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Relationship between photochemical properties and colourfastness due to light-related effects on monoazo reactive dyes derived from H-acid, γ-acid, and related naphthalene sulfonic acids

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Abstract

Photofading of 15 reactive azo dyes derived from H- (seven), J-, L-, R-, 2R-, γ-acids (three), pyrazoline and a reactive copper-complex dye on cellophane under wet conditions was examined to estimate the essential properties: photo-oxidisability (k_0: the reactivity with molecular singlet oxygen), photosensitising ability (f) and photo-reductivity. The relationships between the essential properties of these dyes and the lightfastness (LF) as well as the perspiration-light-fastness (PLF) on cotton fabrics are discussed. A linear correlation between the logarithmic product, log ($f\,k_0$), and the LF ratings of dyes on dry cotton fabric was found when plots of reactive dyes with low LF and those of the vat dyes examined in a previous paper were added because the ratings of 11 red dyes out of 15 dyes examined had a narrow range. It showed that LF of monoazo red reactive dyes on dry cotton fabric is very dependent on photo-oxidative fading. A linear correlation was also found between logarithms of f-values and the relative initial rates of photo-reductive fading, except for dyes with very high photosensitising ability. A conflicting relationship between the k_0-values and the photo-reductivity could be shown for dyes derived from H- and γ-acids, an unsolved restriction on synthesis of azo dyes with excellent LF as well as PLF. Azo dyes derived from γ- and 2R-acids possess smaller f but larger k_0 values than those derived from H-acids. The photofading of dyes on cotton fabrics in the presence of artificial perspiration was explained in terms of the essential properties. The substrates promoted photo-reduction and suppressed photo-oxidation.

Keywords: Reactive azo dye from H- and γ-acids; Lightfastness; Photosensitising ability; Photo-reduction; Photo-oxidation; Perspiration-lightfastness

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1. Introduction

During the latter half of the last century, dye manufacturers developed many new reactive groups, most of which subsequently disappeared due to severe commercial selection. At present in Japan, more than 80% of reactive dyes contain vinylsulfonyl (VS) groups and less than 10% of dyes have only monochlorotriazinyl (MCT) groups. Several reactive dyes with excellent lightfastness (LF) have a common chromophore but different reactive groups, although some improvements in methods to combine the reactive groups have been made. From the limitation of intermediates and their combination, partial modification of chromophores for reactive dyes has been made. Von der Eltz [1,2] reported the development and dyeing properties of Remazol dyes in detail except for the improvement of LF.

In the history of vat dyes over the last century, phototendering of cellulosic fibres sensitised by vat dyes has been extensively studied [3–7]. Because vat dyes undergo photosensitisation and photoreduction in the photochemical processes, both processes have various effects on cellulosic substrates, depending on the dye itself and its partner dyes. Besides the degradation of cellulose by UV light, cellulose suffers photosensitised tendering by vat dyes, while vat dyes suffer catalytic fading (or blue eating) in mixed dyeing. Several workers [8–13] and the present authors [14] reported that the photofading and phototendering properties of annelated anthraquinone vat dyes were attributable to the excited triplet $T_1(n\pi^*)$ states of carbonyl groups, while those of tendering active vat dyes were due to excited triplet $T_1(\pi\pi^*)$ states beside the excited triplet $T_1(n\pi^*)$ states of carbonyl groups. The photosensitising ability of vat dyes is proportional to their photo-reductivity. Moreover, dyes on dry cellulose under aerobic conditions suffer oxidative fading in the superficial part of the substrate and simultaneous reductive fading beneath the oxidised parts. Thus, the mechanism of photofading for vat dyes has been clarified to this extent.

The mechanisms of photofading of azo dyes on various polymeric substrates, however, are somewhat controversial [3,5,6,15]. In the case of azo dyes, azo groups are involved in the photo-reduction and photo-oxidation based on different reaction mechanisms depending upon whether the dyes exist as azo or hydrazone tautomers [14,16]. The relationship between the photosensitising ability and the photo-reductivity of azo dyes has not yet been made clear.

On the other hand, several workers [17–30] have studied the relationships between chemical structure and fastness properties for a series of reactive azo dyes from the more practical viewpoint of substitution effect on the fastness than the previous paper [14]. Bredereck and Schumacher studied the acid dissociation, azo-hydrazone tautomerism, dye aggregation [17], stability to hypochlorite bleach [18], stability to peroxide bleach [19] and light stability of dry and wet cotton fabrics in the presence of perspiration [20] for 12 derivatives of C.I. Reactive Red 227 (Red 227) synthesized using different diazo components. Gregory and Stead [21] carried out a systematic study on the stability of a series of 2-arylazonaphthalene sulfonic acids to hypochlorite bleach and discussed the reaction mechanism, which was different from that reported by Bredereck and Schumacher [18]. Omura et al. reported the molecular design of chlorine-fast heterobifunctional reactive dyes [22–26] and formaldehyde-fast diazo dyes [27]. They optimized the fastness properties of mono- and diazo dyes derived mainly from naphthol sulfonic acids by the substitution effect or by changing diazo components and the numbers and positions of the sulfonic acids. Vig et al. [28–30] studied the light and perspiration-light stability of related compounds of C.I. Reactive Red 194 (Red 194) (eight) and Orange 72 (six) by changing reactive groups and connecting ones. They denied the higher light stability of the dye-fibre bonds. Imada et al. [31] examined the perspiration-lightfastness (PLF) for 22 reactive dyes.

The present authors reported the photofading of a series of reactive dyes on cellulose that was dependent primarily upon the chemical structure and secondarily upon the environmental conditions of exposure [32–40]. The photofading of C.I. Reactive Red 4 [37–39], C.I. Reactive Red 22 [33–35], Red 194 [39,40], and Red 227 [39,40] was analyzed in terms of their potential properties by taking the environmental conditions of exposure into consideration. They reported the photochemical reactivity of triphenodioxazine (TPDO) dyes [41–43]. TPDO dyes possessed high PLF due to the effective internal conversion $S_1 \rightarrow S_0$ or low quantum yield to T_1 state but had high thermal reactivity as a shortcoming [43]. The reason vat dyes had the highest LF among dyes for cellulose was attributed to the very low quantum yield to T_1 state and the very small reactivity with $^1O_2$.

In the present paper, photo-sensitised fading, photosensitising ability and the ease with which fifteen azo reactive dyes derived from naphthalene sulfonic acids were photo-oxidised on cellophane were examined under aerobic conditions and photo-reductive fading using DL-mandelate under anaerobic conditions. Fading of dyed cotton fabrics due to the compound effects of light and artificial perspiration is also estimated, and how the fading can be explained by the estimated essential properties of the dyes is discussed.

2. Experimental

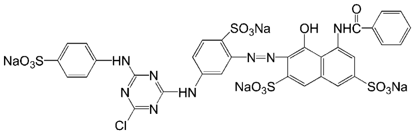
2.1. Materials

2.1.1. Dyes used

Ten VS, one MCT and four mixed-bifunctional reactive dyes derived from H- (seven), J- (one), L- (one), R-(one), 2R- (one), γ-acids (three), and pyrazoline (one) were used. An aminopyrazolinyl azo dye examined in previous studies [33,34] was used as a typical dye with great photo-oxidizability. A copper-complex azo dye of red hue was also used. Except for dyes in the previous studies [32–40] and dyes manufactured by DyStar Japan Ltd., dyes used were prepared according to the usual procedure [44]. The LF and PLF of 15 dyes on cotton dyed in 1/1 and 1/3 of standard depth, estimated by the JIS method [45–47], are listed in Table 1. Using a Y-46 filter, LF was also estimated by the same method. In order to prevent the heating of test fabrics, wood spacers with a thickness of 4.0 mm were set on the two perpendicular edges of the fabric between the filter and fabric. The results are also listed in Table 1.

The chemical structures of these dyes together with C.I. Generic Name, abbreviations in parentheses, C.I. Constitution Number, if available, and the λ_{max} on cellophane films are shown below:

(1) C.I. Reactive Red 4 (Red 4), C.I. 18105, $\lambda_{max} = 551.0$ nm



(2) C.I. Reactive Red 22 (Red 22), C.I. 14824, $\lambda_{max} = 515.0$ nm

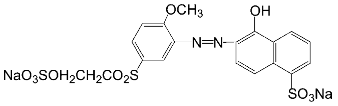


Table 1
Colourfastness of red reactive dyes on cotton fabric

Dye	Light[a]			Perspiration-light[b,c]	
	No filter		Y-46 filter	Acid	Alkaline
Depth	N/3	N/1	N/1	N/3	N/3
Pyr-Yellow	3–4	5	–	4	4–5
Red gVS	5–6	6	6–7	5^-	4–5
Red pgVS	4–5	5	5–6	5^-	3–4
Red mgVS	4–5	4–5	5–6	4–5	3
Red 2RVS	5–6	5–6	6–7	5^-	$2–3^+$
Red TAVS	4–5	5	5–6	3–4	$2–3^+$
Orange JVS	4	4	5–6	4	3–4
Red 4[d]	4	4–5	5–6	2	1
Red 22[d]	3	3–4	5	2	2
Red 23[d]	6	7	7	4–5	4
Red 180[d]	5	5–6	6	2–3	2
Red 194[d]	5	5	6	3–4	2–3
Red 227[d]	5	5	6	3–4	2–3
Red 241[d]	5	5–6	6	3–4	2–3
Red MCVS	5	5	6	3	2–3

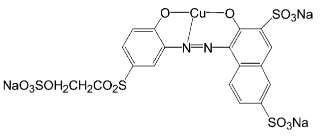
[a] JIS L 0842 (Carbon arc).

[b] JIS L 0888, in which the concentration of histidine in the artificial perspiration is ten times larger than the established one.

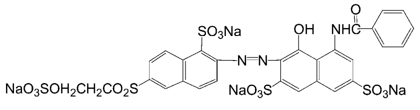
[c] 5^- and $2–3^+$ describe the rating between (4–5) and 5, and that between (2–3) and 3, respectively.

[d] C.I. Reactive Generic Name.

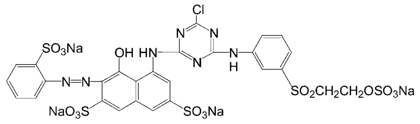
(3) C.I. Reactive Red 23 (Red 23), C.I. 16202, $\lambda_{\max} = 531.0$ nm



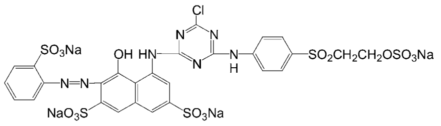
(4) C.I. Reactive Red 180 (Red 180), C.I. 181055, $\lambda_{\max} = 551.0$ nm



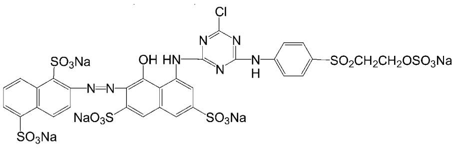
(5) C.I. Reactive Red 194 (Red 194), C.I. 18214, $\lambda_{\max} = 546.0$ nm



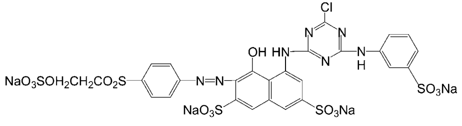
(6) C.I. Reactive Red 227 (Red 227), C.I. 18215, $\lambda_{\max} = 545.5$ nm



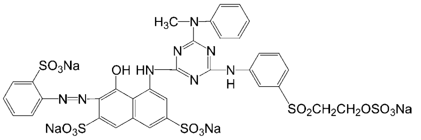
(7) C.I. Reactive Red 241 (Red 241), C.I. 18220, $\lambda_{\max} = 555.0$ nm



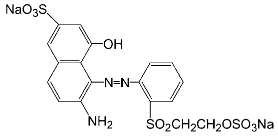
(8) A red dye derived from H-acid having a monochlorotriazinyl group and a VS one (Red MCVS), $\lambda_{\max} = 528.5$ nm



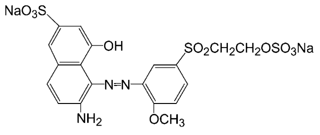
(9) A red dye derived from H-acid having a VS reactive group and a monochlorotriazinyl bridge group (Red TAVS), $\lambda_{\max} = 549.0$ nm



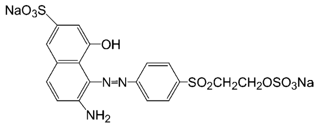
(10) A red dye derived from γ-acid having a VS reactive group (Red gVS), $\lambda_{\max} = 524.0$ nm



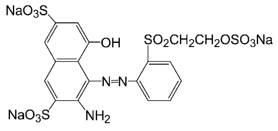
(11) A red dye derived from γ-acid having a 1-methoxy-4-vinylsulfonyl-phenylazo group (Red mgVS), $\lambda_{\max} = 514.0$ nm



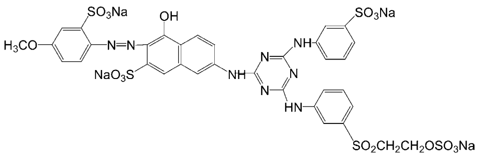
(12) A red dye derived from γ-acid having a *p*-(vinylsulfonyl)phenylazo group (Red pgVS), $\lambda_{\max} = 519.0$ nm



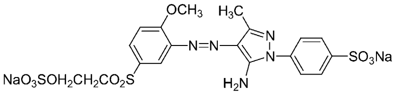
(13) A red dye derived from 2R-acid (Red 2RVS), $\lambda_{\max} = 532.0$ nm



(14) An orange dye derived from J-acid having a VS reactive group and a monochlorotriazinyl bridge group (Orange JVS), $\lambda_{\max} = 509.5$ nm



(15) An aminopyrazolinyl azo dye (Pyr-Yellow) which is very easily photo-oxidized, $\lambda_{max} = 397.0$ nm



2.2. Preparation of dyed samples

2.2.1. Dyeing of cellophane sheets

Cellophane films (Futamura Kagaku Kogyo K.K. #300), cut 3 cm in width and 50 cm in length, were scoured in boiling water for more than 2 h and dyed with each dye by the alkali-shock method to obtain an absorbance between 0.8 and 1.0 at the λ_{max} [33,38,39].

2.2.2. Mixed dyeing of cellophane sheets with Pyr-Yellow and red dyes

Mixed dyeing was carried out by the alkali-shock method for MCT dyes and Pyr-Yellow and by the all-in method at pH 9 for the other VS dyes according to the previous study [43]. After the fixation, the dyed films were repeatedly washed in boiling water to remove the unfixed dyes.

2.3. Estimation of photochemical properties

2.3.1. Estimation of the ease with which dyes are photo-oxidized by use of Rose Bengal

By exposing cellophane films dyed with reactive dyes to a carbon arc on immersing them in aerated aqueous Rose Bengal solution, the relative fading of individual dyes was estimated [33,34]. Because reactive dyes combined with cellulose have different numbers of sulfonic acid groups and further the adsorption of Rose Bengal on dyed cellulose is different from dyes, especially in low concentrations of neutral salt, a high concentration of sodium sulfate (0.5 M) was added to the Rose Bengal solution. The solution was renewed every 5 h during exposure to keep the adsorption of Rose Bengal constant. From the initial rates of fading, the ease with which the dye was photo-oxidized was estimated as values of k_0 (dm^3 mol^{-1} s^{-1}) [33,34].

2.3.2. Estimation of photosensitising ability

For the estimation of photosensitising ability of 14 red dyes, cellophane films dyed in an admixture of red dyes and Pyr-Yellow were exposed through a Toshiba filter Y-46 ($>$ 460 nm) to a carbon arc [33,34]. The values of f were estimated from the rates of fading for Pyr-Yellow of the mixed dyes according to the method of previous studies [33,34,43].

2.3.3. Estimation of the ease with which dyes are photo-reduced

By exposing the dyed cellulosic films to a carbon arc on immersing them in an anaerobic aqueous DL-mandelate (0.05 mol dm^{-3}) solution, to which sodium sulfate (0.5 mol dm^{-3}) was added to prevent the coion exclusion of DL-mandelate, the relative fading, A/A_0, was estimated to exhibit the photo-reductivity of individual dyes [35].

2.3.4. Testing methods for PLF

The recipes of the artificial perspiration in which the test fabric dyed with reactive dyes to be tested was immersed before exposure and the method of exposure were previously reported [39,40]. The testing method is based on JIS L 0888 [47] in which the artificial perspiration is modified.

3. Results and discussion

3.1. Photo-oxidative fading of monoazo reactive dyes

3.1.1. Ease with which dyes are photo-oxidized

In order to estimate the ease with which the azo dyes were photo-oxidized, the photosensitized fading of 15 monoazo reactive dyes on cellulose films immersed in aqueous Rose Bengal solution was examined by exposing to a carbon arc. The fading behaviours for the dyes examined are illustrated in Fig. 1.

The present authors [34] estimated the second-order rate constant, k_0 (mol^{-1} dm^3 s^{-1}), of Pyr-

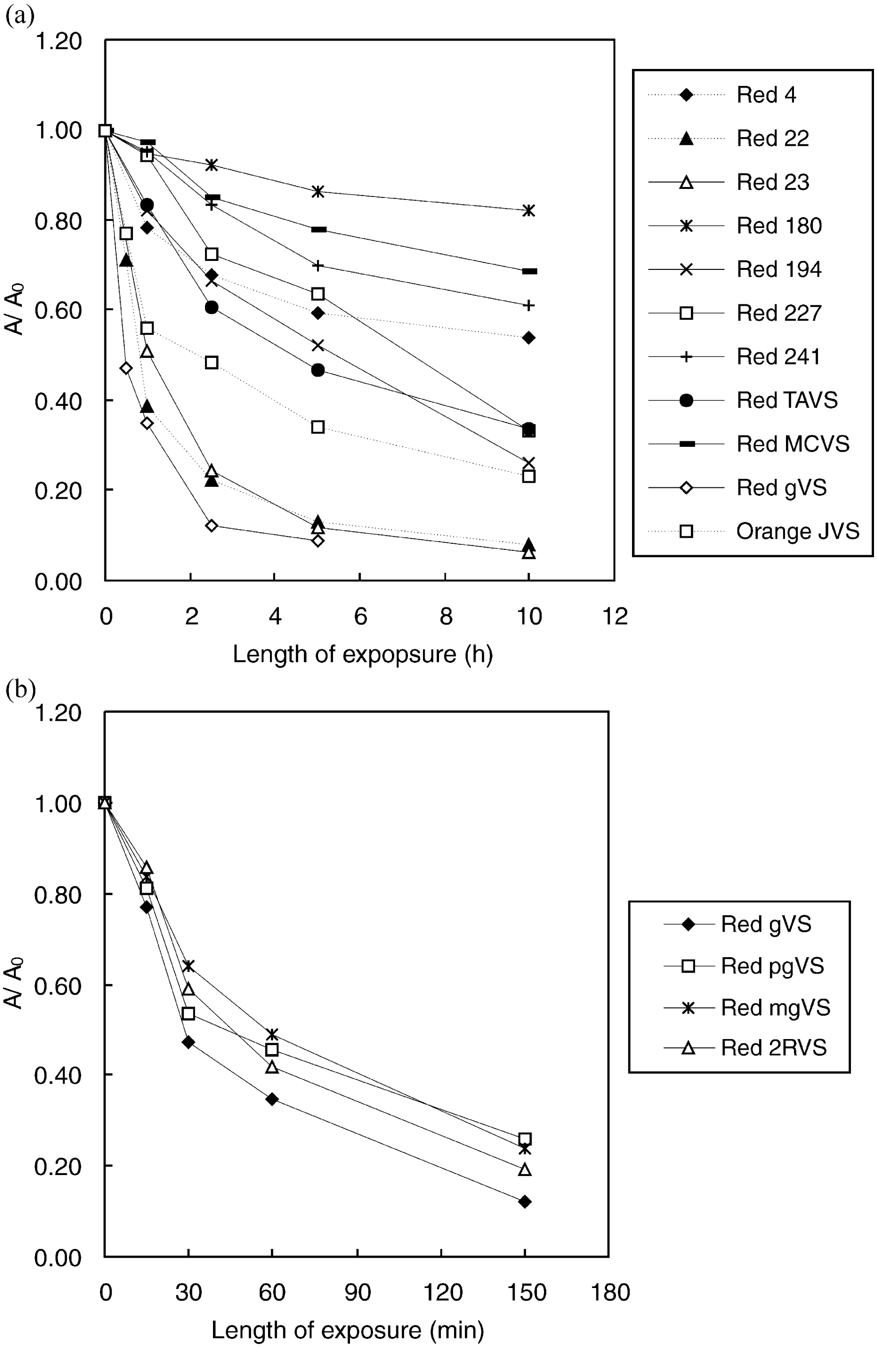


Fig. 1. Fading of reactive azo dyes (a) at lower rate and (b) at higher rate on cellulose films on exposure in aerated aqueous Rose Bengal (3.3×10^{-5} mol dm^{-3} + 0.50 mol dm^{-3} Na_2SO_4) solution. The solution of Rose Bengal was renewed every 5 h. (Fading of Red gVS is illustrated in both figures.)

Yellow for the reaction between the dye and $^1O_2$ generated by Rose Bengal from the rates of fading for the initial time of exposure. This process may be described as follows:

$$D + {}^1O_2 \xrightarrow{k_0} \text{Oxidation product of dyes} \tag{1}$$

$$\frac{d[D]}{dt} = -k_0[{}^1O_2][D] \tag{2}$$

Since the proportion of dyes in the excited states is quite low, oxidation may occur for almost all dyes in the ground state. The oxidation of dyes is controlled not only by the reaction Eq. (2) but also by the quantum yield of $^1O_2$ generation (cf. 3.1.2). These reactions proceed in water-swollen cellulose, a heterogeneous reaction system. As photo-oxidation progresses, the concentration of dyes becomes non-uniform. Since the concentration of oxygen is lower than that of the dyes, oxygen must be supplied from the surface of the substrate by diffusion. Moreover, the excitation of dyes occurs preferentially from the surface due to the filter effect. The photo-oxidation proceeds from the surface from which light enters.

The value of k_0 may be regarded as a measure of the ease with which the dye is oxidized. By a use of the value of k_0 for Pry-Yellow as the reference, the values k_0 for the other dyes were estimated from the rates of fading illustrated in Fig. 1 by the same method as before [33,34,43]. Their values are listed in Table 2. The order of the values of k_0 for these dyes was:

$$\begin{aligned}&\text{Red 180} < \text{Red MCVS} < \text{Red 241} < \text{Red 227}\\&\quad < \text{Red 4} < \text{Red TAVS} < \text{Red 194}\\&\quad << \text{Orange JVS} < \text{Red 23} << \text{Red mgVS}\\&\quad < \text{Red pgVS} < \text{Red 2RVS} < \text{Red 22}\\&\quad < \text{Red gVS} \leqslant \text{Pyr-Yellow}\end{aligned} \tag{3}$$

This order (3) does not correspond to the order of LF (cf. Table 1).

Table 2
Values of the rate constant, k_0 ($dm^3\ mol^{-1}\ s^{-1}$) of the second-order reaction with $^1O_2$, the apparent photosensitivity, f (cf. Table 3), and the values of relative reductive fading, A/A_0, in anaerobic sodium DL-mandelate solution for red reactive dyes on cellulose on exposure to carbon arc under wet conditions

No	Dyes	k_0 (Exp. for 5 h)[b] ($dm^3\ mol^{-1}\ s^{-1}$)	f	f	A/A_0 in MA[c]	
			Y-46 filter	No filter	2 h	4 h
1	Red gVS	0.70	7.42×10^{-4}	–	0.943	0.915
2	Red pgVS	0.59	9.19×10^{-4}	–	0.819	0.591
3	Red mgVS	0.55	3.55×10^{-4}	–	0.923	0.648
4	Red 2RVS	0.62	6.90×10^{-4}	–	0.900	0.618
5	Red TAVS	0.098	0.0017_1	–	0.837	0.707
6	Orange JVS	0.19	0.0016_9	–	0.788	0.389
7	Red MCVS	0.048	0.0020_9	–	0.427	0.236
8	Red 4[a]	0.088	0.0097	0.088[48]	0.758	0.518
9	Red 22[a]	0.66	0.029	0.11 [34]	0.672	0.371
10	Red 23[a]	0.22	0.0022_7	–	0.638	0.058
11	Red 180[a]	0.030	0.0060	–	0.285	0.022
12	Red 194[a]	0.10_2	0.0023_0	–	0.684	0.543
13	Red 227[a]	0.078	0.0028	–	0.703	0.432
14	Red 241[a]	0.064	0.0016_6	–	0.588	0.377
15	Pyr-Yellow	6.9 [34]	5.89×10^{-4}[d]	0.015[34]	1.0 [50]	1.0 [50]
16	Rose Bengal	–	0.76 [49]	0.76 [49]	–	–

[a] C.I. Reactive Generic Name.

[b] In aqueous RB (3.3×10^{-5} M + 0.5 M Na_2SO_4) solution.

[c] In MA = in anaerobic aqueous 0.05 M DL-mandelate (+ 0.5 M Na_2SO_4) solution (pH 6.2).

[d] This value was determined by the extrapolation in Fig. 4.

In a strict analysis, however, the effect of self-sensitization on the fading of each dye should be taken into consideration. Fortunately, since the photosensitising ability, *f*, of the 15 dyes examined was considerably smaller than that of Rose Bengal, the effect may be regarded as negligible. It may be necessary to consider it in the dyes with large *f* values (Red 4 and Red 22) (cf. 3.1.2).

3.1.2. Photosensitisation

In a series of studies on the photofading of reactive dyes on cellulose, the authors [33,34,43] determined the photosensitising ability of dyes by estimating the rates of fading for Pyr-Yellow on cellulose dyed in admixture with the fifteen red dyes to be examined. Unlike the reactive dyes examined previously [33,34], these red dyes produced too little fading of Pyr-Yellow to estimate the values of photosensitising ability. In order to shield Pyr-Yellow from self-sensitization, a yellow filter was used (cf. 2.3.2), and the fading of Pyr-Yellow in the admixture was examined. The results are listed in Table 3, from which the quantum yield, *f*, of the generation of $^1O_2$ for 14 dyes was determined by use of *f*-values for Rose Bengal as the reference value [34,49]. The values of *f* determined are listed in Table 2.

The processes from light absorption to sensitization under aerobic conditions can be expressed as follows [51–53]:

$$^1D_0 + h\nu \rightarrow {}^1D_1 \qquad \text{(excitation)} \tag{4}$$

$$^1D_1 \rightarrow {}^1D_0 + h\nu' \qquad \text{(fluorescence)} \tag{5}$$

$$^1D_1 \rightarrow {}^1D_0 \qquad \text{(internal conversion)} \tag{6}$$

$$^1D_1 \rightarrow {}^3D_1 \qquad \text{(intersystem crossing)} \tag{7}$$

$$^3D_1 \rightarrow {}^1D_0 \qquad \text{(intersystem crossing)} \tag{8}$$

$$^1D_1 + {}^3O_2 \rightarrow {}^3D_1 + {}^1O_2 \quad \text{(singlet sensitisation)} \tag{9}$$

$$^3D_1 + {}^3O_2 \rightarrow {}^1D_0 + {}^1O_2 \quad \text{(triplet sensitisation)} \tag{10}$$

Table 3
Values of A/A_0 for Pyr-Yellow on cellulose dyed in admixture with VS dyes and the initial rate of fading (min^{-1}) on exposure to carbon arc through Y-46 filter under wet conditions. (The values for red dyes are shown in lower column in parentheses.)

No	Dyes	Initial rate of fading[b]	Time of exposure (h)			
			5 h	10 h	20 h	
1	Red gVS	2.42×10^{-5}	0.988 (0.969)	0.975 (0.961)	0.971 (0.948)	
2	Red pgVS	3.00×10^{-5}	0.993 (0.968)	0.978 (0.941)	0.964 (0.940)	
3	Red mgVS	1.16×10^{-5}	0.989 (0.989)	0.989 (0.982)	0.986 (0.978)	
4	Red 2RVS	2.55×10^{-5}	1.0 (0.998)	0.975 (0.985)	0.973 (0.975)	
5	Red TAVS	5.58×10^{-5}	0.969 (0.987)	0.937 (0.962)	0.922 (0.959)	
6	Orange JVS	5.50×10^{-5}	0.972 (0.977)	0.946 (0.985)	0.934 (0.951)	
7	Red MCVS	6.83×10^{-5}	0.955 (0.978)	0.933 (0.963)	0.918 (0.970)	
8	Red 4[a]	3.18×10^{-4}	0.888 (0.961)	0.807 (0.924)	0.618 (0.878)	
9	Red 22[a]	9.47×10^{-4}	0.716 (0.884)	0.531 (0.871)	0.359 (0.837)	
10	Red 23[a]	7.42×10^{-5}	0.985 (0.983)	0.950 (0.952)	0.911 (0.950)	
11	Red 180[a]	1.96×10^{-4}	0.891 (0.987)	0.853 (0.957)	0.765 (0.955)	
12	Red 194[a]	7.50×10^{-5}	0.981 (0.987)	0.956 (0.986)	0.910 (0.977)	
13	Red 227[a]	9.00×10^{-5}	0.923 (0.988)	0.912 (0.980)	0.892 (0.960)	
14	Red 241[a]	5.42×10^{-5}	0.963 (0.981)	0.954 (0.966)	0.935 (0.959)	
			5 min	10 min	15 min	20 min
15	Rose Bengal	2.48×10^{-2}	0.876	0.773	0.616	0.432
	(no filter)	6.50×10^{-2}	0.675	0.441	0.320	0.189

[a] C.I. Reactive Generic Name.
[b] (min^{-1}).

where D denotes dye molecules, left superscripts 1 and 3 singlet and triplet states, respectively, right subscripts 0 and 1 ground and the first (lowest) excited states, respectively.

The process (5) may not occur much since no fluorescence of dyes was observed on the dyed cellulosic substrate. Since the lifetime of $^1D_1$ is much shorter than that of $^3D_1$, process (9) may be rarer than process (10). The values of f may almost correspond to the ratios of [process (10)]/[process (4)]. It is noted that under aerobic conditions, i.e., in cellulosic substrate swollen in aerated water, reaction of $^3D_1$ with hydrogen-donating substrates was strongly inhibited.

The values of f for Red 4 and Red 22, respectively, were a tenth of the corresponding values estimated without a filter (cf. 3.2). The order of magnitude for the f-values was as follows:

$$\begin{aligned}&\text{Pyr-Yellow} < \text{Red mgVS} < \text{Red 2RVS}\\&\quad < \text{Red gVS} < \text{Red pgVS} < \text{Red 241}\\&\quad \doteqdot \text{Orange JVS} \doteqdot \text{Red TAVS} < \text{Red MCVS}\\&\quad < \text{Red 23} \doteqdot \text{Red 194} < \text{Red 227} < \text{Red 180}\\&\quad < \text{Red 4} << \text{Red 22} \qquad (11)\end{aligned}$$

Although the f-value of Pyr-Yellow was previously determined to be 0.015 (cf. Table 2) compared to a blue dye with the lowest value examined [34], it may be considered that the value should be also the lowest shown in the order (11), taking both the photosensitising ability and photo-reductivity for all the dyes examined in the present study into consideration (cf. 3.2.1, Fig. 4). The f-values for Pyr-Yellow determined by extrapolation may correspond to the value by use of the filter.

No correlation between LF and the order may be found (11). Taking both factors of k_0 and f into consideration, an analysis is given below.

3.1.3. Relationship between photo-oxidative fading and LF on cotton fabric

It was reported by the present authors that LF may depend not only upon the k_0-values but also upon the f-values [14,43]. The log (f k_0) was plotted against the rating of LF as shown in Fig. 2. Since the red reactive dyes examined were remarkably influenced by the filter, estimation of LF by the use of a filter was used. Since common red dyes possess LF ratings around 5, plots of the relation centered around these ratings. Plots of dyes with lower LF and those of vat dyes with higher LF were also added to the figure to clarify the essential relationship. This figure indicates an approximate relation between the log (f k_0) and the rating of LF. Plots of reactive dyes other than azo dyes such as Blue 19 [34], phthalocyanine dye [34], and TPDO dyes [43], which were added to the figure, fell into the same line. As shown in the case of vat dyes [14], this relationship may be common to reactive and vat dyes on cellulose. Since the photo-reduced carbonyl groups of vat dyes are

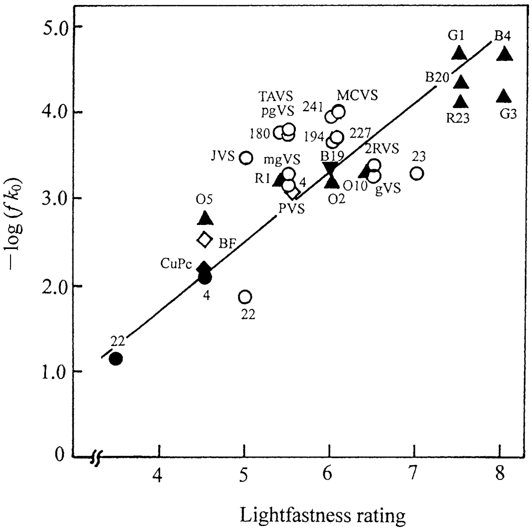


Fig. 2. Correlation between log (f k_0) and the ratings of lightfastness for reactive azo (○, with Y-46 filter; ●, without filter), anthraquinone (▼, C.I. Reactive Blue 19 (B19) without filter [34]), phthalocyanine (◆, VS-CuPc (CuPc) without filter [34]), and triphenodioxazine (◇, PVS-TPDO (PVS) and BF-TPDO (BF) with Y-51 filter [43]) dyes and vat dyes (▲, without filter [14]) on cotton fabric (N/1 depth). (In the figure, symbols of reactive red dyes, used in the present study, are illustrated by numbers or alphabetical symbols without hue names, while symbols for the other reactive dyes are in the parentheses in this caption. Symbols of vat dyes are given by the first character of hue name and its number for C.I. Generic Name.)

completely recovered by air oxidation, which may occur in an inner part of the substrate, the photo-reduction may not contribute to the LF. In the case of azo dyes, however, the photo-reduction of azo groups is not recovered. The photo-reduction of azo groups may make some contribution to the LF of reactive dyes on cotton fabric. However, the contribution may be small since common reactive azo dyes in general possess small quantum yield to the triplet state.

3.2. Photo-reduction of monoazo reactive dyes

3.2.1. Estimation of photo-reductivity

According to van Beek et al. [54–59], photo-reduction of monoazo dyes in solution by the irradiation of UV light generates hydrazyl radical intermediates of dyes, which undergo a disproportional reaction in the dark resulting in the formation of the corresponding amines and iminoquinones as well as the original dyes via different mechanisms depending upon the concentrations of reactants. The intermediates are unstable, have short lifetimes and exist only in low concentration. Although the photoreduction mechanism they proposed may not be acceptable by recent photochemical theories [51–53], their experimental results may be valuable. It was reported also that on irradiation of azo dyes in the presence of substrates such as DL-mandelate and glucose, the formation of active intermediates with strong reducing properties from the substrates, which promoted the formation of amines from azo dyes in the dark, was recognized [54,55]. Although these reactions were carried out homogeneously in solutions, similar reaction behaviours, the stoichiometric generation of amines and little formation of intermediates, were also observed in the present study in water-swollen cellulose [35]. In the electrochemical reduction of azo compounds, mutual interactions between reaction intermediates resulting in the corresponding amines were also reported [60–67].

In the present study, the rates of fading for 15 dyes were determined by irradiating dyed cellophane immersed in an anaerobic aqueous DL-mandelate solution, as shown in Fig. 3. The order of the rates determined was as follows:

$$\begin{aligned}&\text{Pyr-Yellow} << \text{Red gVS} << \text{Red TAVS}\\&\quad < \text{Red mgVS} < \text{Red 2RVS} < \text{Red pgVS}\\&\quad < \text{Red 194} \doteqdot \text{Red 4} < \text{Orange JVS}\\&\quad \doteqdot \text{Red 227} < \text{Red 22} \doteqdot \text{Red 241} << \text{Red 23}\\&\quad \doteqdot \text{Red MCVS} << \text{Red 180}\end{aligned} \qquad (12)$$

The photo-reductivity of Pyr-Yellow was discussed in the previous study [50]. Combining the order of photo-reductivity (12) with the order of photosensitising ability (11), a correlation could be found between the logarithms of photosensitising ability (f) and the relative initial rates of photo-reduction, as shown in Fig. 4. The plots of Red 4 and Red 22 deviated downwards in Fig. 4. This may be attributed to the large influence of the yellow filter as listed in Table 2. Since the Y-46 filter shielded the short wavelength side of the main absorption band of Red 22, which has a small absorption band around 350-380, Red 22 might be strongly influenced by the yellow filter. Similar influences on Red 4 cannot be explained from the absorption spectra. The seven H-acid red dyes had less photosensitising ability than Red 4 in spite of their resemblance in the absorption spectra.

3.3. PLF

As mentioned below, dyes are listed in Table 4 in the descending order of the PLF (cf. Table 1), except for C.I. Reactive Red 23. Although histidine, in general, had a strong effect on the absorption spectra on Cu-complex azo dyes on dyed film immersed in aqueous solution containing histidine, the spectra of Red 23 showed exceptionally little influence [68].

The LF, however, has no such tendency. The potential properties, photosensitising ability, photo-oxidizability, and photo-reductivity, are examined for 15 dyes on cellophane. Why the dyes with these properties undergo fading depending upon the environmental conditions of exposure is discussed.

Evaluation of light-related phenomena by testing methods such as ISO and JIS methods are based on colour variations after exposure of the dyed fabric for a definite time period. The present methods using dyed cellulosic films are to evaluate the potential properties from the initial rates of variation in the absorbance at a definite wavelength. Since the potential properties based on the latter methods can express the essential differences in the LF and the PLF more precisely than the results by the testing methods shown in Figs. 5–12 and Table 4, the three potential properties were used to analyse the photofading phenomenon of azo dyes in the presence of substrates under aerobic conditions.

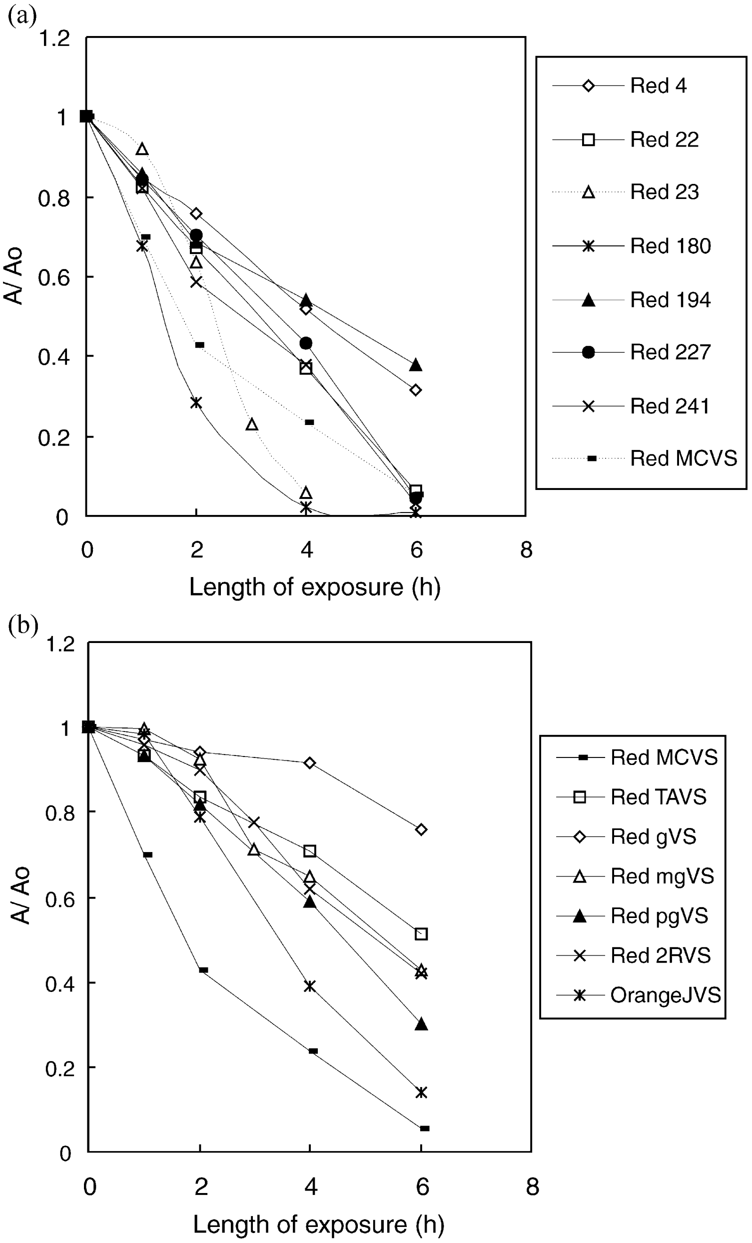


Fig. 3. Fading of reactive azo dyes (a) at higher rate and (b) at lower rate on cellulose films on exposure in anaerobic DL-mandelate (0.050 mol dm^{-3} (pH 6.3) + 0.50 mol dm^{-3} Na_2SO_4) solution. (Fading of Red MCVS is illustrated in both figures.)

Table 4
Values of ΔE^*_{ab}[a], ΔE_{cmc}(2:1)[b], and GS_c(gray scale rating for colour change)[b] for vinylsulfonyl, monochlorotriazinyl and their bifunctional reactive dyes estimated by various testing methods for colourfastness to light and perspiration, and chromaticness values (L^*) of test fabrics (1.0% o.w.f.) by exposure to carbon arc for 8 h and light fastness for 1/1 and 1/6 of standard depth

Colorfastness		Light and perspiration					Light	
Testing method		JIS(8)	ATTS(3.5)	ATTS(8)	LACT	Ever wet[d]	1/6	1/1
Pyr-Yellow	ΔE^*_{ab}	1.82	3.03	2.06	3.15	2.00		
$L^* = 88.78$	ΔE_{cmc}	0.78	1.20	0.85	1.37	0.79	2	5
	ΔE_F(GSc)	1.15(4.5)	1.91(4)	1.15(4.5)	2.15(3.5)	1.20(4.5)		
Red gVS	ΔE^*_{ab}	1.24	2.31	1.09	2.96	26.08		
$L^* = 49.59$	ΔE_{cmc}	0.51	1.02	0.51	1.29	10.97	5–6	6
	ΔE_F(GSc)	0.78(4.5)	1.91(4)	1.04(4.5)	2.49(3.5)	20.38(1)		
Red pgVS	ΔE^*_{ab}	1.63	4.55	4.37	4.48	17.26		
$L^* = 54.23$	ΔE_{cmc}	0.71	2.00	1.88	1.95	7.20	5	5
	ΔE_F(GSc)	1.21(4.5)	3.62(3)	3.35(3.5)	3.57(3)	12.59(1)		
Red mgVS	ΔE^*_{ab}	4.52	2.29	2.23	1.87	12.81		
$L^* = 54.34$	ΔE_{cmc}	2.22	1.02	1.01	0.82	5.69	4	4–5
	ΔE_F(GSc)	3.69(3)	1.90(4)	2.12(3.5)	1.25(4)	10.03(1.5)		
Orange JVS	ΔE^*_{ab}	3.45	3.06	4.57	4.02	4.42		
$L^* = 58.30$	ΔE_{cmc}	1.51	1.43	1.84	1.72	1.78	3	4
	ΔE_F(GSc)	2.99(3)	2.68(3.5)	3.53(3)	3.66(3)	3.21(3)		
Red 2RVS	ΔE^*_{ab}	2.49	4.74	8.51	6.60	5.46		
$L^* = 57.20$	ΔE_{cmc}	1.05	2.00	3.61	2.78	2.32	5–6	5–6
	ΔE_F(GSc)	1.56(4)	3.40(3)	6.55(2)	4.75(2.5)	3.60(3)		
Red TAVS	ΔE^*_{ab}	4.56	4.55	9.33	7.23	2.41		
$L^* = 54.97$	ΔE_{cmc}	1.73	1.82	3.59	2.81	0.94	3–4	4–5
	ΔE_F(GSc)	2.27(3.5)	2.84(3.5)	5.33(2.5)	4.39(2.5)	1.35(4)		
Red 4[c]	ΔE^*_{ab}	7.38	8.88	15.91	11.01	4.40		
$L^* = 59.92$	ΔE_{cmc}	3.07	3.73	6.58	4.63	1.99	3–4	4–5
	ΔE_F(GSc)	4.93(2.5)	6.30(2)	11.69(1)	8.01(2)	3.71(3)		
Red 227[c]	ΔE^*_{ab}	3.82	5.87	15.24	8.87	1.55		
$L^* = 56.96$	ΔE_{cmc}	1.47	2.26	5.93	3.44	0.65	4–5	5
	ΔE_F(GSc)	2.06(4)	3.31(3)	9.59(1.5)	5.41(2.5)	1.29(4)		
Red 194[c]	ΔE^*_{ab}	4.01	5.97	15.37	9.78	2.44		
$L^* = 57.20$	ΔE_{cmc}	1.52	2.31	5.91	3.80	1.21	4–5	5
	ΔE_F(GSc)	2.09(4)	3.44(3)	9.36(1.5)	6.13(2)	2.23(4)		
Red 241[c]	ΔE^*_{ab}	4.94	7.98	16.50	9.48	3.24		
$L^* = 52.35$	ΔE_{cmc}	1.92	3.27	6.51	3.77	1.44	4	5–6
	ΔE_F(GSc)	2.86(3.5)	5.77(2.5)	10.93(1.5)	6.28(2)	2.80(3.5)		
Red 22[c]	ΔE^*_{ab}	6.67	7.88	13.77	12.74	11.53		
$L^* = 61.58$	ΔE_{cmc}	2.77	3.28	5.72	5.39	4.85	3	3–4
	ΔE_F(GSc)	4.47(2.5)	5.87(2)	10.14(1.5)	9.68(1.5)	9.35(1.5)		
Red MCVS	ΔE^*_{ab}	7.67	11.89	22.83	16.59	1.26		
$L^* = 57.07$	ΔE_{cmc}	3.02	4.75	9.14	6.64	0.68	4–5	5
	ΔE_F(GSc)	4.67(2.5)	8.15(2)	16.25(1)	11.63(1)	1.16(4.5)		
Red 180[c]	ΔE^*_{ab}	7.98	11.59	20.39	14.78	1.13		
$L^* = 56.78$	ΔE_{cmc}	3.15	4.63	8.12	5.90	0.60	4	5–6
	ΔE_F(GSc)	4.84(2.5)	7.81(2)	14.00(1)	10.13(1.5)	1.01(4.5)		
Red 23[c]	ΔE^*_{ab}	2.98	4.60	8.52	4.21	2.35		
$L^* = 53.33$	ΔE_{cmc}	1.33	2.03	3.60	1.83	1.11	6	7
	ΔE_F(GSc)	1.97(4)	3.10(3)	5.66(2.5)	2.61(3.5)	1.58(4)		

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

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

[c] C.I. Reactive Generic Name.

[d] Lightfastness on ever wet fabrics estimated by JIS L 0888 method.

3.3.1. Photo-fading of azo dyes in the presence of substrate under aerobic conditions

How the potential properties, illustrated in Figs. 1 and 3 and Tables 1–4, are manifested on exposing 15 dyes on cotton fabric is examined by various testing methods for the PLF. The present authors [38–40] have already assessed whether or not various testing methods can analyze or estimate precisely the potential properties of typical reactive dyes to be examined. From the results of a series of studies, four testing methods, JIS (8), ATTS (3.5), ATTS (8), and LACT, were adopted to examine the fading behaviour of dyes used.

The exposure of wet fabrics was also done. In order to keep the test fabrics wet during the exposure, wet cotton fabrics were set behind the test fabrics, and the other end of the adjacent fabrics was immersed in water in the bottom of a glass vessel. After exposure for a prescribed time period, reflection spectra of test fabrics were measured by a V-560 spectrophotometer and the chromatic values of exposed fabrics were obtained from a computer program equipped with a photometer. The values of colour differences, ΔE^*_{ab}, ΔE_{cmc} (2:1), and ΔE_F, and the gray scale rating for colour changes were obtained using the ISO methods [69,70] as listed in Table 4, where the values of L^* for the test fabric used are also shown.

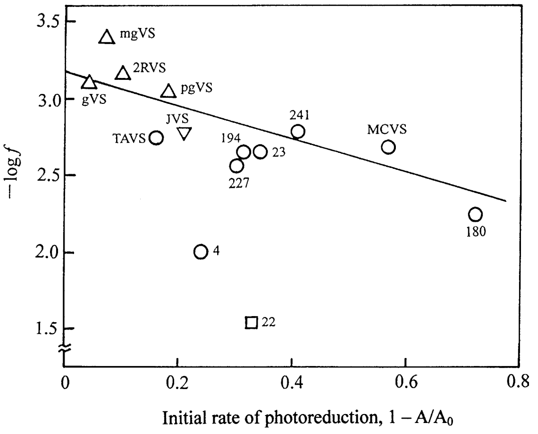


Fig. 4. Correlation between log *f* (*f*-values determined with a Y-46 filter, cf. Table 2) and the relative initial rates of photoreduction, $1 - A/A_0$ for 2 h under anaerobic conditions, for reactive azo dyes from H- (○), γ- (△), J- (▽) and L-acids (□) on cellulosic films on exposure to carbon arc (cf. Table 2). (In the figure, symbols of reactive red dyes are illustrated by numbers or alphabetical symbols without hue names.)

3.3.2. H-acid group

3.3.2.1. Red 4 and Red 180. The relationships between the values of ΔE^*_{ab} and the period of exposure for Red 4 and Red 180 on cotton fabrics immersed in the artificial perspiration are shown in Fig. 5(a) and (b) together with those on dry and ever-wet fabrics. The fading profiles for both dyes were similar to each other in shape except for dry and ever-wet fabrics. The LF of Red 180 was higher than that of Red 4 by 0.5–1.0 times the rating of dry fabrics, while the fastness was 1.5 times the ratings of wet fabrics. The CIELAB values for Red 180 were larger than the corresponding values for Red 4 for four testing methods, but not higher for ever-wet fabrics. The gray scale ratings for the colour variations of two dyes were the same as each other except for the LACT method (0.5 rating) and for the ever-wet method (1.5 rating).

Inspecting further the fading profiles of the two dyes on dry and wet cotton fabrics in detail, the rate of fading for Red 4 on dry fabrics had a positive slope and was definitely larger than that for Red 180. The fading of Red 180 on dry fabrics had a negligible slope, giving it a higher fastness than Red 4, although the CIELAB values for PLF for Red 180 were a little larger than those for Red 4. Red 180 is designed to improve the LF at the cost of PLF (cf. 3.4). Since this dye has the largest photo-reductivity [order (12)] and the least photo-oxidizability [order (3)], the two potential properties among the three are manifested well in the fading profiles estimated by the testing methods for PLF, but another one, the *f*-value, photosensitising ability, seems to play little role in the fading by this testing method. Since substrates on fabric suppress the initial photo-oxidation, the effect of photosensitization may be considerably hidden.

3.3.2.2. Red 194, Red 227, and Red 241. Red 194 and Red 227 are isomers of each other and show similar fading profiles estimated by all the testing methods, as illustrated in Figs. 6 and 7. The ratings estimated for both the dyes coincided in the corresponding items with each other within 0.5

rating. The position of the VS groups has no influences on the fading of these isomers.

When the fading of Red 241 (Fig. 7) is compared with that of Red 194 and Red 227, the ratings estimated by all test methods coincided with each other in the corresponding items within 0.5 rating. Substitution of orthanilic acid by 2-aminonaphthalene-1,5-disulfonic acid brought about little variation in the fading profiles. Compared with the fading of Red 4 and Red 180, these three dyes showed less photo-reductivity than the former two dyes, but the differences in the reductivity among them were too small to realize from the results of the present testing method shown in Figs. 6 and 7 and Table 4.

According to the characterization of photoreduction with DL-mandelate (Red 194 < Red 227 < Red 241) and photo-oxidation with Rose Bengal (Red 241 < Red 227 < Red 194), however, their photochemical properties hold an inverse

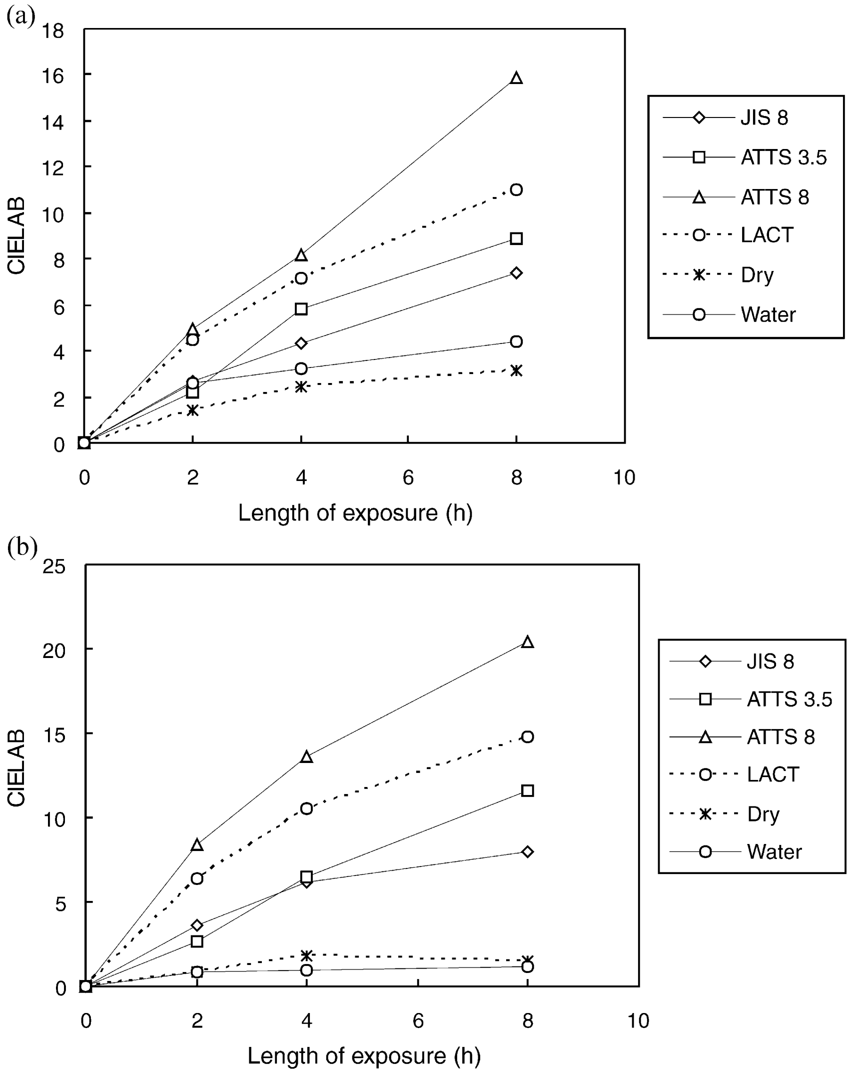


Fig. 5. Fading of (a) C.I. Reactive Red 4 ($X_0 = 38.40$, $Y_0 = 28.03$, $Z_0 = 35.01$) and (b) C.I. Reactive Red 180 ($X_0 = 36.16$, $Y_0 = 24.70$, $Z_0 = 31.38$) on cotton fabric immersed in artificial perspiration on exposure to carbon arc.

relation [cf. order (3) and (12)]. As mentioned below, the photo-reductivity contributes primarily to the PLF. But no order (11) of photosensitising ability (Red 241 < Red 194 < Red 227) seems to correlate with the fading of this case. (The authors considered why the k_0-values correlate inversely with the PLF (cf. 3.4). In spite of the relationship between f-values and the photo-reductivity, $1 - A/A_0$, illustrated in Fig. 4, the correlation between red dyes from H- and γ-acids is not very close. It may be attributed to the use of the filter necessary to estimate the f-values. But, if the relationship is analysed over a wide range of dye structures, the relation may hold as shown in Fig. 4, but within a narrow range. This fact may mean that the filter effects are not the same on all the red dyes.)

No estimation by existing testing methods may be able to differentiate these delicate differences except the film methods with Rose Bengal and DL-mandelate. Red 241 has smaller photo-oxidizability and larger photo-reductivity than the other two red dyes. Since the other red dyes from H-acid

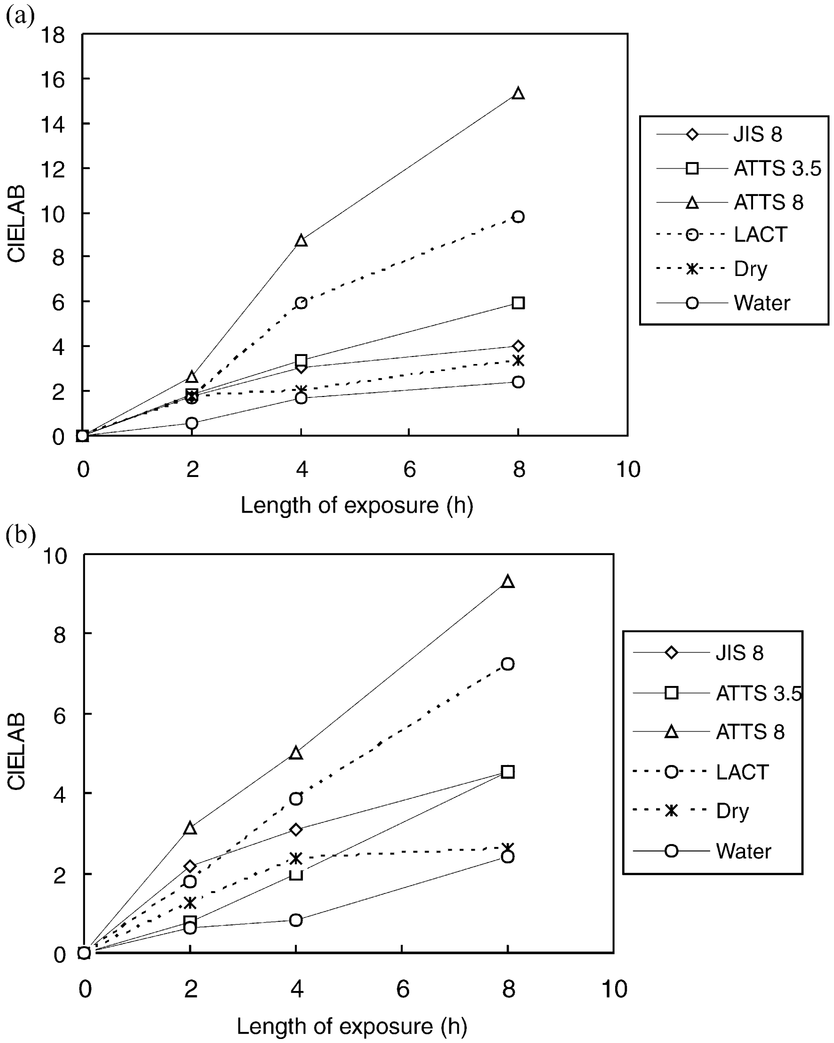


Fig. 6. Fading of (a) C.I. Reactive Red 194 ($X_0 = 38.18$, $Y_0 = 25.13$, $Z_0 = 26.45$) and (b) Red TAVS ($X_0 = 35.24$, $Y_0 = 22.90$, $Z_0 = 26.59$) on cotton fabric immersed in artificial perspiration on exposure to carbon arc.

possess similar properties as mentioned below, the general photochemical properties are discussed in Section 3.3.6.

3.3.2.3. Red MCVS and Red TAVS. When Red MCVS and Red TAVS as well as Red 4 and Red 180 (cf. 3.3.2) are added to the comparison of the above three red dyes, the order of photo-reduction is:

$$\text{Red TAVS} < \text{Red 4} \fallingdotseq \text{Red 194} < \text{Red 227} < \text{Red 241} < \text{Red MCVS} < \text{Red 180}, \quad (13)$$

and that of photo-oxidation is:

$$\text{Red 180} < \text{Red MCVS} < \text{Red 241} < \text{Red 227} < \text{Red 4} < \text{Red TAVS} < \text{Red 194} \quad (14)$$

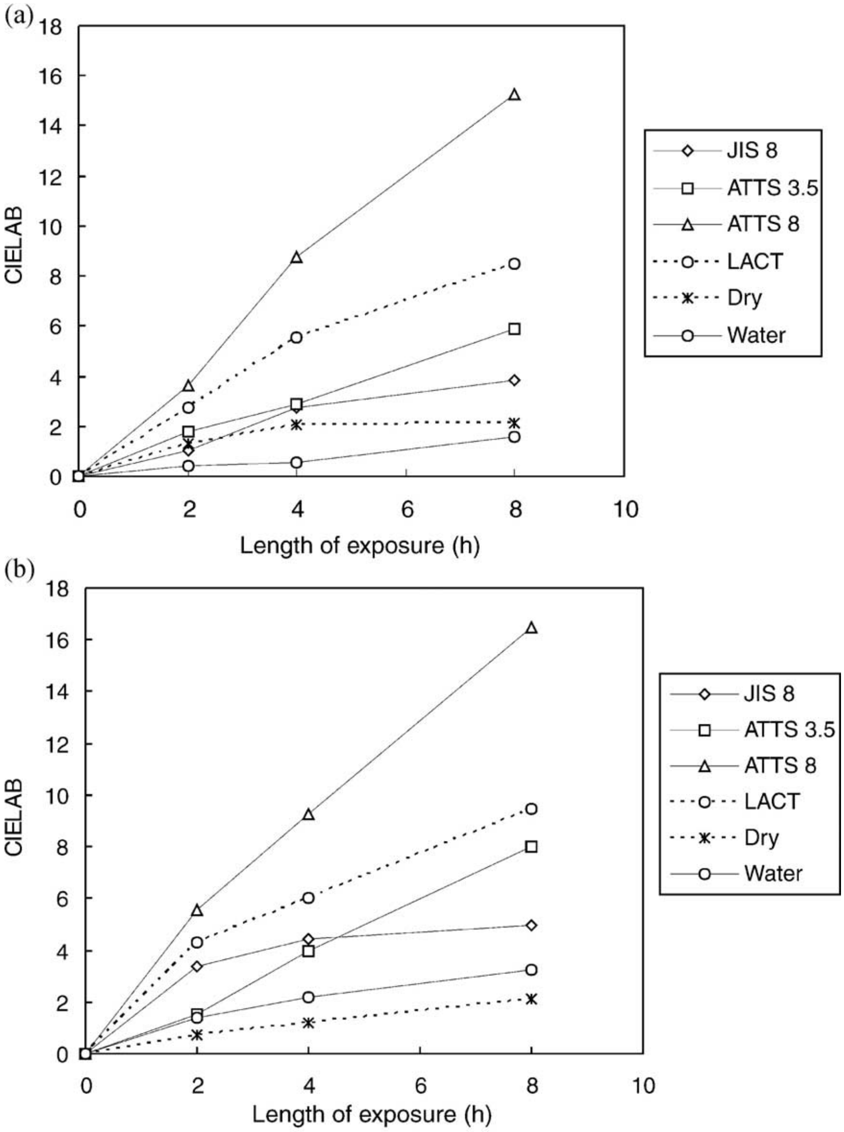


Fig. 7. Fading of (a) C.I. Reactive Red 227 ($X_0 = 37.74$, $Y_0 = 24.88$, $Z_0 = 26.77$) and (b) C.I. Reactive Red 241 ($X_0 = 31.62$, $Y_0 = 20.46$, $Z_0 = 26.17$) on cotton fabric immersed in artificial perspiration on exposure to carbon arc.

The order (13) is a partial extract from the order (12), while the order (14) is from the order (3). As shown by the order, all the dyes from H-acid hold the inverse relationship. But the order of photosensitising ability is:

$$\text{Red 241} < \text{Red TAVS} < \text{Red MCVS} < \text{Red 194} < \text{Red 227} < \text{Red 180} < \text{Red 4} \qquad (15)$$

No good correlation is found between (15) and (13) or (14).

The fading profiles of these two dyes are shown Figs. 5 and 7. As implied by the inverse relationship, the fading profile of Red MCVS is between Red 180 and Red 241 from order (3) and (12). In the photosensitising ability, some other factors may contribute to the order (15). In practice, the fading of Red MCVS on dry cotton is smaller than that of the other red dyes, although there is no difference in the rating of LF for these red dyes. The fading on wet fabrics is considerably suppressed, a merit of this dye, at a cost of PLF, a demerit. The fading behaviour of Red MCVS is nearly similar to that of Red 180 from the results of the PLF test.

It is noted that the introduction of an *N*-methylanilino group in stead of a chloride one in the triazine nucleus makes little improvement over Red 194 in the stability to both the oxidative and reductive attacks by the film tests. The results by the testing methods of PLF for dyed fabrics showed only some small improvements but at a cost of LF (cf. Tables 1 and 4, and Section 3.4).

3.3.3. Pyr-Yellow, Red gVS, Red mgVS, Red pgVS, and Red 2RVS

The fading profiles of these five dyes on cotton fabric are shown in Figs. 8–10. Red gVS, Red mgVS, and Red pgVS are isomers that have VS groups at different positions, except for the methoxy group of Red mgVS. Red 2RVS from 2R-acid has an additional sulfonic acid group for the γ-acid dye group. The five dyes show similar fading profiles due to the common structure of γ-acid. It can be noted that these dyes and the H-acid dye group (cf. 3.3.2) are poles apart in photochemical reactivity. Inspecting the profiles in detail, Pyr-Yellow and four red dyes from γ- and 2R-acids showed characteristic fading: the greatest fading (rating 2) of Pyr-Yellow on dry fabrics and the greatest fading (rating 1–3) of the red dyes on wet fabrics. The latter abnormal fading on wet fabric may be attributed to its large (or usual) photosensitising ability, while the former fading to the very small photosensitising ability [34], but Pyr-Yellow suffers catalytic fading in mixture dyeing especially on wet fabrics [32,33]. Three red dyes from γ-acid may possess the same property as Pyr-Yellow. Introduction of a sulfonic acid group (Red 2RVS) improves the LF on wet fabric but unfortunately at a cost of PLF. These dyes from γ-acid suffer little fading in the presence of substrates because substrates act as a radical scavenger of $^1O_2$ to suppress the oxidative fading. Then, they have excellent PLF: ratings 3–4.5, while the rating for Red 2RVS is not always fair (cf. Table 1). The fading behaviour of Red 2RVS is between the other three red dyes from γ-acid and dyes from H-acid. Thus, dyes from γ-acid should not be used on wet fabric, although they have good PLF. The fading after immersing in artificial perspiration even at pH 8 was almost completely suppressed for Red gVS and Pyr-Yellow, and was considerably suppressed for Red pgVS and Red mgVS. The latter two dyes showed fading behaviour between the dyes from H-acid and the former two dyes.

3.3.4. Orange JVS and Red 22

Compared with the other dyes, the fading behaviour of these two dyes was very complex, as shown in Fig. 11. Red 22 undergoes exceptional fading that is different from the other dyes [34]. It is caused by its high photosensitising ability and the very great ease with which it is photo-reduced and oxidized [35]. On exposure under wet conditions, it suffered great initial oxidative fading, but after drying during exposure the fading by JIS 8 and ATTS (3.5) methods was almost suppressed accompanying thorough fading from the surface, less fading than that of ever-wet wet fabric. The preferential surface fading of Red 22 was also observed in ever-wet fabric, but this dye shows little fading on dry fabric, compared with that in the other test methods. This dye has good photostability only on dry fabric, and Red 22 should be avoided in dyeing cotton that has a chance of exposure to wet conditions.

Orange JVS, on the other hand, as a whole showed the smallest fading among dyes examined on exposure by various testing methods. Thus, the PLF was estimated to be 3–3.5, but the LF was also of this magnitude. Since this dye exists at the middle position of the orders (3) and (12), commercial dyes seem to improve the LF at the cost of PLF or by decreasing the photo-oxidizability and increasing simultaneously the photo-reductivity. As can be seen from Red 22, Red 4 and Orange JVS, dyes located in the middle position of the redox series may not be considered excellent dyes.

3.3.5. Red 23

This is one of dyes with the highest LF of the reactive dyes, as well as excellent PLF (cf. Tables 1 and 4). Testing methods of PLF for most Cu-

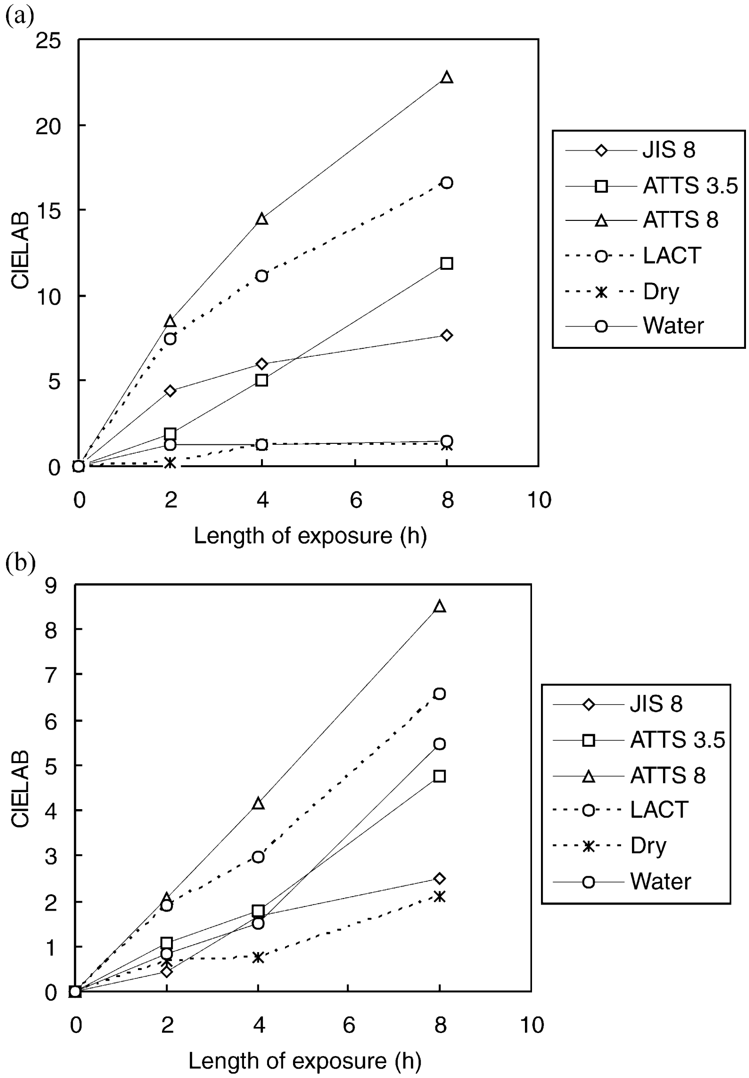


Fig. 8. Fading of (a) Red MCVS ($X_0 = 36.73$, $Y_0 = 25.00$, $Z_0 = 27.85$) and (b) Red 2RVS ($X_0 = 35.05$, $Y_0 = 25.12$, $Z_0 = 29.65$) on cotton fabric immersed in artificial perspiration on exposure to carbon arc.

complex azo dyes, which use histidine, results in low ratings of fastness, since histidine coordinates to copper atoms of Cu-complex dyes to give high adsorption on cellulose [71]. Some testing methods use a large concentration of histidine in the artificial perspiration to strengthen the effect of the substrates [68,72,73]. As shown in Fig. 12, however, Red 23 had very little effect on the colour variation or the abstraction of copper atoms on immersing and exposing after the immersion. Since the rates of abstraction of copper atoms increase with an increase in the pH of the aqueous artificial perspiration in spite of the least colour change of the dye, the ATTS (8) method resulted in colour variations with the time of exposure, giving a low PLF, but the other methods give good or excellent PLF. Therefore, the LACT method without histidine gave an excellent PLF.

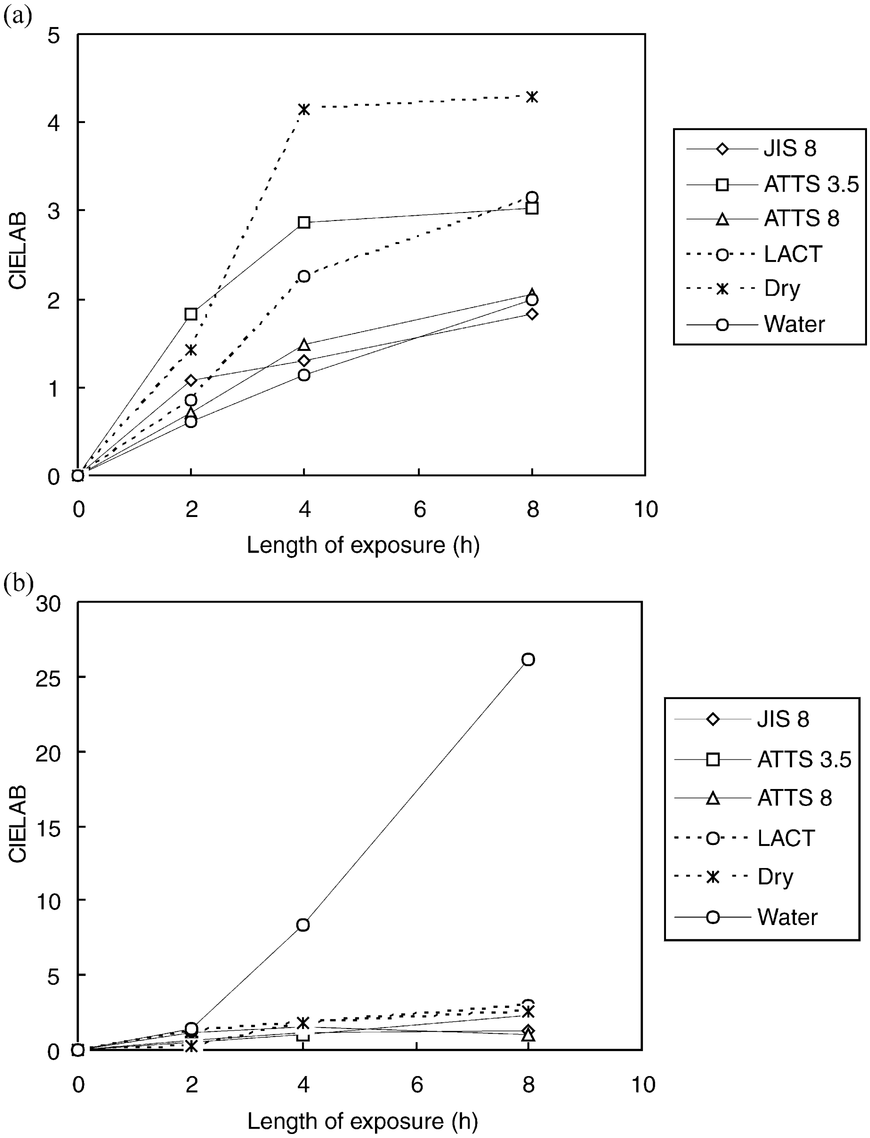


Fig. 9. Fading of (a) Pyr-Yellow ($X_0 = 64.94$, $Y_0 = 73.65$, $Z_0 = 31.50$) and (b) Red gVS ($X_0 = 27.11$, $Y_0 = 18.08$, $Z_0 = 19.61$) on cotton fabric immersed in artificial perspiration on exposure to carbon arc.

3.3.6. General photo-fading of reactive azo dyes on cotton fabric in the absence and presence of substrates

3.3.6.1. Exposure of the dyes on dry cotton fabrics in air. Prolonged exposure to light in air produces characteristic colour variations indicating photo-reduction in cotton fabric dyed with vat dyes [14]. The photo-reduction occurred in the inner part of fabric, while the photo-oxidative fading proceeded preferentially from the interfacial part [14]. This mechanism of photo-fading should also hold for the reactively-dyed fabric (cf. 3.1), since the formation of photo-reduction products were confirmed from the absorption spectra of the exposed sample in air [36]. In general, it is difficult to prove the occurrence of photo-reduction of reactive dyes

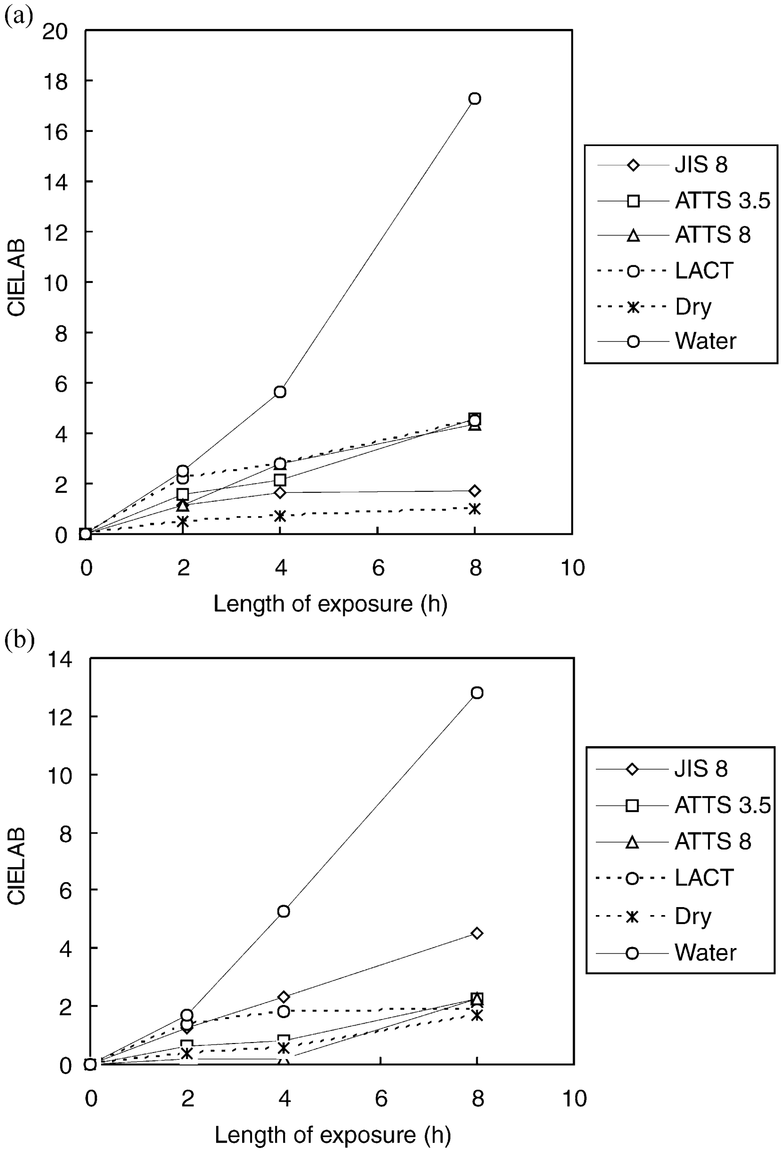


Fig. 10. Fading of (a) Red pgVS ($X_0 = 31.77$, $Y_0 = 22.19$, $Z_0 = 21.56$) and (b) Red mgVS ($X_0 = 30.42$, $Y_0 = 22.29$, $Z_0 = 19.96$) on cotton fabric immersed in artificial perspiration on exposure to carbon arc.

in the inner part of cellulose due to the small relative fading and lack of a characteristic spectrum of reaction products.

Photo-reduction of vat dyes is reversible, while that of azo dyes irreversible. It is natural that the photo-fading of vat dyes is attributed to photo-oxidation [14]. As mentioned above, it was demonstrated that the fading of cotton fabric dyed with reactive azo dyes is dependent upon photo-oxidation (cf. 3.1.3). This fact may imply that the contribution of photo-reduction to the fading is relatively small. Moreover, in practice, due to the transmittance of the dyed substrate, the incident light is absorbed preferentially at the surface, a filter effect, and the photo-fading may advance from the surface, but at much lower rates in the inner part.

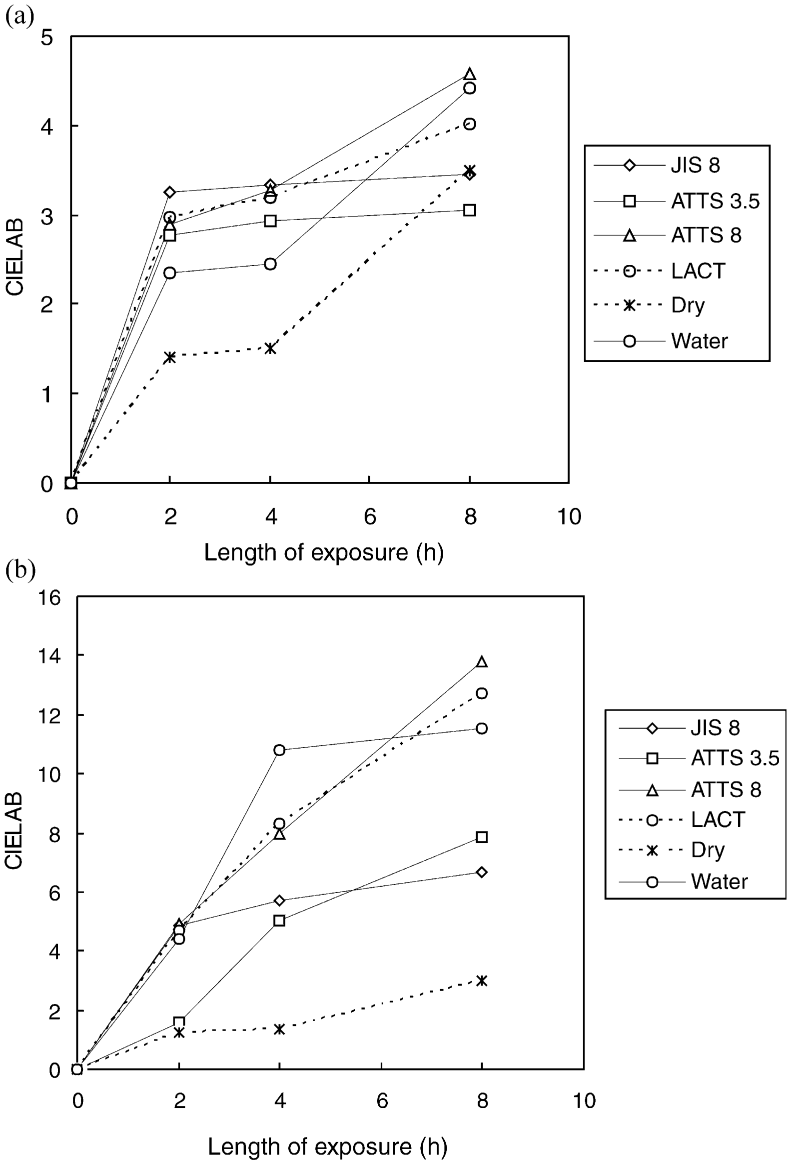


Fig. 11. Fading of (a) Orange JVS ($X_0=38.23$, $Y_0=25.96$, $Z_0=14.02$) and (b) C.I. Reactive Red 22 ($X_0=40.92$, $Y_0=29.91$, $Z_0=29.82$) on cotton fabric immersed in artificial perspiration on exposure to carbon arc.

3.3.6.2. Exposure after immersing in artificial perspiration. In the presence of substrates such as perspiration, the photochemical processes are the exposure of dyes on cotton fabrics containing substrates of low molecular weight in air and in some cases under aerobic wet conditions. According to the spectral analyses of photo-decomposed products, the oxidative and reductive fading occurred simultaneously at the beginning of exposure, and later the oxidative fading was suppressed depending upon the concentrations of oxygen and substrates [35]. Since substrates such as amines usually act as radical scavengers, they may suppress the initial photo-oxidative fading and promote the subsequent photo-reductive one, while oxygen has the reverse effects. (For example, wool plays the role, and the LF is markedly increased.) The initial suppressive effect, however, was not easily recognized in the fading on cotton fabric, but the promotion effect was remarkable.

The photo-fading of individual azo dyes in the presence of substrates was analysed and summarized above (cf. Figs. 5–12 and Table 4). The fading could be explained qualitatively in terms of the three essential properties, but not quantitatively. The difficulties of explanation may be attributed to both the physically heterogeneity in respective positions of dyed substrate where the photochemical reaction takes place and changeable environmental conditions with time.

3.4. Conflicting relationship between photo-oxidisability and reductivity

In order to illustrate the relationships between the photo-reductivity, $1 - A/A_0$, and the k_0-values, their plots are shown in Fig. 13, a rectangular hyperbola. For the azo dyes from H- and γ-acids examined in the present study, the products of the values of $(1 - A/A_0)$ and of k_0 are roughly constant, indicating that the parameters possess conflicting properties with each other. Within azo dyes from H-acid, these properties can be surely recognized, but can not within ones from γ-acid. Since the latter dyes have narrow range of properties, it may not be recognized unless they are considered together with dyes from H-acid, although they have little photo-reductivity but

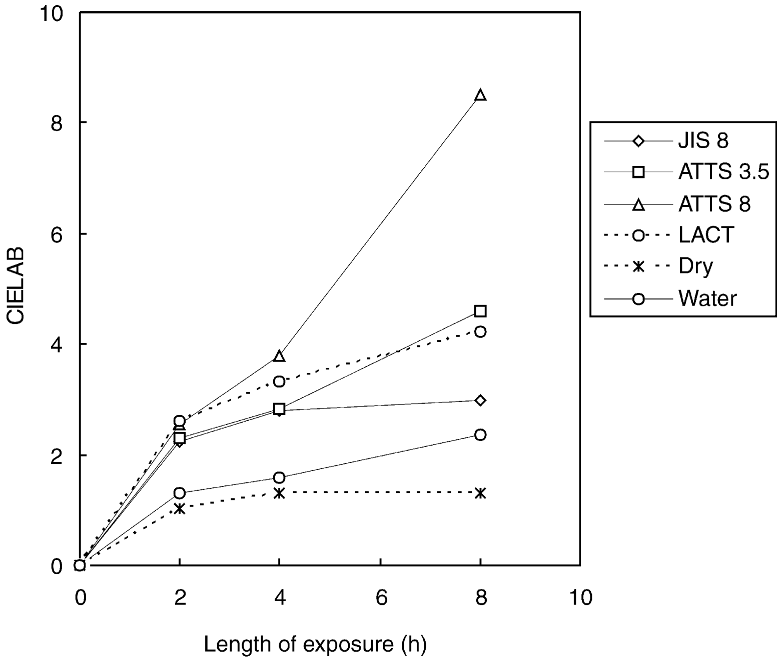


Fig. 12. Fading of C.I. Reactive Red 23 ($X_0 = 30.60$, $Y_0 = 21.35$, $Z_0 = 24.03$) on cotton fabric immersed in artificial perspiration on exposure to carbon arc.

large values of k_0. Both parameters for Red 22 and Orange JVS did not fit with the rectangular hyperbola, but they did not deviate greatly. As a whole, the conflicting relationship may hold roughly for azo dyes, but approximately within a narrow range of structures.

As mentioned above, the k_0-values express the reactivity of azo dyes in the ground state against $^1O_2$, while the photo-reductivity may depend upon the photophysical and chemical properties of the T_1 state [8–14]. Although it was observed in Fig. 4 that the latter physical properties are proportional to the initial rates of photo-reduction and to the quantum yield of $^1O_2$ under the conditions that allow only the photo-oxidative reactions to occur, no one has reported the reason a correlation such as that illustrated in Fig. 13 exists in the chemical properties between ground and excited states. Although photo-reduction may depend on the values of pK_a of azo groups in the T_1 state, Fig. 4 seems to imply little dependence upon the pK_a, but only upon the quantum yield of the T_1 state. Since van Beek et al. [54,55] also reported that the photo-reduction of monoazo dyes had a close correlation with the electron affinity of the dyes from the reduction potential, further examination is required to elucidate the correlation. This is the same result as the present study, if the reciprocal relationship between reduction and oxidation of the dyes in the ground state is taken into consideration. This relationship is a controversial property that gives a high PLF to azo dyes as well as a high LF for photo-oxidative fading. If the inverse relation is an inevitable property for azo dyes, or if no method is found to minimize the ease with which they undergo both photochemical reactions, no one may be able to design azo dyes from H- and γ-acids with excellent LF as well as excellent PLF. Azo dyes from H-acid were examined for a limit of direction to minimize the k_0-values, while those from γ-acid were to minimize the f-values. Dyes with intermediate values possess lower PLF than the dyes from H- and γ-acids have.

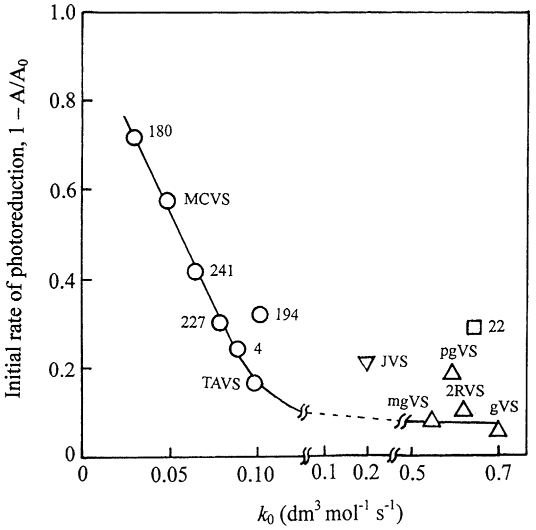


Fig. 13. Relationship between the k_0-values (cf. Table 2) for azo dyes from H- (○), γ- (△), J- (▽) and L-acids (□) on cellulosic films and the relative rates of reductive fading ($1 - A/A_0$ for 2 h; cf. Fig. 3 and Table 2). (In the figure, symbols of reactive red dyes are illustrated by numbers or alphabetical symbols without hue names.)

4. Summary

Potential properties, photo-oxidizability (f: the quantum yield to generate $^1O_2$), photo-reductivity (relative initial rates of photo-reduction by immersing in anaerobic DL-mandelate solution), and photo-oxidisability (k_0: the ease with which the dye is oxidized by $^1O_2$), for fifteen reactive monoazo dyes were estimated by use of dyed cellulosic films, and the photofading of reactively-dyed cotton fabric was analysed in terms of the potential properties to elucidate the mechanism.

The reactive azo dyes examined were found to show the following photo-fading characteristics:

1. The ratings of LF of fifteen reactive dyes on cotton fabric had a close relationship with the logarithmic product of f and k_0, indicating that the dye fading was due to photo-oxidation and that the LF depends upon both the f- and k_0-values.
2. The photo-reductivity of reactive dyes was proportional to the f-values. The photo-fading occurred via the T_1 state, which generated $^1O_2$ to undergo photo-oxidation under the aerobic conditions and abstrac-

ted hydrogen atoms from substrates to form corresponding amines under the anaerobic conditions.

3. A contradictory relationship between the photo-reductivity and the ease with which the dyes were photo-oxidised was found for azo dyes, but the reason why azo dyes possess the restriction could not be elucidated. The design of azo dyes with excellent LF as well as PLF is impossible unless this restriction is overcome.

The three potential properties for photo-fading of dyes were determined from the initial rates of variation in the absorbance of dyed cellulosic films due to exposure, while the ratings of colourfastness were determined by measuring the colour differences after a long definite time of exposure. The latter methods are not suitable to analyse the photochemical properties of dyes. Testing methods for light-related properties of dyes are required to utilize the initial slope in the colour variation, which all scientific or physico-chemical analyses use.

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References

[1] von der Eltz H-U. Zur Geschichte der Sortimentes der Remazol-Farbstoffe. Textil-Praxis International 1982;37:1312–20.

[2] von der Eltz H-U. 10 Jahre Erfahrungen mit Remazol-Farbstoffen in der Färberei. Zeitschrift gesamte Textilindustrie 1968;70:824–30.

[3] Evans NA, Stapleton IW. Structural factors affecting the lightfastness of dyed fibers. In: Venkataraman K, editor. The chemistry of synthetic dyes, vol. VIII. New York: Academic Press; 1978. p. 221–77 [Chapter VI].

[4] Allen NS, McKellar JF. Photosensitized degradation of polymers by dyes and pigments. In: Allen NS, McKellar JF, editors. Photochemistry of dyed and pigmented polymers. London: Applied Science Publishers Ltd.; 1980. p. 247–78 [Chapter 5].

[5] Baumgarte U, Wegerle D. Veränderung von Cellulosefärbungen durch Lichteinwirkung. Melliand Textilberichte 1986;67:567–72, 640–7.

[6] Venkataraman K. The action of light on dyes and dyed fibers In: Chemistry of synthetic dyes, vol. 2. New York: Academic Press; 1952. p. 1210–52 [Chapter 40].

[7] Baugh PJ. Photodegradation and photooxidation of cellulose. In: Allen NS, editor. Developments in polymer photochemistry, vol. 2. London: Applied Science Publishers; 1981. p. 165–214.

[8] Baugh PJ, Phillips GO, Worthington NW. Photodegradation of cotton cellulose. II. Effect of the vat dyes Caledon Yellow GN, 5GK, and 4G. The Journal of the Society of Dyers and Colourists 1970;86:19–24.

[9] Baugh PJ, Phillips GO, Worthington NW, Photodegradation of cotton cellulose I. Reactions sensitised by anthraquinone sulphonates. The Journal of the Society of Dyers and Colourists 1969;85:241–5.

[10] Schorer M, Dörr F. Über die Photoakitivität anthrachinoider Küpenfarbstoffe. Berichte der Bunsengesellschaft für physikalishe Chemie 1964;68:478–81.

[11] Nitzl K, Dörr F. Optische Eigenschaften und photochemisches Verhaltens einiger Anthrachinon-Farbstoffe: Pyranthron, Flavanthron, Indanthrenblau RS. Melliand Textilberichte 1964;45:893–7.

[12] Dörr F. Ursachen der Eigenschaften von Farbstoffen als Faserschädiger und-nichtschädiger. Modellvorstellungen zur primärreaktion Chimia 1961;15:63–7.

[13] Dörr F. Faserschädigung durch anthrachinonide Farbstoffe. In: Foerst W, editor. Optische Anregung organischer Systeme; Aufnahme und Umwandlung von Lichtenergie durch Farbstoffe und die Einflüsse des Mediums. [2. Internationale Farbensymposium, 21–24 April 1964, Schloss Elmau]. Weinheim: Verlag Chemie; 1966. p. 732–43.

[14] Hihara T, Okada Y, Morita Z. Photo-oxidation and -reduction of vat dyes on water-swollen cellulose and their lightfastness on dry cellulose. Dyes and Pigments 2002; 53(2):153–77.

[15] Leaver IH. Photooxidation and photoreduction of dyes in polymers. In: Allen NS, McKellar JF, editors. Photochemistry of Dyed and Pigmented Polymers. London: Applied Science Publishers Ltd.; 1980. p. 161–245 [Chapter 4].

[16] Morita Z, Hada S. A semiempirical molecular orbital study on the reaction of an aminopyrazolinyl azo dye with singlet molecular oxygen. Dyes and Pigments 1999;41(1):1–10.

[17] Bredereck K, Schumacher C. Structure reactivity correlations of azo reactive dyes based on H-acid. I. NMR chemical shift values, pK_a values, dyestuff aggregation and dyeing behaviour. Dyes and Pigments 1993;21:23–43.

[18] Bredereck K, Schumacher C. Structure reactivity correlations of azo reactive dyes based on H-acid. II. Dye degradation by hypochlorite. Dyes and Pigments 1993;21:45–66.

[19] Bredereck K, Schumacher C. Structure reactivity correlations of azo reactive dyes based on H-acid. III. Dye degradation by peroxide. Dyes and Pigments 1993;23:121–33.

[20] Bredereck K, Schumacher C. Structure reactivity correlations of azo reactive dyes based on H-acid. IV. Investigations into the lightfastness in the dry state, in the wet state, and in presence of perspiration. Dyes and Pigments 1993;23:135–47.
[21] Gregory P, Stead CV. The degradation of water-soluble azo compounds by dilute sodium hypochlorite solution. Journal of the Society of Dyers and Colourists 1978;94: 402–7.
[22] Omura T, Kayane Y, Tezuka Y. Design of chlorine-fast reactive dyes. Part 1: the role of sulphonate groups and optimization of their positions in an arylazoarylamine system. Dyes and Pigments 1992;20:227–46.
[23] Omura T. Design of chlorine-fast reactive dyes. Part 2. the role of sulphonate groups and optimization of their positions in an arylazoarylamine system. Dyes and Pigments 1993;23:179–96.
[24] Omura T. Design of chlorine-fast reactive dyes. Part 3: structure–fastness relationship in twice-coupled H-acid dyes and their analogues. Dyes and Pigments 1994;24:125–41.
[25] Omura T. Design of chlorine-fast reactive dyes. Part 4: degradation of amino-containing azo dyes by sodium hypochlorite. Dyes and Pigments 1993;23:179–96.
[26] Omura T, Yokogawa K, Kayane Y, Tezuka Y. Design and properties of reactive dyes with heterobifunctional reactive systems. Dyes and Pigments 1995;29:1–21.
[27] Omura T. Formaldehyde-induced discoloration: design of formaldehyde-fast bisazo dyes. Dyes and Pigments 1993; 22:99–116.
[28] Csepregi Zs, Aranyyosi P, Rusznák I, Töke L, Frankl J, Víg A. The light stability of azo dyes and azo dyeings I. Light stability of dyeings with reactive and non-reactive derivatives, respectively, of two selected azochromophores. Dyes and Pigments 1998;37:1–14.
[29] Csepregi Zs, Aranyyosi P, Rusznák I, Töke L, Víg A. The light stability of azo dyes and azo dyeings II. Perspiration-light stability of dyeings with reactive and non-reactive derivatives, respectively, of two selected azochromophores. Dyes and Pigments 1998;37:15–31.
[30] Aranyyosi P, Csepregi Zs, Rusznák I, Töke L, Víg A. The light stability of azo dyes and azo dyeings III. The effect of artificial perspiration on the light stability of reactive and non-reactive derivatives of two selected azochromophores in aqueous solution. Dyes and Pigments 1998;37:33–45.
[31] Imada K, Harada N, Takagishi T. Fading of azo reactive dyes by perspiration and light. Journal of the Society of Dyers and Colourists 1994;110:231–4.
[32] Okada Y, Kato T, Motomura H, Morita Z. Catalytic fading of vinylsulfonyl reactive dye mixtures on cellulose under wet conditions. Dyes and Pigments 1990;12:197–211.
[33] Okada Y, Hirose M, Kato T, Motomura H, Morita Z. Photofading of vinylsulfonyl reactive dyes on cellulose under wet conditions. Dyes and Pigments 1990;14:113–27.
[34] Okada Y, Hirose M, Kato T, Motomura H, Morita Z. Fading of vinylsulfonyl reactive dyes on cellulose in admixture under wet conditions. Dyes and Pigments 1990; 14:265–85.
[35] Okada Y, Motomura H, Morita Z. Simultaneous oxidative and reductive photofading of C.I. Reactive Red 22 and Black 5 on cellulose in presence of oxygen and substrate under wet conditions. Dyes and Pigments 1990;16: 205–21.
[36] Okada Y, Morita Z. Fading of some vinylsulfonyl reactive dyes on cellulose under various conditions. Dyes and Pigments 1992;18:259–70.
[37] Okada Y, Sato E, Motomura H, Morita Z. Photofading of monochlorotriazinyl reactive dyes on cellulose under wet conditions. Dyes and Pigments 1992;19:1–19.
[38] Okada Y, Fukuoka F, Morita Z. Estimation of potential photochemical properties for monochlorotriazinyl reactive dyes and their manifestation in the fading of dyed cellulose. Dyes and Pigments 1997;35:311–30.
[39] Okada Y, Fukuoka F, Morita Z. Environmental effects of oxygen on the fading of monochlorotriazinyl reactive dyes on cotton fabrics. Dyes and Pigments 1998;37:47–64.
[40] Okada Y, Sugane A, Fukuoka F, Morita Z. An assessment of testing methods for colour fastness to light, water and perspiration, and related methods with some reactive dyes. Dyes and Pigments 1998;39:1–23.
[41] Hihara T, Okada Y, Morita Z. Aggregation of triphenodioxazine reactive dyes in aqueous solution, on cellulose and nylon substrates. Dyes and Pigments 2000;45:131–43.
[42] Hihara T, Okada Y, Morita Z. Reaction of triphenodioxazine dyes with bleaching agents, hypochlorite and hydrogen peroxide, in aqueous solution. Dyes and Pigments 2000;46:181–92.
[43] Hihara T, Okada Y, Morita Z. Photofading, photosensitization, and effect of aggregation on fading of triphenodioxazine and copper phthalocyanine dyes. Dyes and Pigments 2001;50(3):185–201.
[44] Zollinger H. Methods for the preparation of aromatic and heteroaromatic diazo compounds. In: Diazo Chemistry. I. Aromatic and Heteroaromatic Compounds, Weinheim: VCH; 1994. p. 11–37 [Chapter 2].
[45] Japanese Industrial Standard Association. Testing method for colour fastness for daylight, JIS L 0841-1992.
[46] Japanese Industrial Standard Association, Testing method for colour fastness for ultraviolet carbon arc lamp light, JIS L 0842-1996.
[47] Japanese Industrial Standard Association. Testing method for colour fastness to light and perspiration, JIS L 0888-1988 (Reaffirmed 1992).
[48] Okada Y, Kato T, Motomura H, Morita Z. Photosensitization and simultaneous reductive or oxidative fading of monochlorotriazinyl reactive dyes on cellulose under wet conditions. Dyes and Pigments 1992;20:123–35.
[49] Gandin E, Lion Y, Van de Vorst A. Quantum yield of singlet oxygen production by xanthene derivatives. Photochemistry and Photobiology 1983;37:271–8.
[50] Okada Y, Kato T, Motomura H, Morita Z. Fading mechanism of reactive dyes on cellulose by simultaneous

effects of light and perspiration. Sen'i Gakkaishi 1990; 46(8):346–55.

[51] Gilbert A, Baggott J. Essentials of molecular photochemistry. Blackwell Scientific Publications; 1991.

[52] Rabek JF. Mechanisms of photophysical processes and photochemical reactions in polymers, theory and applications. Wiley; 1987.

[53] Klessinger M, Michl J. Excited states and photochemistry of organic molecules. VCH; 1995.

[54] van Beek HCA, Heertjes PM, Houtepen C, Retzloff D. Formation of hydrazyl radicals and hydrazo compounds by photoreduction of azo dyes. Journal of the Society of Dyers and Colourists 1971;87:87–92.

[55] van Beek HCA, Heertjes PM, Schaafsma K. Photoreduction of azo dyes by reducing agents formed upon photoexcitation of some aliphatic and aromatic compounds. Journal of the Society of Dyers and Colourists 1971;87: 342–8.

[56] van Beek HCA, Heertjes PM, Rutges AAM. The photofading of mixtures of azo dyes and mixtures of an azo dye and oxygen in aqueous solution containing dl-mandelic acid. Journal of the Society of Dyers and Colourists 1973; 89:389–96.

[57] Heijkoop G, van Beek HCA. Decomposition and disproportionation of hydrazyl radicals and hydrazo compounds derived from azo dyes. Recueil Travaux Chimiques des Pay-Bas 1976;95:6–10.

[58] Heijkoop G, van Beek HCA. ESR investigation of the radical intermediates formed in the photoreduction of azo dyes. Recueil Travaux Chimiques des Pay-Bas 1977;96:83–5.

[59] Neevel JG, van Beek HCA, den Ouden HHI, van de Graaf B. Photo-oxidation of azo dyes in the presence of biacetyl and oxygen. Journal of the Society of Dyers and Colourists 1990;106:176–81.

[60] Conant JB, Pratt MF. The irreversible reduction of organic compounds. III. The reduction of azo dyes. Journal of the American Chemical Society 1926;48:2468–84.

[61] Florence TM, Aylward GH. Electrochemical studies on Eriochrome Violet B and its lanthanide complexes. I. Behaviour of Eriochrome Violet B and its lanthanide complexes at the dropping mercury electrode: D.C., A.C., and cathode ray polarography. Australian Journal of Chemistry 1962;15:65–81.

[62] Florence TM, Aylward GH. Electrochemical studies on Eriochrome Violet B and its lanthanide complexes. II. Controlled-potential coulometric studies. Australian Journal of Chemistry 1962;15:416–24.

[63] Florence TM, Farrar YJ. Polarography of azobenzene and its p-sulphonic acids. Australian Journal of Chemistry 1964;17:1085–97.

[64] Florence TM, Polarography of aromatic azo compounds I. Effects of substituents on the electroreduction of azo compounds. Australian Journal of Chemistry 1965;18: 609–18.

[65] Florence TM. Polarography of aromatic azo compounds. II. Kinetic study of the disproportionation of 4-aminohydrazobenzene-4′-sulphonic acid. Australian Journal of Chemistry 1965;18:619–26.

[66] Boto KG, Thomas FG. The, D.C. and A.C. polarography of some substituted azobenzenes in acetonitrile. Australian Journal of Chemistry 1971;24:975–80.

[67] Boto KG, Thomas FG. The polarography of some substituted azobenzenes in acetonitrile. II. Identification of reduction products. Australian Journal of Chemistry 1973; 26:1251–8.

[68] Okada Y, Asano M, Morita Z. The influence of histidine on the color of Cu-complex azo dyes on cellulose. Dyes and Pigments 1996;31(1):53–67.

[69] International Standard. Textiles—tests for colour fastness—part J03: calculation of colour differences, ISO 105-J03:1995.

[70] International Standard. Textiles—tests for colour fastness—part A05, Instrumental assessment of change in colour for determination of grey scale rating, ISO 105-A05:1996.

[71] Okada Y, Kawanishi T, Morita Z. Coordination of histidine to the copper atom of a metal-complex reactive azo dye on cellulose. Dyes and Pigments 1994;24:99–111.

[72] Okada Y, Nagashima T, Iizuka H, Asano M, Morita Z. Color variations of cotton dyes with reactive Cu-complex azo dyes by histidine, and testing methods for color fastness to perspiration. Dyes and Pigments 1997;33(3):239–50.

[73] Okada Y, Sugane A, Watanabe A, Morita Z. Effect of histidine on the fading of Cu-complex azo dyes on cellulose and testing method for color fastness to light and perspiration. Dyes and Pigments 1998;38(1-3):19–39.