was faded completely after 4–6 h of exposure. The fading of this dye on initially wet fabrics was much lower than that on 'ever-wet' fabrics. The subsequent fading on wet fabrics became very much greater than that on dry fabrics. The subsequent fading of Orange BF especially on 'ever-wet' fabrics was accelerated by a considerably greater factor compared with the fading on dry fabrics, although little effect on the initial fading was observed.

The initial and subsequent fading of Cu-Pc and CI Reactive Black 5 was accelerated, while only the rates of subsequent fading for Yellow was promoted without change in the magnitude of the initial fading.

The O_2-suppressive mechanism may still be operative on wet fabrics. With CI Reactive Red 4, Cu-Pc, and Orange, the subsequent fading was suppressed on 'ever-wet' fabrics, although the initial fading was increased. But, since the absolute value of fading for Cl Reactive Red 4 was large, this dye has a low fastness to light, as well as to light and water. In contrast, since the absolute values of the fading of CI Reactive Blue 2, CI Reactive Blue 19, and Brown were small, it may be concluded that the small acceleration effects of water were observed practically on fading, although the promotion factors were estimated as considerable. These dyes have a high colorfastness to light and water.

Since on wet fabrics the rate of oxidative fading is promoted, how large ease with which the dyes are oxidized may be examined by the promotion effect on fading by water. The fact that the fading of most dyes was increased by water implies that these dyes suffer oxidative attack promoted by water. The suppressive effect of the fading by oxidative attack shows that the dyes undergo reductive fading, although the dye has a shortcoming in that the reductive fading is accelerated by the presence of a substrate such as histidine, lactic acid, textile resins, etc (cf. 3.4).

The AATCC testing methods for the colorfastness to light and water may not therefore be able to fully estimate these potential properties, although this test method has practical aspects.

From the fading behavior illustrated in Fig. 2, the magnitudes of total fading for dyes with high light stability on wet cotton fabrics are in the following order:

$$\begin{aligned}&\text{Brown} < \text{Blue 19} \approx \text{Yellow BF} \approx \text{Blue 2} \approx \text{Red 194} < \text{Red 227}\\&< \text{Cu-Pc} < \text{Orange} < \text{Yellow R}\end{aligned} \qquad (2)$$

From the order (1), CI Reactive Black 5 and Orange BF were excluded.

3.3 Differences among ΔE^*_{ab}, $\Delta E_{cmc}(2,1)$, and ΔE_F by exposure

On exposure of dyed fabrics previously immersed in artificial perspiration, the fading of all the dyes, except for anthraquinones and Cu-Pc, occurred without change in shade, i.e. azo dyes underwent fading by an increase in the reflection parameters the principal band. But a small decrease in the reflection of exposed fabrics was observed at wavelengths longer than that of the main absorption band, although the decrease was not perceptible as color variations by the naked eye.

From the reflection spectra of dyed fabrics before and after exposure, the values of three kinds of color differences, i.e. ΔE^*_{ab}, ΔE_F, and $\Delta E_{cmc}(2,1)$, were estimated as listed in Table 3. The ratios for $\Delta E^*_{ab}/\Delta E_F$ were 1.4–2.1 for the yellow, orange, and red dyes (and including also CI Reactive Blue 19), although the ratios by the different methods were nearly constant for individual dyes, with a few exceptions. In the case of the blue, brown, and black dyes (except for CI Reactive Blue 19) the ratios were around unity. Smaller values of $\Delta E^*_{ab}/\Delta E_F$ than those by other methods were found in the exceptional cases of low fading undergone by dyes such as CI Reactive Blue 2, Cl Reactive Blue 19, and four bifunctional dyes by the JIS (5.5) method and Brown by the two JIS methods. These effects may lower the gray scale rating for the color change in these cases by about 0.5 units.

The values for ΔE_{cmc} shown in Table 3, on the other hand, were always smaller than those for ΔE^*_{ab} and ΔE_F. The ratios of $\Delta E^*_{ab}/\Delta E_{cmc}$ for individual dyes were not changed by the testing methods, but varied with different dyes. The exceptional cases of small ratios of $\Delta E^*_{ab}/\Delta E_F$ held also for the ratios of $\Delta E^*_{ab}/\Delta E_{cmc}$, with a few exceptions. These tendencies of the two ratios were also observed in the cases of low fading for these dyes exposed on wet fabrics (cf. the last two columns of Table 3).

3.4 Testing methods for colorfastness to light and perspiration

Some testing methods for the colorfastness to light and perspiration were applied to reactive dyeings to elucidate whether or not the methods could estimate their properties. In order to assess these testing methods, color variations of 14 dyes on exposure were analyzed in terms of the conjoint effects of substrate and pH. The fading behavior is shown in Figs 3–8 and the results are summarized as color differences and gray scale ratings by the methods in Tables 3 and 4.

On exposure, all the fabrics began to dry gradually. In general, the presence of substrate suppresses the oxidative fading and promotes reductive fading, irrespective of whether the dyes exist in the azo or hydrazone form. If the amounts of substrate are not sufficient to suppress the oxidative fading,

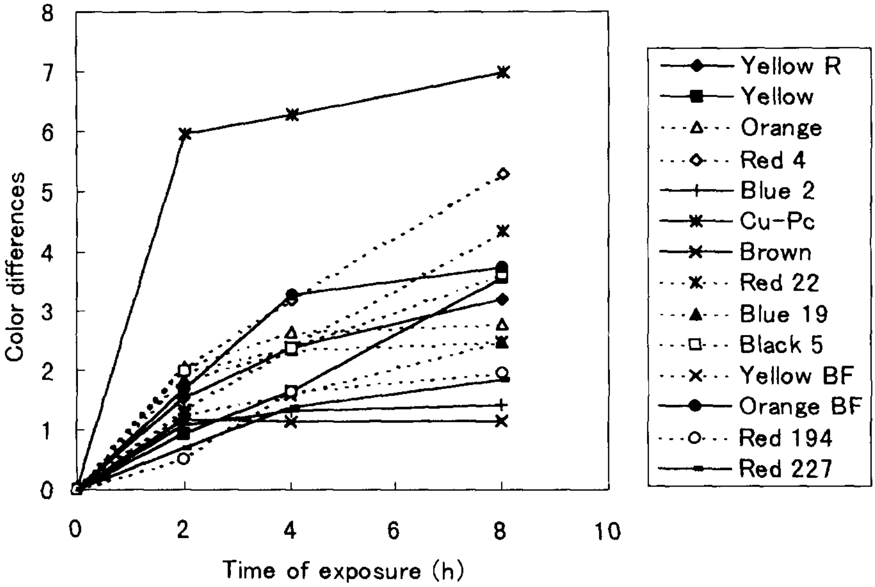

Fig. 3. Relationships between ΔE^*_{ab} and time of exposure for the reactive dyes on cotton fabrics previously immersed in the prescribed artificial perspiration of the JIS (5.5) method, on exposure to a carbon-arc fadeometer.

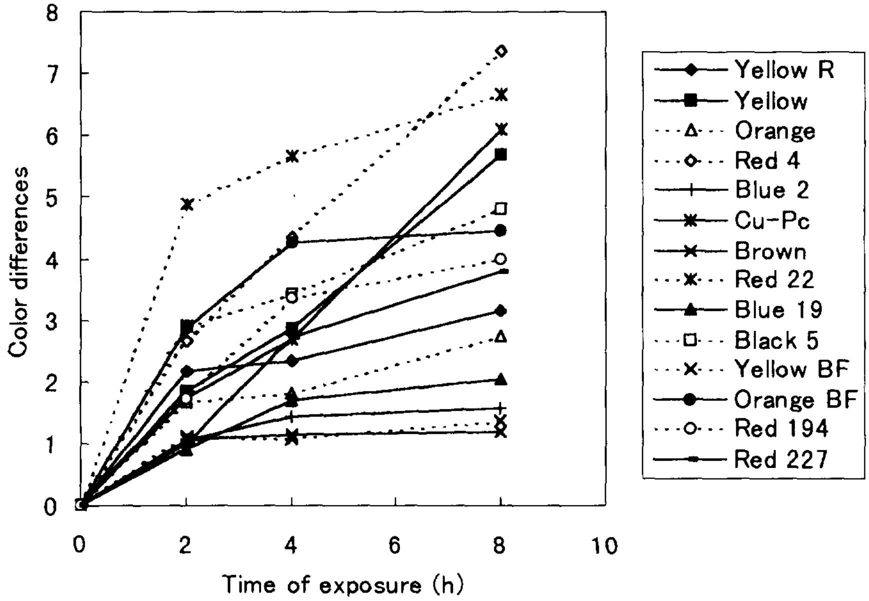

Fig. 4. Relationships between ΔE^*_{ab} and the time of exposure for the reactive dyes on cotton fabrics previously immersed in the prescribed artificial perspiration of the JIS (8) method, on exposure to a carbon-arc fadeometer.

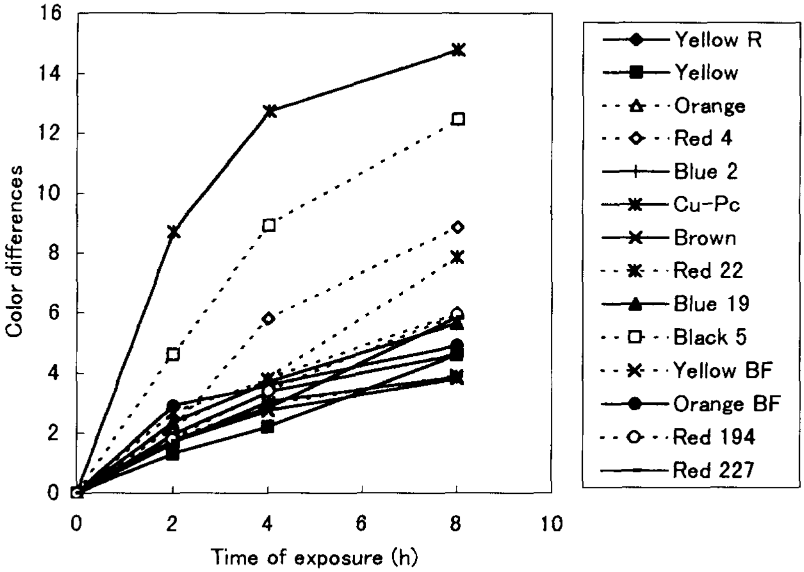

Fig. 5. Relationships between ΔE^*_{ab} and time of exposure for the reactive dyes on cotton fabrics previously immersed in the prescribed artificial perspiration of the ATTS (3.5) method, on exposure to a carbon-arc fadeometer.

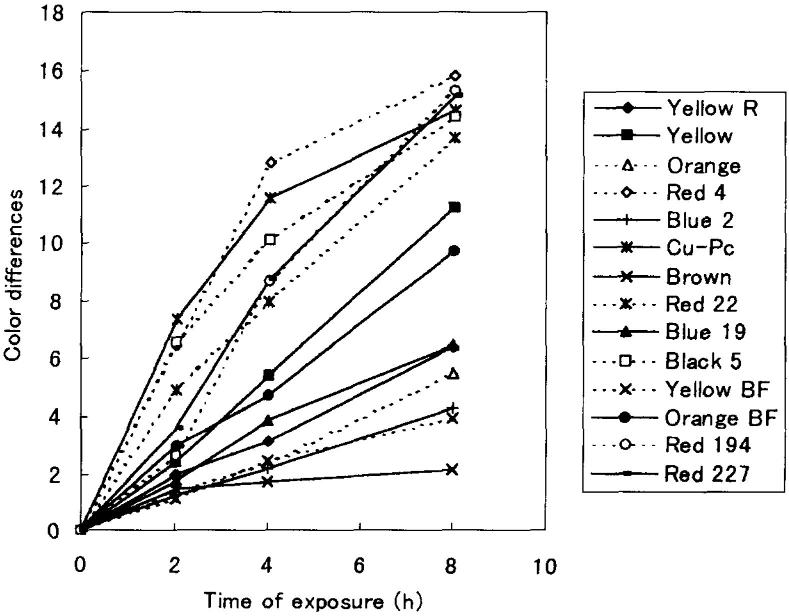

Fig. 6. Relationships between ΔE^*_{ab} and time of exposure for the reactive dyes on cotton fabrics previously immersed in the prescribed artificial perspiration of the ATTS (8) method, on exposure to a carbon-arc fadeometer.

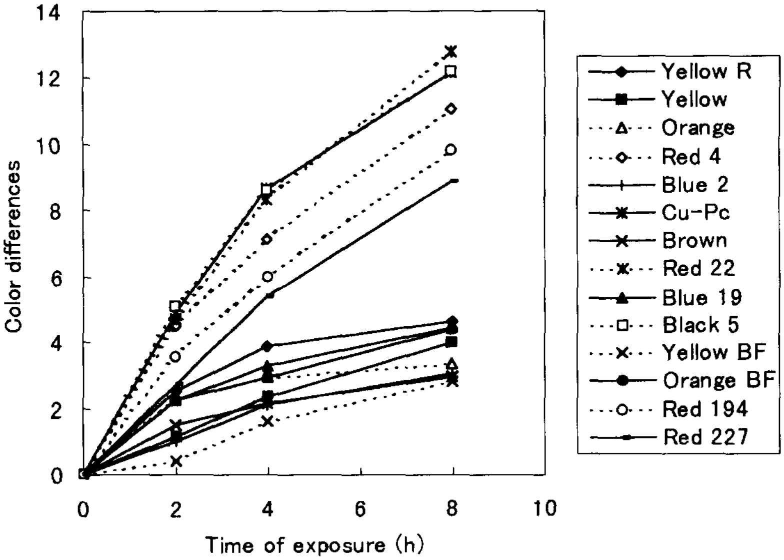

Fig. 7. Relationships between ΔE^*_{ab} and time of exposure for the reactive dyes on cotton fabrics previously immersed in the prescribed artificial perspiration of the LACT method, on exposure to a carbon-arc fadeometer.

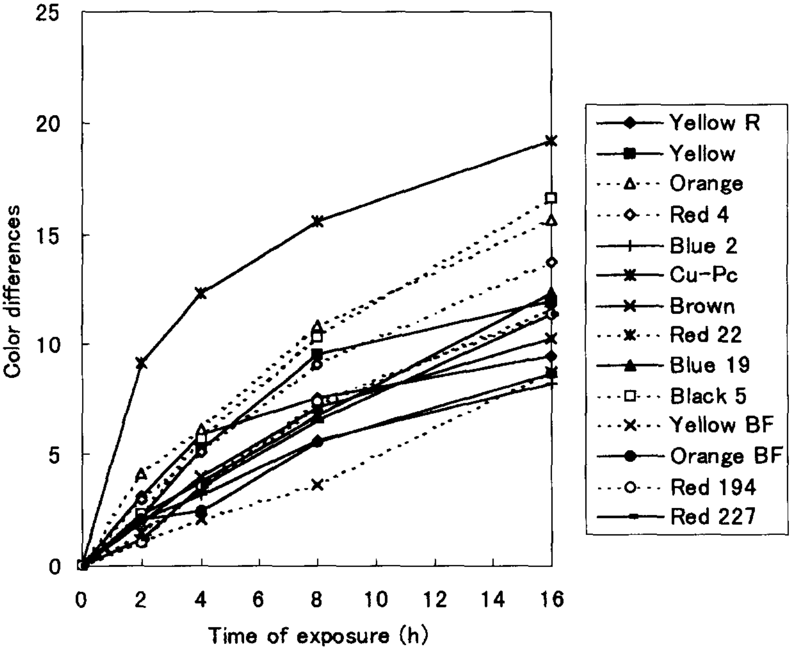

Fig. 8. Relationships between ΔE^*_{ab} and time of exposure for the reactive dyes on cotton fabrics previously immersed in the prescribed artificial perspiration of the MZN method, on exposure to a carbon-arc fadeometer.

TABLE 4
Values of ΔE^*_{ab} for Reactive Dyes on Cotton Fabrics Estimated by Different Testing Methods

Dye	*JIS(5.5)*		*JIS(8)*		*ATTS(3.5)*		*ATTS(8)*		*LACT*		*MZN*	
	Init.[a]	*Sub.*[b]	*Init.*[a]	Sub[b]	*Init.*[a]	*Sub.*[b]	*Init.*[a]	*Sub.*[b]	*Init.*[a]	*Sub.*[b]	*Init.*[a]	*Sub.*[b]
Yellow R	1.6	1.6	2.2	1.0	2.0	2.6	2.0	4.5	2.5	2.1	3.1	4.4
Yellow	1.0	2.6	1.9	3.8	1.3	3.3	2.4	8.9	1.1	2.9	2.2	7.3
Orange	2.1	0.7	1.7	1.0	2.2	3.8	1.4	4.1	2.3	1.0	4.1	6.8
CI Reactive Red 4	2.0	3.4	2.7	4.7	4.4	4.5	6.4	9.5	4.5	6.5	2.9	6.2
CI Reactive Blue 2	1.1	0.3	1.1	0.5	1.7	2.2	1.3	3.1	1.0	2.0	2.1	3.5
Cu-Pc	6.0	1.0	1.7	4.4	8.7	6.1	7.3	7.4	4.9	7.2	9.1	6.5
Brown	1.2	0	1.1	0.1	1.7	2.1	1.5	0.7	1.5	1.4	1.9	5.2
CI Reactive Red 22	1.3	3.1	4.9	1.8	2.7	5.2	4.9	8.9	4.7	8.0	1.4	5.8
CI Reactive Blue 19	1.8	0.7	0.9	1.2	2.5	3.2	1.8	4.7	2.2	2.2	2.3	4.4
CI Reactive Black 5	2.0	1.7	2.9	1.9	4.6	7.9	6.6	7.9	5.1	7.1	2.3	8.1
Yellow BF	1.3	1.2	1.1	0.3	1.8	2.1	1.1	2.9	0.4	2.4	1.1	2.5
Orange BF	1.7	2.1	2.9	1.6	2.9	2.0	3.0	6.8	2.2	2.1	2.0	3.6
CI Reactive Red 194	0.5	1.5	1.7	2.3	1.8	4.2	2.7	12.7	3.6	6.2	1.1	6.3
CI Reactive Red 227	0.7	1.2	1.0	2.8	1.8	4.1	3.6	11.6	2.7	6.2	1.2	5.3

[a] ΔE^*_{ab} after 2 h of exposure.
[b] Difference of ΔE^*_{ab} between 2 h and 8 h of exposure.

oxidative fading may initially occur followed by reductive fading, the rates of which depend on the testing methods.

The influence of pH on the fading mechanism is also noted. An increase in the pH of the aqueous solution in which the test specimen was dipped can activate singlet oxygen and shift the azo-hydrazone tautomerism to the azo side [34–36]. The conjoint effects of substrate and pH on the fading behavior may therefore be too complex for a clear analysis. For dyes whose azo-hydrazone tautomerism or redox potential is not profoundly influenced by change in pH, the effect of substrate on the fading may be simplified, as in the cases of 3.4.1–3.4.5 (except for Yellow BF). Since many dyes may however exist as a mixture of azo and hydrazone forms which are influenced by change of pH, variations in the fading behavior of each dye are very complicated, depending on the dye structure and on the testing methods, as in the cases of the other five dyes (cf. 3.4.6–3.4.10).

3.4.1 Yellow

In neutral and acidic regions, this dye exists predominantly in the hydrazone form. The initial oxidative fading on wet fabrics is then suppressed by the addition of substrate in the case of JIS (5.5), ATTS (3.5). The rates of subsequent (probably reductive) fading by all the methods were larger than those on dry fabrics, although the JIS (5.5) method, where oxidative fading occurs can be excluded. The fading by the JIS (5.5) method is mainly oxidative, while that by the other methods may be initially oxidative and subsequently reductive.

3.4.2 Orange

The magnitudes of the initial (oxidative) fading were suppressed by all the testing methods, other than the MZN method, while the rates of subsequent reductive fading were increased due to the presence of substrate. However, the total fading of this dye is small compared with that of the other dyes. This is an excellent dye which has high photostability to both oxidative and reductive attack.

3.4.3 CI Reactive Blue 2 and CI Reactive Blue 19

Compared with the initial fading on wet fabrics, the initial fading was little influenced by the testing methods applied, since the fading was small. The JIS methods had no effect on the rates of subsequent fading, while all the other methods showed acceleration effects. The probably negligible initial oxidative fading is immediately followed by reductive fading promoted by the substrate, since this dye has low photosensitivity.

In the case of CI Reactive Blue 19, all the methods promoted the initial and subsequent fading, although the effects varied with methods. The effects on the subsequent fading of CI Reactive Blue 19 by the JIS (5.5) method, and on the initial fading by the JIS (8) method were small, while those on subsequent fading by the ATTS (3.5), ATTS (8), and MZN methods were larger.

3.4.4 Brown

Compared with the fading on wet fabrics, all the methods promoted the initial and subsequent fading, since oxidative fading is almost completely suppressed by the substrate. The promotion effects were small, i.e. the colorfastness of Brown was relatively high compared with other dyes. This is an excellent dye with high photostability to both the oxidative and reductive attacks, like Orange.

3.4.5 Bifunctional reactive dyes

(a) Yellow BF. Compared with the fading on wet fabrics, which was smaller than that on dry fabrics, the ATTS (3.5) method showed on acceleration effect on the initial fading, while the LACT method had a suppressive effect. Although the JIS (5.5), JIS (8), ATTS (8), and MZN methods had little effect, the subsequent reductive fading was promoted by all the methods, except for the JIS (8) method. Thus, this dye has high photostability to both oxidative and reductive attack.

(b) CI Reactive Red 194 and CI Reactive Red 227. Compared with the fading on wet fabrics, the JIS (5.5) method had no effect on the fading for both the dyes, while all the other methods had promotion effects on both the initial and subsequent fading. The ATTS (8), LACT, and MZN methods especially gave a large subsequent reductive fading. This shows that those two dyes have a high photostability to oxidative attack, but a substantially low one to reductive attack. Although they are isomers in which only the position of the vinylsulfonyl groups is different, they have similar photochemical properties.

(c) Orange BF. This dye showed larger fading on wet fabrics than that of the other bifunctional dyes by all the testing methods used although nearly the same fading as that of Yellow BF occurred on dry fabrics. Compared with the fading on wet fabrics, the JIS (5.5) and MZN methods had no effect on the initial fading, while the JIS (8), ATTS (3.5), ATTS (8), and LACT methods showed an acceleration effect. Except for the ATTS (8) method, all the methods suppressed the subsequent reductive fading, implying that this dye is readily photo-oxidized compared with the other bifunctional dyes. This dye therefore, has a lower photostability to oxidative attack than the two red dyes, but a higher one to reductive attack.

3.4.6 Yellow R

Yellow R exists mainly in the azo form and has some ease with which it is photo-oxidized as well as photo-reduced [5, 6]. Compared with the fading on wet fabrics, the JIS (5.5) method suppressed the initial fading of this dye, but the JIS (8), ATTS (3.5), and ATTS (8) methods had little effect on it, and the LACT and MZN methods promoted it (cf. Figure 2 and Table 4). In the cases of the LACT and MZN methods, initial oxidative fading occurs, followed immediately by a reductive fading promoted by the large amount of substrate. Thus, the presence of substrate suppressed the initial fading and promoted subsequent fading, except for in the case of the JIS method.

In the case of the ATTS (8) method, the initial fading disappeared and subsequent reductive fading occurred substantially. Due to the larger amounts of substrate in the ATTS methods than those in the JIS methods and the shift to the azo form at pH 8, the rates of subsequent reductive fading by the ATTS (8) method were considerably larger than those by the ATTS (3.5) and JIS (5.5) methods.

3.4.7 CI Reactive Red 4

This dye was sensitive to changes in the environment, such as humidity, pH, the addition of substrate, etc. The variations of initial fading with different testing methods were complicated, since this dye exists as a mixture of azo and hydrazone forms highly sensitive to change in pH. Compared with the fading on 'ever-wet' fabrics, the JIS (5.5), JIS (8), and MZN methods suppressed the initial oxidative fading by the presence of substrate, while only the ATTS (8) method accelerated the initial fading. The rates of subsequent fading were substantially promoted by substrate.

3.4.8 CI Reactive Red 22

As in the case of CI Reactive Red 4, the fading of this dye was also sensitive to the change in environment, since the azo-hydrazone tautomerism is also sensitive to a change in pH. Compared with the case of wet fabrics where a large fading was observed, the JIS (5.5), ATTS (3.5) and MZN methods suppressed the initial fading, while the other methods promoted it. The ATTS (8) and LACT methods promoted subsequent reductive fading, but the other methods suppressed it. The high photosensitivity of this dye is diminished by substrate.

3.4.9 Cu-Pc

Except for the case of the initial fading by the JIS (8) method, all the methods promoted the initial fading as well as subsequent fading, compared with the case of wet fabrics. The considerable ease with which Cu-Pc is photo-oxidized seems to be lessened, while the high ease with which it is photo-reduced is further promoted by substrate, depending on the methods. Since the redox potential of this dye is sensitive to a change in pH [37], this dye showed the same pH effects on the fading behavior as those for azo dyes. Thus, an increase in pH promotes photo-reduction and a decrease in photo-oxidation.

3.4.10 CI Reactive Black 5

All the methods promoted the initial and subsequent fading, although the effects varied with the methods. This dye has a rather high photostability to oxidative attack rather than a reductive one. The testing methods using acid artificial perspiration gave smaller initial fading to that at pH 8, while those at pH 8 and in the neutral range showed a larger initial and subsequent fading than that in the acid region, although the ATTS (3.5) method accelerated both the initial and subsequent fading. The ATTS, LACT, and MZN methods, especially, strongly enhanced the subsequent fading. A change in pH affects the azo-hydrazone tautomerism, but since this dye has two kinds of azo groups, the pH effect is very complex.

3.5 Assessments of the testing methods

3.5.1 JIS methods [12]

The JIS methods gave ratings between 2.5 and 4.5 for the 14 dyes examined. From the values of ΔE^*_{ab}, the JIS (5.5) method distinguished Cu-Pc from the other dyes, in which differences in the fading behavior were small, while the JIS (8) method distinguished CI Reactive Red 4, CI Reactive Red 22, Cu-Pc, and Yellow from the other dyes (Figs 3 and 4). Thus, these methods could classify the grade of dyes with low fastness. The differences in the ratings estimated by the JIS (5.5) and JIS (8) methods were within 0.5 of GS_c. The JIS L 0888 method should be modified to improve the shortcomings due to too small an amount of substrate.

Although the fading behavior by the JIS methods was considerably different from that on initially wet and 'ever-wet' fabrics (cf. Figs 2–4), the gray scale ratings determined by JIS methods were almost similar to those determined on wet fabrics, except for Cu-Pc (cf. Table 3). The JIS methods estimate firstly the effect of water and secondarily the effects of pH and substrate on the fading behavior of the dyes examined.

3.5.2 ATTS methods [13, 14]

The ATTS (3.5) method gave the ratings between 1 and 4 for the 14 dyes examined, while the ATTS (8) method gave ratings between 1 and 3.5. the fading behavior by both the ATTS methods differed considerably (Figs 5 and 6). The differences in the fading behavior can be attributed to pH effects, including the differences in the adsorption of histidine on cellulose [10], since the concentrations of substrate are the same. The ATTS (3.5) method distinguished Cu-Pc, CI Reactive Red 4, and CI Reactive Black 5 from the other dyes. The differentiation or grading of dyes by this method seems to be insufficient, although it can use for a rough estimation.

The ATTS (8) method classified the ratings well, depending upon the subsequent fading, since little initial fading was observed as illustrated in Fig. 6. Since the fading behavior by this method diverged after exposure longer than 4 h, differentiation between the dyes examined was excellent. The method seems to be too severe to estimate the colorfastness to light and perspiration for the 14 dyes investigated. However, this method is an excellent one which can estimate the photostability of dyes to both oxidative and reductive attack.

3.5.3 LACT methods [16]

This method has been proposed to estimate mainly the photo-reductivity of dyes. It gave the ratings between 1 and 4.5 for the 14 dyes used. The fading behavior in Fig. 7 implies that this method can estimate the photo-reductivity of the dyes to an acceptable level and distinguish dyes with low and high stability to photo-reductive attack. Testing methods other than the LACT method use artificial perspiration at pH 3.5, 5.5, or 8 from the similarity to the testing method for colorfastness to perspiration. The present authors, however, have an opinion that an aqueous neutral perspiration should be used to estimate the compound effects of light and perspiration on the photochemical properties of dyes, because, as shown by the differences in the fading behavior with pH in the JIS and ATTS methods, no viable results could be extracted from the differences, unless they were analyzed in detail. The results obtained imply that the LACT method is an adequate method.

3.5.4 Mizuno method [15]

The MZN method gave ratings between 1 and 3 for the dyes used. Since it estimates the colorfastness or the spectrum of photochemical properties for reactive dyes as ratings over a narrow range, the method cannot differentiate the properties of the dyes examined, as shown in Fig. 8. The method assessed Orange, Yellow, CI Reactive Red 227, and CI Reactive Red 194 as having low ratings. Since, except for bifunctional reactive dyes, the other methods gives higher ratings for Orange than the MZN method, the estimation by the MZN method may be inappropriate or too severe for existing reactive dyes.

Differences larger than 1.0 between the ratings estimated by the LACT and MZN methods were observed for Yellow, Orange, CI Reactive Blue 2, CI Reactive Blue 19, Brown and Yellow BF. Except for Yellow and Orange as mentioned above, estimation by the MZN method for the other four dyes may be imprecise, since they are determined to have high ratings by testing methods other than the MZN method.

3.5.5 Comparison of testing methods used

There is a essential problem in estimating the properties of reactive dyes, i.e., whether stability only to photo-reductive attack, or stability to both photo-reductive and oxidative attack, is to be examined. The JIS, ATTS, and MZN methods estimate the stability to both attacks, and the LACT method only the stability to reductive attack. The former may be ideal, although the ratings obtained cannot reveal the essential properties of the dye. The one-point measurements by these testing methods cannot represent both properties, since the 14 dyes used have diverse properties whose fading behavior appears dependent upon the environmental conditions.

In the present assessment, using cotton fabrics dyed with 14 reactive dyes, the ATTS and LACT methods were acceptable, but not the JIS and MZN methods. In the ATTS methods, the ATTS (8) method may be more reasonable for the fading behavior than ATTS (3.5). As mentioned above (cf. 3.5.3), the use of alkaline and acid perspiration seems to be fruitless, if no Cu-complex azo dyes are applied.

If the dyes which have substantive stability to the compound effect of both light and perspiration are selected from the dyes used in the present study, the order of the stability may be estimated from the results of GS_c (Table 3) as follows:

$$\text{Yellow BF} < \text{Orange} \approx \text{Brown} < \text{Blue 2} \approx \text{Blue 19} \approx \text{Yellow R} \leq \text{(Yellow)} \quad (3)$$

If the photo-oxidizability is not fully regarded, Yellow may be added to this list.

4 SUMMARY

In order to assess the testing methods for colorfastness to light, light and water, and light and perspiration, the fading behavior of cotton fabrics dyed with 14 reactive dyes was analyzed in terms of their potential photochemical properties and environmental conditions. On exposure of cotton fabrics dyed with reactive dyes by these methods, oxidative and/or reductive fading occurred, depending firstly on the chemical structure of dyes and secondarily on the environmental conditions. Since the addition of substrate promoted reductive fading or suppressed oxidative fading, how the potential photochemical properties were influenced by environmental conditions was evaluated with respect to the testing methods.

Reactive dyes, however, have potentially diverse properties which are sometimes contradictory to each other and undergo various kinds of photodecomposition on cellulose depending on the environmental conditions. It was shown that no practical testing methods could strictly estimate whether oxidative or reductive fading of a reactive dye occurred. However, practical testing methods aim to estimate the stability to both oxidative and reductive attacks. Judging from the fading of the 14 reactive dyes on cotton fabrics by these methods, only a limited number of methods were shown to be adequate.

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REFERENCES

1. Okada, Y., Hirose, M., Kato, T., Motomura, H. and Morita, Z., *Sen'i Gakkaishi*, 1990, **46**, 346–355.
2. Okada, Y., Motomura, H. and Morita, Z., *Dyes and Pigments*, 1991, **16**, 205–221.
3. Okada, Y., Hirose, M., Kato, T., Motomura, H. and Morita, Z., *Dyes and Pigments*, 1990, **14**, 113–127.
4. Okada, Y., Hirose, M., Kato, T., Motomura, H. and Morita, Z., *Dyes and Pigments*, 1990, **14**, 265–285.

5. Okada, Y., Sato, E., Motomura, H. and Morita, Z., *Dyes and Pigments*, 1992, **19**, 1–19.
6. Okada, Y., Motomura H. and Morita, Z., *Dyes and Pigments*, 1992, **20**, 123–135.
7. Okada, Y., Asano, M. and Morita, Z., *Dyes and Pigments*, 1996, **31**, 53–67.
8. Okada, Y., Nagashima, T., Iizuka, H., Asano, M. and Morita, Z., *Dyes and Pigments*, 1995, **33**, 239–250.
9. Okada, Y., Kawanishi, T., Motomura, H. and Morita, Z., *Dyes and Pigments*, 1994, **24**, 99–111.
10. Okada, Y., Kawanishi, T. and Morita, Z., *Dyes and Pigments*, 1995, **27**, 271–285.
11. Okada, Y., Asano, M. and Morita, Z., The 17th IFATCC Congress, June 5–7, 1996, Vienna.
12. Japanese Standards Association, JIS (Japanese Industrial Standard) L 0888-1990.
13. Urahata, T., Noshi, H. and Noda, K., *Descente Sports Science*, 1986, **7**, 74–84.
14. Urahata, T., Noshi, H. and Noda, K., *Descente Sports Science*, 1987, **8**, 32–54.
15. Mizuno Co. Ltd., Testing Method for Colour Fastness to Light and Perspiration.
16. Okada, Y., Murata, J. and Morita, Z., *Sen'i Seihin Shohi Kagaku*, 1993, **34**, 678–685.
17. International Standard, ISO 105-J03, 1995.
18. International Standard, ISO 105-A05, 1996(E).
19. Okada, Y., Orikasa, K., Motomura, H. and Morita, Z., *Dyes and Pigments*, 1992, **19**, 203–214.
20. Okada, Y., Fukuoka, F. and Morita, Z., *Dyes and Pigments*, 1998, **35**, 311–330.
21. Okada, Y., Fukuoka, F. and Morita, Z., *Dyes and Pigments*, 1998, **37**, 47–64.
22. International Standard, ISO 105-B02, 1988.
23. Japanese Standards Association, JIS L 0842-1996, JIS L 0843-1988.
24. Lyčka, A. and Macháček, V., *Dyes and Pigments*, 1986, **7**, 171–185.
25. Mustroph, H., Potocnak, J. and Grossmann, N., *Journal für praktische Chemie*, 1984, **326**, 979–984.
26. Datyner, A., Nicholls, C. H. and Pailthorpe, M. T., *Journal of the Society of Dyers and Colourists*, 1977, **93**, 213–216.
27. Giles, C. H., Shah, C. D., Johari, D. P. and Sinclair, R. S., *Journal of the Society of Dyers and Colourists*, 1972, **88**, 59–62.
28. Ball, P. and Nichollas, C. H., *Dyes and Pigments*, 1982, **3**, 5–26.
29. Gabor, G., Frei, Y., Gegiou, D., Kaganowitch, M. and Fischer, E., *Israel Journal of Chemistry*, 1967, **5**, 193–212.
30. Bell, S. J., Mazzola, E. P. and Coxon, B., *Dyes and Pigments*, 1989, **11**, 93–99.
31. Blus, K. and Kraska, J., *Dyes and Pigments*, 1992, **18**, 163–177.
32. AATCC Test Method 125-1986.
33. AATCC Test Method 126-1986.
34. Bonneau, R., Pottier, R., Bagno, O. and Joussot-Dubien, J., *Journal of Photochemistry and Photobiology*, 1975, **21**, 159–163.
35. Sysak, P. K., Foote, C. S. and Ching, T.-Y., *Photochemistry and Photobiology*, 1977, **26**, 19–27.
36. Papeschi, G., Monici, M. and Pinzauti, S., *Medecine, Biologie, Environnement*, 1982, **10**, 245–250.
37. Lever, A. B. P., Milaeva, E. R., and Speier, G., The redox chemistry of metalophthalocyanines in solution, In *Phthalocyanines, Properties and Applications*, Vol. 3, ed. C. C. Lenznoff and A. B. P. Lever. VCH Publishers, Inc., New York, 1993, Chapter 1, pp. 1–69.