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Photo-oxidation and -reduction of vat dyes on water-swollen cellulose and their lightfastness on dry cellulose

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Abstract

Photostability of nine (seven anthraquinone and two thioindigoid) vat dyes on cellulosic films was examined. The ease (k_0) with which the dyes were photo-oxidized was estimated by the relative fading of vat dyes on cellophane immersed in aqueous Rose Bengal solution on exposure, a condition resulting in only the photo-oxidative fading. The photosensitivity (f) was estimated by the relative fading of an aminopyrazolinyl azo vinylsulfonyl dye on cellophane dyed in admixture with vat dyes examined under the same conditions as above. The values of k_0 were small, compared with those of reactive dyes, while those of f comparable. The lightfastness of nine vat dyes on dry cotton fabric had close correlation with log ($f\,k_0$). This fact shows that the fading of vat dyes on dry cellulose occurs mainly by photo-oxidation on exposure in air. On exposure of vat dyes on cellulosic substrate in an aqueous anaerobic DL-mandelate solution, a condition resulting in only the photo-reduction, vat dyes displayed a colour change in the direction of the acid leuco-compounds, many of which returned to the original dyes by re-oxidation. Vat dyes with high photo-reductivity showed the same colour change on dry cellulose by long exposure, implying that photo-oxidation occurs in the superficial part of fibre substrate and photo-reduction in the inner part. The photofading properties of anthraquinone vat dyes were attributed to the excited triplet $T_1(n\pi^*)$ state of the carbonyl groups. The quantum yields to $T_1(\pi\pi^*)$ was very small by an effective internal conversion of the exited singlet states. Since the $\pi\pi^*$ absorption of the annelated anthraquinones with the large extinction coefficients shielded the carbonyl groups with the small coefficients from the $n\pi^*$ absorption, the photofading of the vat dyes with the highest lightfastness became very small. As a result, those vat dyes perform the highest lightfastness. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Vat dye; Photosensitisation; Photo-oxidation; Photo-reduction; Lightfastness; Phototendering; Internal conversion

1. Introduction

At present, there is no true alternative to vat dyes [1], although the total number of vat dyes on the market has drastically diminished [2]. The light and wet fastness of reactive dyes as the actual alternative has not yet reached the level of anthraquinone vat dyes invented a century ago. Reactive dyes for cellulose have held more important position than vat dyes despite the lower lightfastness and lower colour fastness to various wet treatments than their fastness of vat dyes.

Baumgarte reviewed the present state or the last development and withdrawal of vat dyes [2]. In the

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shortcomings of vat dyes, phototendering of cellulose and nylon and tendering by dyeing have been well-known effects by yellow and orange anthraquinone dyes [3–7]. Two essential mechanisms, the oxidation of cellulose by singlet molecular oxygen generated by photosensitization and the hydrogen abstraction by the excited states of vat dyes, have been proposed. Although extensive studies were so far reported, no decisive conclusion seems to be attained. According to Allen and McKellar [4], a series of studies by Egerton et al. [8–11] on the phototendering of cellulose, wool and nylon dyed with vat dyes are summarized as follows: (1) the existence of oxygen as the necessity, (2) the marked acceleration effect of water, and (3) substrate specificity of cellulose and nylon, (4) non-tendering of wool, and (5) no obvious correlation between chemical structure of vat dyes and tendering activity. Baumgarte and Wegerle [7] wrote in 1986 that it had not still finalized which mechanism held in the fibre tendering caused by anthraquinone vat dyes.

In the field of vat dyes, we have a lot of research papers including PB reports since the beginning of last century. They have focused on the fields of vat dyeing, photofading including photochemistry, polymer stabilization (mainly cellulose and polyamide), and the syntheses or manufacturing processes of vat dyes and pigments and the other fields than dye chemistry. There are another series of researches on the oxidative and reductive photofading of dyes on cellulosic substrate. Several workers [12–15] proposed the possibility of photoreduction of dyes on cellulose including vat dyes with strong tendering property [7] by exposure in the presence of textile resins and perspiration (cf. 3.4). The present authors [16,17] studied the mechanism of photofading of reactive dyes on cellulose in presence of various components of perspiration and showed that substrates such as amines, lactic acid, amino acids etc. quenched the singlet oxygen generated by the photosensitisation of the dyes to cause the photo-reductive fading. In cases where the concentrations of substrates are low, it was proved that the oxidative fading occurred initially, was suppressed gradually, and then the reductive fading began depending upon the concentration of substrates. Under the anaerobic conditions the reductive fading of azo dyes occurred from the start of exposure even in the absence of substrate, while simultaneous oxidative and reductive fading occurred on dry cellulose [18,19].

In the previous papers [20–22], the present authors reported that the photofading of vinylsulfonyl (VS) and monochlorotriazinyl (MCT) dyes with various chemical structures such as azo, anthraquinone, triphenodioxazine (TPDO) and copper phthalocyanine (CuPc) etc. occurs via photo-oxidation mechanism on cellulose on exposure in air. In presence of substrate such as amines, amino acids, lactic acid etc., they suffer reductive fading especially under anaerobic conditions. Although these reactive dyes with high lightfastness are designed to possess very small photosensitivity, their lightfastness is still considerably inferior to that of some vat dyes.

From the present viewpoint, therefore, above features summarized by Allen and McKellar [4] seem to be good markers of diagnostic test [16–19,23,24], which suggest the singlet oxygen mechanism. In spite of these extensive studies on phototendering of vat dyes reported so far [7–11,24–31], the essential reason giving the highest lightfastness to vat dyes among various kinds of dyes for cellulose seems believed to have not completely been elucidated.

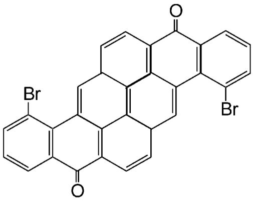
In the present study, we examine the photo-oxidative and reductive fading of nine vat dyes with no or mild tendering property on water-swollen cellulose under aerobic or anaerobic conditions where either photo-oxidation by singlet oxygen or photo-reduction by hydrogen abstraction has been confirmed to occur (cf. 3.1, 3.2 and 3.4). Comparing the results of the simplistic views on the oxidative and reductive fading on water-swollen cellulose with the real lightfastness on dry cotton, we analyse to which oxidative or reductive action the fading resulting in the lightfatness on dry cotton is attributed. Utilizing the results of phototendering and catalytic fading so far reported using many vat dyes with strong tendering properties, we explain the preferential surface oxidative fading and simultaneous inner reductive fading on dry cellulose. We analyze all the photochemical behaviors to elucidate why some of them have the highest lightfastness among dye classes for cellulose.

2. Experimental

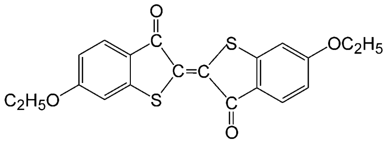
2.1. Dyes used

Nine typical vat dyes (two thioindigoid dyes and seven annelated anthraquinone dyes containing indanthron, violanthron and pyranthron, perylene-tetracarboxylic diimide) were used. Lightfastness and perspiration-light fastness of vat dyes used on cotton fabrics are listed in Table 1. They have small or no tendering property but strong one. In order to estimate the photosensitivity of vat dyes, an aminopyrazolinyl azo dye was used as previously [16–19]. C.I. Generic Name, C.I. Constitution Number, the λ_{max} of UV absorption band and main color band on cellophane, the commercial names of vat dyes used, abbreviation in parenthesis, the method of vat dyeing in the last parenthesis [32], and the chemical structures are shown below:

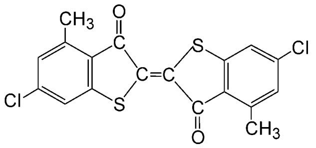
1. C.I. Vat Orange 2, C.I. 59705 (Position of bromine atoms [33]), λ_{max} = 250.0, 457.0 nm, Mikethren Orange RRTS (Orange 2) (IN)



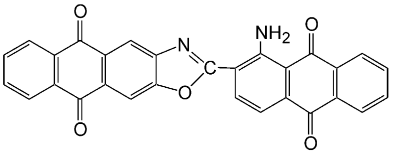
2. C.I. Vat Orange 5, C.I. 73335, λ_{max} = 501.0 and 522.0 nm, Mikethren Orange R (Orange 5) (SR 1)



3. C.I. Vat Red 1, C.I. 73360, λ_{max} = 513.5 nm, Indanthren Brilliant Pink R (Red 1) (SR 1)



4. C.I. Vat Red 10, C.I. 67000, λ_{max} = 267.0, 510.0 nm, Mikethren Red FBB (Red 10) (IW)



5. C.I. Vat Red 23, C.I. 71130, λ_{max} = 213.5, 459.0 nm with a large plateau on the long wavelength side, Indanthren Red FGL (Red 23) (IW)

Table 1
Colour fastness, catalytic fading and phototendering of vat dyes on cotton fabrics

Dye[a]	Light fastness[b]		Perspiration-light[c]		Catalytic fading[d] [7]	Phototendering[d] [7]
	N/1	N/12	Acid	Alkaline		
Vat Orange 2[e]	6	4	4–5	4–5	Weakly active	−2
Vat Orange 5[f]	4–5	3–4	3–4	3–4	Weakly active	−2
Vat Red 1[e,f]	5–6	4	3–4	3–4	Weakly active	−2
Vat Red 10[e]	6–7	5	4–5	4–5	Slightly active	−1
Vat Red 23	7–8	6	5	5	Slightly susceptible	0
Vat Blue 4	8	7	4–5	4–5	Slightly susceptible	+4
Vat Blue 20	7–8	5	4–5	4–5	Slightly susceptible	0
Vat Green 1	7–8	6	5	5	Slightly susceptible	+1
Vat Green 3	8	7	5	5	Slightly susceptible	+3

[a] C.I. Generic Name.

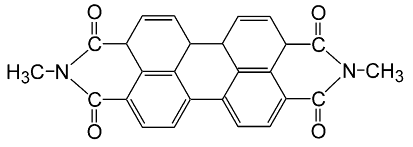
[b] JIS L 0842 (Carbon arc).

[c] JIS L 0888, in which the concentration of histidine in the artificial perspiration is ten times larger than the established one. Dyeing depth = N/3.

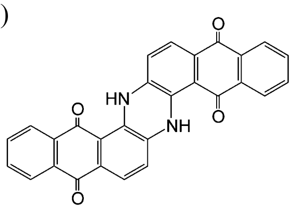
[d] − = damaging action; + = protective action (The authors filled the blanks of Ref. [7].)

[e] Protect unoxidised dyeings from direct sunlight.

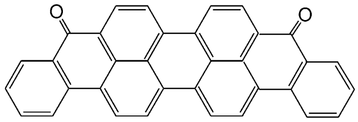
[f] accelerate tendering on exposure to light (Colour Index 3rd Edition). (According to ref. [32], the first column becomes: Orange 2[e,f]; Red 1[f]; Blue 20[e]; and the other dyes are the same.)



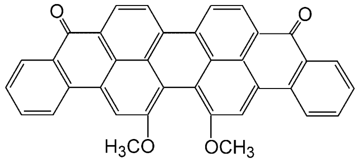
6. C.I. Vat Blue 4, C.I. 69800 (Indanthron), λ_{max} = 276.0, 601.5 nm, Mikethren Blue RSN (Blue 4) (IN)



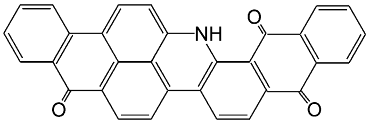
7. C.I. Vat Blue 20, C.I. 59800 (Violanthron), λ_{max} = 227.0, 523.0 nm, Indanthren Dark Blue BOA (Blue 20) (IN)



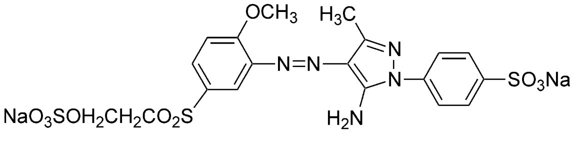
8. C.I. Vat Green 1, C.I. 59825, λ_{max} = 221.0, 249.5, 405.0, 620.0 nm, Mikethren Brilliant Green FFB (Green 1) (IN)



9. C.I. Vat Green 3, C.I. 69500, λ_{max} = 223.0, 266.5, 626.0 nm, Indanthren Olive Green B (Green 3) (IN)



10. An aminopyrazolinyl azo dye, λ_{max} = 218.0, 397.0 nm, (Pyr-Yellow)



2.2. Dyeing of cellulose film

Cellophane films (Futamura Kagaku Kogyo K.K. #300), cut into tapes of 3 cm wide, were dyed by IN, IW or SR 1 method at the prescribed temperature to obtain dyeings of a prescribed depth (Absorbance at λ_{max} of visible absorption band = 0.75–0.9) [32]. After dyeing, oxidation was carried out in water at room temperature at least overnight and 'soaping' or rinsing in boiling water for 20 min. Through dyeing and 'soaping,' a thorough purification of dyes has been made on the films.

2.2.1. Mixture dyeing with Pyr-Yellow

Cellophane films dyed previously by each vat dye were further dyed by a vinylsulfonyl reactive dye, Pyr-Yellow, to estimate the photosensitivity of vat dyes using the alkali-shock method [22] to obtain the prescribed concentrations of both the dyes (Absorbance of Pyr-Yellow at λ_{max} of 397 nm = ca. 0.3, that of vat dyes, see 2.2).

2.3. Exposure of dyed cellophane

2.3.1. Photofading of dyes on water-swollen cellophane films

The relative fading, A/A_0 (the ratio of the absorbance of the initial and exposed dyed samples), at λ_{max} of colour band was estimated by exposing the dyed films immersed in aerated water to carbon arc light. In cases where the second dye, which has an influence on the absorption of λ_{max}, exists, the absorbance at the other wavelength was used (cf. Table 2). By exposing the dyed films when immersed in an aqueous Rose Bengal (RB) solution (3.3×10^{-4} mol dm^{-3} + 0.05 M Na_2SO_4), the ease with which the dyes were photo-oxidized was estimated [18,22]. The aqueous RB solution was renewed every ten hours during exposure to maintain the concentration of RB, adsorbed from the aqueous solution in which the dyed film was immersed, on the film to be constant. RB adsorbed by cellophane during exposure was washed off by boiling water, by 10% aqueous dimethylformamide solution at 50 °C and, if not possible, treated by an aqueous hypochlorite solution (0.05 g available chlorine dm^{-3}; pH 8, 25 °C). It was confirmed before the treatments that these conditions had no

Table 2
Relative fading, A/A_0, of vat dyes on cellulose immersed in aerobic Rose Bengal solution on exposure to carbon arc and that on cellulose immersed in anaerobic DL-mandelate solution

C.I. vat dye	Oxidative fading by Rose Bengal[a]				Reductive fading by DL-mandelate[b]		
	Time of exposure			Initial rate of fading (min^{-1})	Time of exposure		Wavelength observed (nm)
	10 h	20 h	40 h		5 h	10 h	
Orange 2	0.990	0.955	– [c]	3.75×10^{-5}	1.064	1.080	457
Orange 5	0.970	0.949	0.909	5.13×10^{-5}	0.973	0.966	521
Red 1	0.999	0.963	0.941	3.08×10^{-5}	0.850	0.777	514
Red 10	0.980	0.937	0.908	5.13×10^{-5}	0.911	0.863	510
Red 23	0.972	– [c]	– [c]	4.67×10^{-5}	0.992	0.964	458
Blue 4	0.940	0.880	0.778	9.63×10^{-5}	0.813	0.734	750
Blue 20	0.998	0.980	0.950	1.67×10^{-5}	0.902	0.882	625
Green 1	0.946	0.917	0.904	7.96×10^{-5}	0.966	0.940	720
Green 3	0.916	0.853	0.825	1.36×10^{-4}	0.952	0.935	725

[a] Exposure in aqueous RB (3.3×10^{-4} M + 0.05 M Na_2SO_4) solution.
[b] Exposure in anaerobic aqueous 0.05 M DL-mandelate (+0.05 M Na_2SO_4) solution (pH 6.2)
[c] After exposure in aqueous Rose Bengal solution, little fading was observed.

effect on the absorption spectra of vat dyes examined but that of RB.

2.3.2. *Estimation of the photosensitivity of vat dyes*

Exposing film samples that had been dyed in admixture with the vat dye and Pyr-Yellow, which had very large ease of photo-oxidation and small photosensitivity, to carbon arc light without or behind a Toshiba filter Y-46 (>470 nm), the photosensitivity of vat dyes was estimated [19,22]. Since some vat dyes showed much smaller photosensitivity than Pyr-Yellow, the influence of the photosensitivity of Pyr-Yellow itself on the estimation for vat dyes may not be neglected. In order to minimize the influence, the absorbance of Pyr-Yellow at λ_{max} in the mixture dyeing with vat dyes was adjusted so as to be constant ratio (in this case; about a third of that for vat dyes) and a yellow filter was used to remove the effect of self-photosensitivity of Pyr-Yellow on fading.

2.3.3. *Estimation of the photo-reductivity of vat dyes*

The values of A/A_0 were estimated by exposing the dyed films immersed in a deaerated DL-mandelate (+0.05 M Na_2SO_4) solution (pH 6.2–6.6) [16]. The dyed film was set on the inner surface of a glass cell on a cell folder placed in a glass vessel and was exposed to the carbon arc light in a fade-ometer. Modifying a sample holder for JIS L 0888 made the cell holder with which a glass vessel was equipped. Under the anaerobic conditions a pair of two sheets of cellophane of the same size as the sample, all the films of which were previously impregnated by the DL-mandelate solution, was set in front of and behind the sample film (Total: five sheets) inside the front glass of a glass cell for exposure. On the rear side of the films, a glass plate was put for preventing penetration of trace oxygen. After evacuating a glass vessel, nitrogen of ordinary pressure was filled in the glass vessel in which the glass cell was set. Under the anaerobic conditions, a sheet of the dyed film was set in the glass cell, which was set in the glass vessel mentioned above, was allowed to keep for 24 h before exposure.

3. Results and discussion

3.1. *Ease with which the dye is photo-oxidized*

Exposing vat-dyed cellophane films immersed in an aqueous RB solution to carbon arc, ease with which the dye was photo-oxidized was determined. Under these conditions, it was confirmed by several diagonistic tests that the photo-oxidation by singlet oxygen occurred in water-swollen cellulose [18].

The second-order rate constant, k_0 ($\mathrm{mol^{-1}\ dm^3\ s^{-1}}$), of a dye in the reaction with ${}^1O_2$ generated by RB may be estimated from the rates of fading for the initial period of exposure. This process may be described as follows:

$$D + {}^1O_2 \xrightarrow{k_0} \text{Oxidation products of dyes} \qquad (1)$$

$$\frac{\mathrm{d}[D]}{\mathrm{d}t} = -k_0[{}^1O_2][D] \qquad (2)$$

Since the concentration of dyes in the excited states is low and the lifetime is very short, the oxidation may almost occur for dyes in the ground state. The steady state condition was assumed by the continuous exposure; the concentration of ${}^1O_2$ was given by the product of the solubility of dioxygen in water and the quantum yield of ${}^1O_2$ by RB. These reactions proceed in water-swollen cellulose, a heterogeneous reaction system. It was assumed that the reaction system is treated homogeneous in the initial period of exposure where the fading of dyes is small, since the concentration of RB is kept constant (cf. 2.3.1).

The initial rates of photo-oxidation of vat dyes photosensitized by RB are listed in Table 2, and the values of k_0, of reaction between dye and ${}^1O_2$, in Table 3 using the value of k_0 of Pyr-Yellow as the reference, the same methods as used previously [18,22]. The values of k_0 range from 0.0018 to 0.014 $\mathrm{mol^{-1}\ dm^3\ s^{-1}}$, the latter is the same as the least value of k_0 for reactive dyes examined [19,22] and the former may be the least values of organic dyes attained.

Vat dyes have very high stability to the oxidative attacks, compared with usual reactive dyes examined previously [19,22]. Although the differences in the magnitudes of photo-oxidizability were small, the order of the ease of photo-oxidizability was as follows:

$$\text{Green 3} > \text{Blue 4} > \text{Green 1} > \text{Red 10} \div \text{Orange 5} > \text{Red 23} > \text{Orange 2} > \text{Red 1} > \text{Blue 20} \qquad (3)$$

This order seems to have no correlation with the lightfastness listed in Table 1, although the small values of k_0 must be one of the absolute necessities that vat dyes have the highest lightfastness in the single dyeings and avoid suffering from catalytic fading in the mixture dyeings. It is noteworthy that thioindigo dyes have not larger values of k_0 than anthraquinone dyes have, despite of the lower lightfastness than that of anthraquinone dyes. These facts imply that the differences in the light stability on cellulose are not attributed only to the differences in the values of k_0. Some factors

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

No.	Dyes	k_0[a] ($\mathrm{mol^{-1}\ dm^3\ s^{-1}}$)	f (–) Y-46 filter	f (–) No filter	Rate of photo-reduction in MA[b] ($\mathrm{min^{-1}}$)
1	Vat Orange 2	0.0039_8	0.19	0.22	1.6×10^{-4}
2	Vat Orange 5	0.0054_5	0.32	0.45	7.3×10^{-5}
3	Vat Red 1	0.0032_7	0.25	0.26	4.4×10^{-4}
4	Vat Red 10	0.0054_5	0.100	0.16	2.6×10^{-4}
5	Vat Red 23	0.0049_6	0.016	0.016	4.3×10^{-5}
6	Vat Blue 4	0.0102_2	1.65×10^{-3}	2.29×10^{-3}	5.3×10^{-4}
7	Vat Blue 20	0.0017_7	0.036	0.028	2.6×10^{-4}
8	Vat Green 1	0.0084_5	1.92×10^{-3}	2.15×10^{-3}	1.1×10^{-4}
9	Vat Green 3	0.014_4	2.68×10^{-3}	5.46×10^{-3}	1.3×10^{-4}
10	Reactive Blue 19	0.014 [34]	–	0.027 [34]	1.4×10^{-4} [16]
11	CuPc (VS)	0.081 [34]	–	0.095 [34]	8.0×10^{-4} [16]
12	Pyr-Yellow	6.9 [34]	–	0.015 [34]	0.0 [16]
13	Rose Bengal		(0.76)	0.76 [36,37]	–

[a] Exposure in aqueous RB (3.3×10^{-4} M + 0.05 M Na_2SO_4) solution (cf. Table 4).

[b] Exposure in an anaerobic aqueous 0.05 M DL-mandelate (+ 0.05 M Na_2SO_4) solution (pH 6.6) (cf. Table 2).

other than the photo-oxidizability may also contribute to the extent of lightfastness on cellulose.

3.2. Photosensitization of vat dyes

Lightfastness of reactive dyes on cellulose has close relation with the photosensitivity of themselves [4,19,22]. Azo dyes with high lightfastness are reported to possess small photosensitivity [16,34,35]. In order to estimate what degree of the photosensitivity vat dyes have, the relative fading of Pyr-Yellow on cellophane dyed in admixture with vat dyes is examined using the same method applied previously to reactive dyes [19,22].

3.2.1. Estimation of apparent photosensitivity f without filter

Exposing the mixture-dyed cellophane in aerated water without filter, the values of A/A_0 of Pyr-Yellow are listed in Table 4, from which the values of initial rate of fading were determined as shown in the 8th column of Table 4. Using the value of Pyr-Yellow on cellophane immersed in an aqueous RB solution as the reference value [36,37], the apparent photosensitivity, f (–), of vat dyes or apparent quantum yield to generate singlet molecular oxygen was determined, based on the same assumption as in Section 3.1, as shown in the fifth column of Table 3.

The order of the apparent photosensitivity of vat dyes determined without filter was as follows:

$$\text{Orange 5} > \text{Red 1} > \text{Orange 2} > \text{Red 10} >> \text{Blue 20} > \text{Red 23} > (\text{Pyr-Yellow}) >> \text{Green 3} > \text{Blue 4} > \text{Green 1} \quad (4)$$

The value of f for Pyr-Yellow was smaller than those of vat dyes such as thioindigos and larger than those of some anthraquinone dyes. If the photosensitivity of mixture dyeing emerges additively as an overlapping effect of component dyes,

Table 4
Values of A/A_0 for Pyr-Yellow on cellulose dyed in admixture with vat dyes on exposure to carbon arc directly or behind Y-46 filter under wet conditions[a]

No.	C.I. vat dyes	Filter	Time of exposure				Initial fading (min^{-1})	
			10 min	20 min	30 min	60 min	Rate	Difference
1	Orange 2	No filter	0.811 (0.977)	0.632 (0.988)	0.467 (0.963)	0.247 (0.979)	1.89×10^{-2}	1.2×10^{-2} (2.7)[b]
		Y-46	0.969 (1.0)	0.885 (0.976)	0.823 (0.988)	0.575 (0.990)	7.08×10^{-3}	
2	Orange 5	No filter	0.615 (0.986)	0.337 (0.973)	0.177 (0.991)	<0.01 (0.981)	3.85×10^{-2}	2.7×10^{-2} (3.2)[b]
		Y-46	0.880 (0.991)	0.725 (0.983)	0.734 (0.977)	0.468 (1.0)	1.20×10^{-2}	
3	Red 1	No filter	0.789 (0.976)	0.572 (0.977)	0.333 (0.992)	0.186 (0.990)	2.20×10^{-2}	1.3×10^{-2} (2.4)[b]
		Y-46	0.940 (1.0)	0.813 (0.970)	0.697 (0.997)	0.599 (1.0)	9.35×10^{-3}	
4	Red 10	No filter	0.863 (1.0)	0.782 (0.981)	0.704 (0.999)	0.478 (0.988)	1.37×10^{-2}	1.0×10^{-2} (3.7)[b]
		Y-46	0.964 (0.977)	0.921 (1.00)	0.885 (0.983)	0.767 (0.989)	3.72×10^{-3}	
			1 h	2 h	4 h	10 h		
5	Red 23	No filter	0.917 (1.0)	0.837 (1.0)	0.674 (1.0)	0.521 (0.979)	1.38×10^{-3}	8.0×10^{-3} (2.4)[b]
		Y-46	0.965 (1.0)	0.944 (1.0)	0.917 (1.0)	0.794 (1.00)	5.83×10^{-4}	
6	Blue 20	No filter	0.855 (0.983)	0.768 (0.990)	0.630 (1.0)	0.204 (0.979)	2.42×10^{-3}	1.1×10^{-3} (1.8)[b]
		Y-46	0.920 (0.977)	0.839 (0.961)	0.770 (1.0)	0.571 (0.982)	1.33×10^{-3}	
			5 h	10 h	20 h			
7	Blue 4	No filter	0.913 (1.0)	0.880 (1.0)	0.765 (1.0)		1.96×10^{-4}	1.3×10^{-4} (3.2)[b]
		Y-46	0.937 (0.992)	0.973 (1.0)	0.974 (1.0)		6.17×10^{-5}	
8	Green 1	No filter	0.949 (1.0)	0.848 (0.999)	0.789 (0.981)		1.84×10^{-4}	1.1×10^{-4} (2.6)[b]
		Y-46	0.983 (0.983)	0.957 (1.0)	0.990 (0.993)		7.17×10^{-5}	
9	Green 3	No filter	0.860 (0.993)	0.770 (1.0)	0.582 (1.0)		4.67×10^{-4}	3.7×10^{-4} (4.7)[b]
		Y-46	0.946 (1.0)	0.940 (0.993)	0.958 (1.0)		1.00×10^{-4}	

[a] Values in parentheses are A/A_0 for vat dyes.

[b] Ratio (–) of the initial rates of fading of Pyr-Yellow by exposure with and without filter.

the values of f obtained must be larger than 0.015 (f of Pyr-Yellow). All the vat dyes examined did not satisfy the condition, although Pyr-Yellow may have some effects. In the mixture dyeing with C.I. Vat Blue 4, Green 1 and Green 3, Pyr-Yellow had little effect on the photosensitivity. Three vat dyes may act as a filter of Pyr-Yellow but the other vat dyes. Before why these dyes have the shielding effect is discussed, exposure of mixture-dyed cellophane by use of a yellow filter is carried out.

3.2.2. Estimation of f *by use of filter*

Results of exposure of mixture-dyed cellophane behind a yellow filter are shown in Table 4 (A/A_0 for different times of exposure and the initial rates of fading of Pyr-Yellow) and in Table 3 (f-values). There is a problem of reference for the f-values, because no reference value by exposure behind a Y-46 filter exists. The same reference value as that without filter was employed. (Then, this is described as the f-value in parenthesis in Table 3). The filter lowered the initial rates of fading of Pyr-Yellow without exception, although degree of influences varied with dyes.

The order of the apparent photosensitivity of vat dyes determined by exposure behind a Y-46 filter was as follows:

$$\begin{aligned}&\text{Orange } 5 > \text{Red } 1 > \text{Orange } 2 > \text{Red } 10 >> \\ &\text{Blue } 20 > \text{Red } 23 > (\text{Pyr-Yellow}) >> \\ &\text{Green } 3 > \text{Green } 1 > \text{Blue } 4 \qquad (5)\end{aligned}$$

Except for the formal reversal between C.I. Vat Green 1 and Blue 4 in the orders (4) and (5) due to the very small difference in the initial rates of fading, the orders (4) and (5) coincide each other, indicating no effect of yellow filter. The ratios of the initial rate of fading with and without use of filter ranged from 1.8 to 4.7, while the differences in the initial rates of fading were also small. They are listed in the last column of Table 4 (the ratios in parenthesis). The fact that yellow filter has little effect on the fading of Pyr-Yellow shows that anthraquinone vat dyes possess shielding effect in the molecule itself (cf. 3.5.6), which makes the yellow filter invalid. The fact that three anthraquinone dyes exhibit small photosensitivity and small decreases in the apparent photosensitivity by use of yellow filter means that these vat dyes have possibilities to act as potential suppressor of photosensitization or coloured UV-absorber and that the excited states of these dyes by visible absorption near-UV region and UV-absorption are deactivated effectively by internal conversion, since these dyes have no fluorescence. This is also one of the absolute necessities why anthraquinone vat dyes have very high lightfastness on cellulose as well as on wool and nylon.

In order to examine to what degree photosensitivity determines the lightfastness of vat dyes, relationship between lightfastness on cotton fabric and log f, estimated with and without filter, was plotted as shown in Fig. 1(a). As can be seen, a

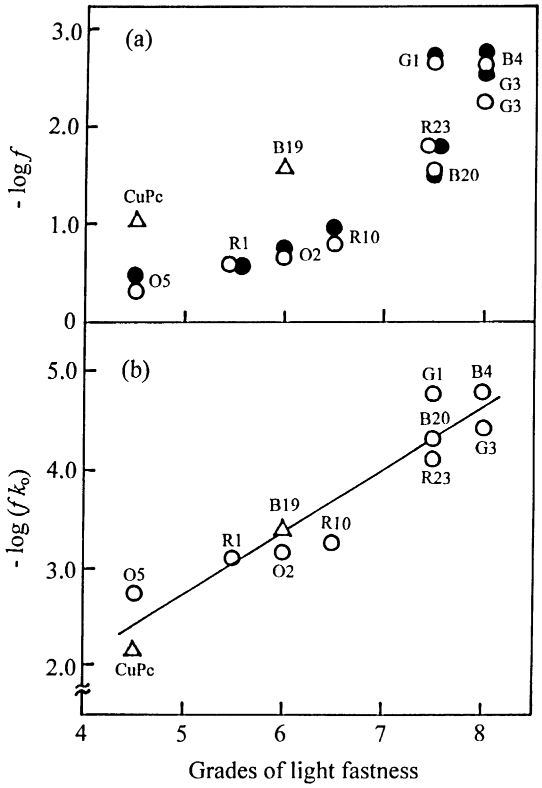


Fig. 1. (a) Relationships between the grade of light fastness on cotton fabrics and log f, and (b) those between the grade of light fastness and the logarithmic product of k_0 and f for vat (○) and reactive (△) dyes on cellophane films determined without filter (open symbols) and with Y-46 filter (closed symbols) (cf. Table 3). Position of plots is described by the initial letter of C.I. Generic (Colour) Name accompanied with the number except for CuPc [34].

rough correlation exists in the figure. In case of vat dyes, shielding effect seems to be small. But, this figure indicates as well that the photosensitivity contributes dominantly to the lightfastness of vat dyes on cellulosic substrate, as in the case of reactive dyes [22,34,35].

3.3. Relationship between lightfastness on cellulose and oxidative fading

In the previous paper [22], it was reported that high lightfastness of triphenodioxazine dyes on cellulosic substrate is attributed to the very small photosensitivity in spite of their relatively large values of k_0, compared with those of azo and anthraquinone dyes with high lightfastness [34,35]. The stability of dyes on cellulose to photo-oxidative attack may depend upon the products of the values of k_0 and f, and upon the environmental conditions under which the substrate exists. In order to examine this relation for vat dyes used, the logarithmic products of the values of k_0 and f, listed in Table 3, were plotted against the lightfastness on cellulose, as being illustrated in Fig. 1(b). Some data of reactive dyes [34], listed in Table 3, were also added. It shows that there exists a clear correlation between lightfastness on cotton fabrics and log (fk_0). Comparing two figures of (a) and (b) each other, superposition of two factors, k_0 and f, improved considerably the scatter in the relationships. This indicates that the values of k_0 contribute also to the lightfastness. This fact shows that the lightfastness of vat dyes is almost determined by the photo-oxidative fading on cellulosic substrates. It is worth noting that both the parameters on abscissa were determined on water-swollen cellulose under aerobic conditions, on which only oxidative fading should occur, while the ratings of lightfastness on dry cotton fabric on ordinate.

It is concluded that the lightfastness of dyes on cellulose depends primarily on the photosensitivity and secondarily on the ease of photo-oxidation, the lightfastness ratings being proportional to log (fk_0). Vat dyes with the highest lightfastness possess extremely small values of f as well as k_0 among dyes for cellulose.

Above observation implies us an important fact that photo-oxidative fading of vat dyes should take place preferentially from the surface of cellulosic substrate, because it may occur only under aerobic conditions. The photo-reduction of dyes should occur in the inner part of cellulosic substrate, whenever it does on dry cellulose in air, since the environment in which the reduction progresses must be kept anaerobic.

3.4. Photo-reduction of vat dyes

The photo-reduction of vat dyes was studied as the photochromism [38,39] and as a result of promotion effect by environmental conditions such as oxygen content [40] and existence of substrates [41,42]. Since the quantum yields of the $T_1(n\pi^*)$ states have a close relation both the photo-oxidation and reduction, the tendency of photo-reduction may be roughly proportional to that of photo-oxidation. In order to examine to what degree the photo-reduction of nine vat dyes with low or no tendering activity proceeds, cellophane films dyed with vat dyes were exposed to carbon arc on immersing in an aqueous anaerobic DL-mandelate solution and the absorption spectra were measured immediately after the exposure as immersed in the mandelate solution. Since it has been confirmed that only the photo-reduction of various reactive dye occurred under this experimental condition [16], the similar mechanism may hold for vat dyes. [When the $T_1(n\pi^*)$ states of carbonyl groups in vat dyes abstract a hydrogen atom, a semiquinone dye radical and a cellulose radical are formed, depending on the kinds of carbonyl groups in vat dyes. Although no structure of the dye radical was assigned, a mixture of dye radicals is referred (acid) leuco-compounds.]

The absorption spectra displayed gradual variations with time of exposure, implying a progress of photo-reduction, as illustrated in upper part of Figs. 2–6 as the typical examples of nine dyes. When exposed cellophane films were allowed to immerse in water or to dry in air at least overnight after measuring the spectra as exposed, re-oxidation of photo-reduced species occurred gradually. The absorption spectra on dry film after complete re-oxidation were measured. They are illustrated in lower part of each figure. The spectral changes of dyes on cellulosic films during exposure under

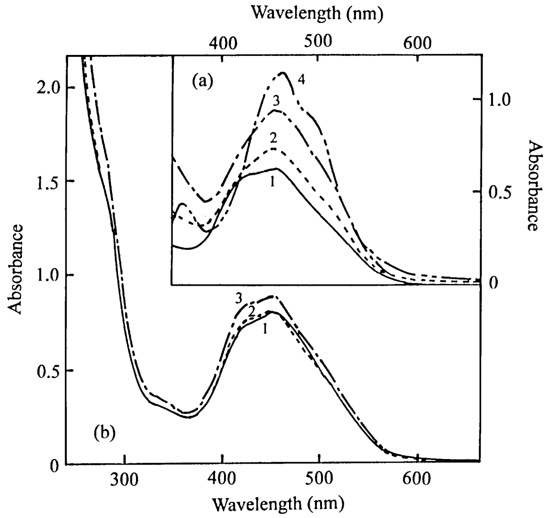


Fig. 2. (a) Absorption spectra (measured as immersed) of C.I. Vat Orange 2 on cellophane after exposure for 0 h (1), 5 h (2), 10 h (3) on immersing in aqueous anaerobic DL-mandelate solution, and thermal reduction (4) in formamidinesulfinic acid (0.10 M) in 0.5 M phosphate buffer (0.25 M Na_2HPO_4 + 0.25 M Na_2HPO_4) for 10 min at 40 °C (complete return to the original spectrum was confirmed) and (b) those on dry cellophane of corresponding photo-reduced sample after complete re-oxidation.

anaerobic conditions and after the re-oxidation of every exposure are summarized in Table 5.

In general, by exposure under the anaerobic conditions, slow formation of semi-reduced species or apparent colour changes of vat dyes in the direction of acid leuco-compounds under neutral conditions occurred, while little photo-reductive decomposition of the compounds proceeded (cf. 3.5).

3.4.1. C.I. Vat Orange 2

With time of exposure under anaerobic conditions, the intensity of visible absorption band was increased as illustrated in Fig. 2(a). But the spectra were considerably different from those of thermally reduced species, indicating different structure of the photo-reduced species from thermally reduced ones. After the exposed samples were re-oxidized, the spectrum of 5 h-exposed sample showed a small change from the original one, while the spectrum of 10 h-exposed sample a considerable increase of visible absorption band [Fig. 2(b)].

The lability of halogen atoms in some vat dyes was reported to high vatting temperatures [33] and light [43–45]. Cooper and Stonehill [43] reported that the irradiation of C.I. Vat Orange 2 in chlorobenzene resulted in dehalogenation showing a red shift of visible band with a hyperchromic change, which may be the same spectral changes illustrated in Fig. 2.

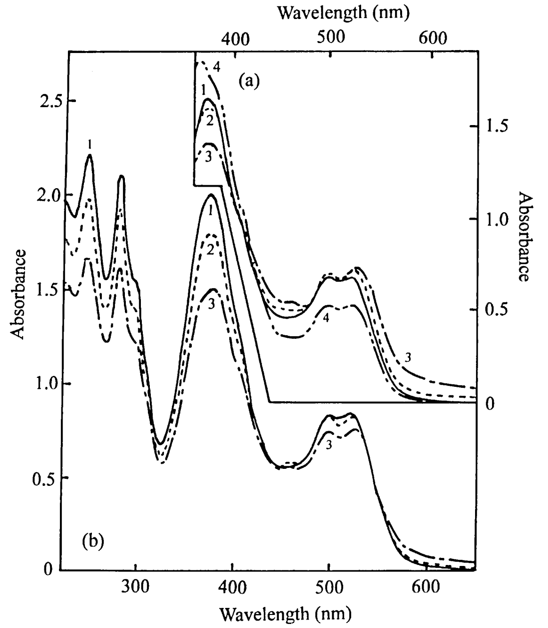


Fig. 3. (a) Absorption spectra (measured as immersed) of C.I. Vat Orange 5 on cellophane after exposure for 0 h (1), 5 h (2), 10 h (3) on immersing in aqueous anaerobic DL-mandelate solution, and thermal reduction (4) in $Na_2S_2O_4$ (4.0 g dm^{-3}) in 0.1 M phosphate buffer for 10 min at 40 °C (complete return to the original spectrum was confirmed), and (b) those on dry cellophane of corresponding photo-reduced sample after complete re-oxidation.

Halogenation brings about an improvement in the dyeing property of indigoid, thioindigoid and anthraquinone vat dyes [33]. C.I. Vat Orange 2 has a rather low stability to photo-reductive attacks. Since the spectral variations as a result of photo-reduction occur in a direction to cancel the result of photo-reduction, this dye may be estimated to have higher stability than the real. Bromination is not a modification to give very high light stability.

3.4.2. Thioindigoid dyes, C.I. Vat Orange 5 and Red 1

On wool, indigos and the halogenated indigos have excellent lightfastness (grade 8), and a grade

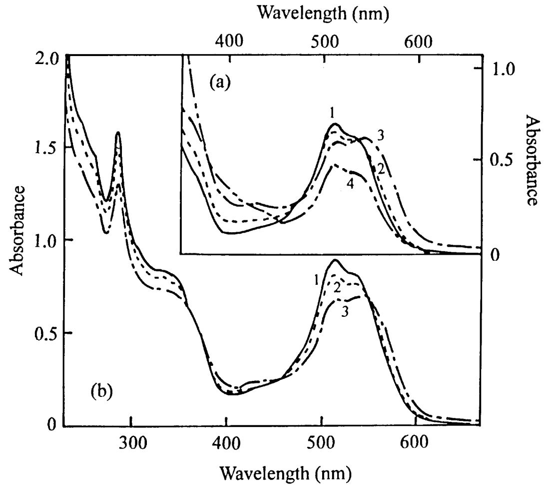


Fig. 4. (a) Absorption spectra (measured as immersed) of C.I. Vat Red 1 on cellophane after exposure for 0 h (1), 5 h (2), 10 h (3) on immersing in aqueous anaerobic DL-mandelate solution, and thermal reduction (4) in $Na_2S_2O_4$ (4.0 g dm^{-3}) in 0.1 M phosphate buffer for 10 min at 40 °C (complete return to the original spectrum was confirmed), and (b) those on dry cellophane of corresponding photo-reduced sample after complete re-oxidation.

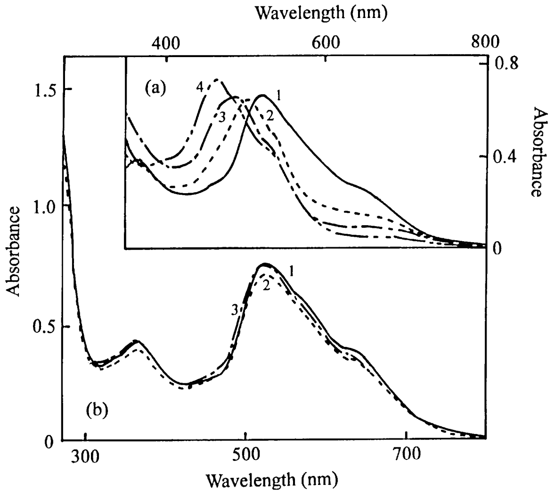


Fig. 5. (a) Absorption spectra (measured as immersed) of C.I. Vat Blue 20 on cellophane after exposure for 0 h (1), 5 h (2), 10 h (3) on immersing in aqueous anaerobic DL-mandelate solution, and thermal reduction (4) in $Na_2S_2O_4$ (4.0 g dm^{-3}) in 0.1 M phosphate buffer for 10 min at 40 °C (complete return to the original spectrum was confirmed), and (b) those on dry cellophane of corresponding photo-reduced sample after complete re-oxidation.

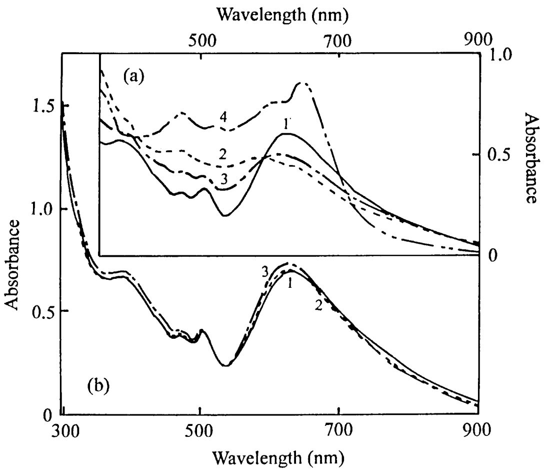


Fig. 6. (a) Absorption spectra (measured as immersed) of C.I. Vat Green 3 on cellophane after exposure for 0 h (1), 5 h (2), 10 h (3) on immersing in aqueous anaerobic DL-mandelate solution, and thermal reduction (4) in formamidinesulfinic acid (0.10 M) in 0.5 M phosphate buffer (0.25 M Na_2HPO_4 + 0.25 M Na_2HPO_4) for 10 min at 40 °C (complete return to the original spectrum was confirmed), and (b) those on dry cellophane of corresponding photo-reduced sample after complete re-oxidation.

of 6–8 is attained by many indigos and thioindigoid dyes on the protein fibre [46]. Photo-oxidative fading may be suppressed, since singlet molecular oxygen is almost quenched by wool substrates. On cotton, indigo and other indigoid dyes usually have lightfastness only of the grade 3–4; but a few magenta and pink thioindigoid dyes have higher fastness (grade 5–6) (cf. Table 1). They have, however, the perspiration-light fastness of grade 3–4 on cotton, indicating that they undergo also photo-reduction depending upon the environmental conditions. Exposing the vat-dyed cellulosic films immersed in an aqueous anaerobic DL-mandelate solution, only the photo-reduction should proceed.

1. *C.I. Vat Orange 5*: Absorption of longer wavelength side of double peak and that at wavelengths longer than the peak was increased with exposure, while absorption band with λ_{max} of 380 nm was decreased, as being illustrated in Fig. 3(a). Absorption spectrum of photo-reduced species was similar to that of thermally reduced species by sodium dithionite or formamidinesulfinic acid (FSA). This dye suffered reductive decomposition

Table 5
Photo-reduction of vat dyes on cellulose by exposure immersing in aqueous anaerobic DL-mandelate solution and the re-oxidation in air

Dye	Spectra of photo-reduced dye (measured on wet film as photo-reduced)	Spectra of re-oxidized dye (measured on dry film after air oxidation)	Figure illustrated
Orange 2	Increase of visible absorption band due to photo-reduction and debromination	Almost complete return from photo-reduction from 5 h-exposure and small fading by 10 h-exposure	Fig. 2(a), (b)
Orange 5	Decrease of main absorption band of double peak around 500 nm, and large decrease of A/A_0 at 380 nm	Distinct decrease with time of exposure after air oxidation	Fig. 3(a), (b)
Red 1	Spectral change with two isosbestic points, implying partial variation of structure (dechlorination)	Spectral change with three isosbestic points, implying partial variation of structure (dechlorination)	Fig. 4(a), (b)
Red 10	Decrease of A/A_0 at λ_{max} with time of exposure. Same spectra after exposure and re-oxidation.	Small decrease of A/A_0 by photo-reduction at λ_{max} with time of exposure	–
Red 23	Decrease of A/A_0 at λ_{max} with time of exposure	Complete return from 5 h-exposure but a small decrease of A/A_0 at λ_{max} with time of exposure more than 5 h.	–
Blue 4	Blue-shift of λ_{max} (increase by 5 h-exposure (change to brownish) and decrease by 10 h-exposure)	Increase of main absorption at 590–600 nm with exposure, but a small decrease of A/A_0 at >700 nm.[a]	–
Blue 20	Blue-shift of λ_{max} with time of exposure	Almost complete return of spectrum by re-oxidation, but a small decrease of A/A_0 at >600 nm.	Fig. 5(a), (b)
Green 1	Blue-shift of λ_{max} or increase of the absorption around 500 nm (change to brownish) with time of exposure	Almost complete return of spectrum by re-oxidation, but a small decrease of A/A_0 at >650 nm.	–
Green 3	Spectral change with two isosbestic points	Almost complete return of spectrum by re-oxidation, but a small decrease of A/A_0 at >700 nm.	Fig. 6(a), (b)

[a] Colour changes (the maximum around 750 nm, cf. Table 2 and 3) occurred simultaneously in the photo-reduction/re-oxidation processes, but no change on exposure longer than 10 h.

by FSA with ease, when strong conditions were applied. After re-oxidation, both the absorption of the double peak and the UV-peak was decreased with exposure (Fig. 3(b) and Table 5). Thus, exposing under anaerobic conditions, distinct reductive fading of this dye, a decomposition of thioindigo, was observed. This dye has low stability to photochemical and thermal reductive attacks.

2. *C.I. Vat Red 1*: With time of exposure, the absorption spectra showed gradual change with two isosbestic points, as illustrated in Fig. 4(a). After re-oxidation, the gradual changes in the spectrum with at least three isosbestic points were observed [Fig. 4(b) and Table 5]. By mild thermal reduction, the absorption spectra reversible to the original one by re-oxidation were observed, while the changes in the spectrum by photo-reduction were completely irreversible, although the spectra changed accompanying with isosbestic points, implying dehalogenation.

Hibbert et al. [47,48] reported that isatin and dibromoisatin were isolated from the photodegradated cotton fabric dyed with indigo and tetrabromoindigo, respectively, indicating the oxidation of indigoes and dehalogenation during exposure. Dehalogenation from anthraquinone vat dyes often occurs thermally in an aqueous solution under reducing atmosphere as well as by the irradiation of the leuco salt solution [33,43–46]. This may be an evidence to show that the photo-oxidation and photo-reduction took place under the circumstances.

3.4.3. C.I. Vat Red 10 and Red 23

Although these two dyes have different chemical structures and absorption spectra, photo-reductive fading behaviours were similar to each other. With time of exposure under anaerobic conditions, the absorption of visible absorption band of two dyes was gradually decreased (Table 5). This was also observed for the re-oxidized species on dry film. Absorption spectra of photo-reduced species were almost similar to those of the original oxidized species, although those of thermally reduced species were quite different. Exposing under anaerobic conditions, the photo-reductive fading proceeded with time. These dyes have rather low stability to photo-reduction, but have a low tendering activity. Tendering activity may be proportional to photo-reductivity with exception such as C.I. Vat Yellow 1 (cf. Table 6), since both the processes occur via the same $T_1(n\pi^*)$ states.

3.4.4. C.I. Vat Blue 4 and Green 1

Although these two dyes have different chemical structures and absorption spectra, photo-reductive fading behaviours were similar to each other (Table 5). On exposure of C.I. Vat Blue 4 under anaerobic conditions, small blue shift of all over the colour band with λ_{max} of 595 nm was observed. Compared with the spectra of the original sample, absorption spectra of re-oxidized species on dry film showed a very small increase at the peak and a gentle decrease of ridgeline in the long wavelength side of the peak. C.I. Vat Green 1 showed little spectral variation (more tiny one than that of C.I. Vat Blue 4) by the exposure as well as by the re-oxidation. The excited singlet states of these dyes may perform internal conversion of very high efficiency, as was discussed in a previous paper [22]. The absorption spectra of thermally reduced species of both the dyes show a

Table 6
Fading behaviours of vat-dyed nylon fabric on exposure under different environmental conditions [40] and the lightfastness of vat dyes used on cellulose and polyamide

Vat Dyes	C.I. Vat Yellow 1	C.I. Vat Yellow 2	C.I. Vat Green 1
Lightfastness on cellulose[a]	Good lightfastness on viscose rayon: 6 (ISO), 2–3 (AATCC), –[b]	Very poor lightfastness on viscose rayon: 4–5 (ISO)	Good lightfastness on viscose rayon: 7–8 (ISO)
Lightfastness on polyamide	Hue is so sensitive to photo-reductive attack that becomes greenish by short exposure to light [49].	Nylon: 3–4	Nylon: 5–6
		Wool: 3–4 Silk: 4–5	Wool: 7–8 Silk: 7–8
Exposure in vacuum[c]	Reduced; greatest change in shade[e]	Reduced; next greatest change in shade[e]	Reduced; least change in shade.
	Some loss in depth, i.e. some destruction of dye	Some loss in depth, i.e. some destruction of dye	Some loss in depth, i.e. some destruction of dye
Exposure in moist air[d]	Changed shade more slowly in "reduced" direction[f]	Changed shade slowly in "reduced" direction[f]	Very little change of shade.
	More loss in depth.	More loss in depth.	More loss in depth.
Exposure in moist oxygen[d]	Changed shade more slowly than in air.	Changed shade more slowly than in air.	No change of shade.
	More loss in depth.	More loss in depth	More loss in depth.

[a] Data from Colour Index 3rd Edition. Depth: N/1.

[b] Dyeing of 2N/1 depth shows photochromism; returns to original hue in air or on mild soaping.

[c] In a vacuum the presence of the dyes does not accelerate tendering.

[d] In air, the dyes have a marked tendering effect, whilst in pure oxygen the effect is the greatest in all cases. The dye fades in a vacuum and in oxygen and during fading shows by its colour the presence of the leuco-compound. The reduction of the dye which accompanies fading takes place very readily in a vacuum. It takes place less readily in presence of air and least rapidly in pure oxygen.

[e] The magnitudes of shade change are proportional to the tendering activity with exceptions such as C.I. Vat Yellow 1 which is non-tenderer [7,33,46,49].

[f] In the direction of the vat acid.

blue shift accompanied with hyperchromic change, a formation of leuco-compounds whose carbonyl groups were reduced and then ionized depending upon pH. Although little photo-reduction was observed, photo-reduced species may have different structures, one of whose carbonyl groups was reduced, from that of the thermally reduced species. Thus, these dyes may cause practically no reductive fading and even little temporary formation of acid leuco-compounds under anaerobic conditions.

3.4.5. C.I. Vat Blue 20

Exposing under anaerobic conditions, large blue shift of main colour band with λ_{max} of 520 nm accompanying no shift of broad absorption band with λ_{max} of the longest wavelength (670 nm), a gradual colour change, was observed with time, as illustrated in Fig. 5(a). Although, within 10 h of exposure, the ultimate spectrum of photo-reduced species was not attained, it seemed to approach to the absorption spectrum of thermally reduced species (Table 5).

In spite of the large blue shift or apparent remarkable colour change by exposure, the complete return to the original oxidized species was observed [cf. Fig. 5(b)]. Although the photo-reduction of the first stage, whose structure resemble to that of thermally reduced species, occurs with ease, the photo-reduced species of the first stage may not suffer further photo-reduction of the second stage.

3.4.6. C.I. Vat Green 3

Although the structure and the absorption spectra of this dye are different from those of C.I. Vat Blue 20, the spectral variation behaviours by exposure under anaerobic conditions resemble each other, as shown in Fig. 6(a), (b) and Table 5. Large blue shift of main colour band with λ_{max} of 620 nm and small bands with λ_{max} of 500 and 470 nm, a gradual colour change, was observed with time. The absorption spectra of photo-reduced species were quite different from that of thermally reduced species. In spite of large colour change by exposure, complete return of absorption spectra to the original oxidized ones was observed. Although the photo-reduction of the first stage occurs with ease like C.I. Vat Blue 20, the photo-reduced species of the first stage may not suffer further photo-reduction of the second stage.

3.4.7. General behaviour of photo-reduction

As being mentioned above, no photo-decomposition of C.I. Vat Blue 4, Blue 20, Green 1 and Green 3 progressed on exposure in the anaerobic DL-mandelate solution. They may undergo the repetition of partial photo-reduction and re-oxidation on cellulose by daily exposure to sunlight, a reversible photo-reductive colour change [40,49,50], although the extent of colour changes varies with dyes; that of C.I. Vat Blue 20 being the largest.

In the cases of C.I. Vat Red 10 and Red 23, the rates of colour change by the exposure were faster than those of above blue and green dyes. It may be because the red dyes have larger quantum yields of triplet states than the blue dyes. It is obviously inferred from the values of f listed in Table 3. Although the photo-reduction of anthraquinone dyes may be also related to the acid-base properties of carbonyl groups in the triplet states [51], the photo-reductivity may be roughly proportional to the values of f, estimated by the photo-oxidizability.

In the cases of C.I. Vat Orange 2, Orange 5 and Red 1, they underwent irreversible photo-reduction, dehalogenation and/or the decomposition of thioindigoid structure (Red 1). This is also due to their larger quantum yields of triplet states than the dyes with high stability, indicating an approximate proportionality of the photo-reductivity to the values of f.

Exposing dyed cellophane immersed in an aqueous anaerobic DL-mandelate solution is a severe condition for dyes to cause the photo-reduction [16]. The azo dyes on cellulose are photo-reduced to give the corresponding amino compounds without exception at a rate depending upon the chemical structure of dyes. Anthraquinone vat dyes with both the low photo-reductivity and the low oxidizability result in the highest lightfastness as well as a property of non-tendering. There are some proofs to indicate that the photo-oxidation and reduction of azo dyes occur simultaneously on dry cellulose in air, the former taking place at the superficial part, while the latter in the inner part [19]. To develop azo dyes with higher lightfastness, dye chemists have tried to find azo dyes with lower quantum yields to T_1 states. Unfortunately, since the photo-reduction of azo dyes is irreversible, enhancement of lightfastness is limited. Anthraquinone vat dyes have sophisticated molecular mechanisms, though not intended, to lower the quantum yields and to make the photo-reduction reversible.

The rates of photo-reduction were estimated by measuring a decrease of absorption at a given wavelength by exposure and after re-oxidation, whose behaviours are described in Table 5 and their values in Tables 2 and 3, although no advance of reductive fading, a complete return of the spectrum by photo-reduction/re-oxidation processes, was observed by further exposure longer than 10 h. It may be regarded that no values of the rates describe the real rates of photo-reduction, although the photo-reductivity is apparently proportional to the values of f, as discussed above.

3.5. Photochemical properties of vat dyes on dry cellulose

Baumgarte and Wegerle [7] summarized the knowledge and experiences of vat dyes for dyeing cellulosic fibres as follows: (1) damage of cellulose by dyeing, (2) catalytic fading or "blue-eating" and (3) phototendering, besides the excellent performance on light and wet treatment. Using three vat dyes, two with large ease and one with very small ease of the spectral changes by the photo-reduction, Boulton [40] reported typical photochemical behaviours of vat-dyed nylon by daily exposure to sunlight, although the differences between cellulose and nylon must be taken into consideration (cf. Table 6). Observing similar phenomena on vat-dyed cellulose by very long exposure to sunshine, Müller [49] reported crucial data on photofading properties of vat dyes on cellulose (cf. 3.5.5). Landolt [50] observed also such phenomena. It is more suitable to observe the photo-reductive colour variations of vat dyes on nylon than to do on cellulose. Vat dyes perform photo-reduction more easily on nylon than on cellulose. Besides cellulosic substrate, studies on the lightfastness and phototendering of vat dyes on nylon, wool and polyester substrates were also reported [10,29–31]. Then, some vat dyes on wool have the highest lightfastness and don't act as phototenderer but on nylon. Some vat dyes have also the highest lightfastness on polyester substrate. As being mentioned above, these fading behaviors of vat dyes seem to indicate singlet oxygen mechanism.

Photofading of vat dyes on cellulose, on the other hand, has been studied in connection with photochromism [38,39] and catalytic fading [33,49,52,53]. The former is due to the photo-reduction and the return to the original hue by re-oxidation, while the latter is a typical behaviour by photo-oxidative fading. Although the rates and the extents of photo-reductive and oxidative reactions differ with dyes and depend upon the environmental conditions, both the reactions of vat dyes must simultaneously occur in various substrates. As being shown in Table 6, oxygen promotes the photo-oxidation and suppresses the photo-reduction, while nitrogen promotes the photo-reduction and inhibits the photo-oxidation. The antagonistic photo-oxidation/reduction behaviour can be often observed in the compound effects of light and substrate on reactive-dyed cellulose [16,17] and on vat-dyed cellulose [39,41,42]. With an increase in the concentration of substrates on cellulose and with a decrease in the concentration of oxygen, the rates of photo-reduction were increased, and vice versa. In spite of the absence of substrates, dye chemists [40,49–51] observed the photo-reduction of vat dyes on dry cellulose by prolonged exposure in air or under the aerobic conditions. We must consistently explain these apparently contradicting observations. It is required to explain why the photo-oxidative and reductive phenomena occur simultaneously on dry cellulose and the other textiles in the absence of substrates, which promote reductive fading.

These fading phenomena of vat dyes on exposure in air may be interpreted as a result of photo-oxidative fading that occurs from the surface of polymer substrate and simultaneous photo-reductive fading in the inner part of the substrate. Moreover, the former fading occurs preferentially, because the dyes that exist nearer to the incident light in the polymer substrate have a filter effect [54] on the dyes that exist in the more inner part of the substrate and because oxygen is supplied from the surface, depending upon the dye concentration and the concentration distribution in the substrate as dyed and/or as exposed for a definite time (a sample of preferential surface fading). In the boundary where photo-oxidation and reduction compete with each other, the reductive fading may be suppressed by oxygen. The boundary may advance toward the inner direction, since as the oxidative fading progressed, the consumption of oxygen in nearer part to the surface may diminish with fading. In case of the exposure of the dyed cellophane immersed in aerated water in the present study in the absence of substrates such as amines and lactic acid, the dyes in the water-swollen cellulose may be kept under aerobic conditions and suffer only oxidative fading, since sufficient air may be supplied due to the diffusion of air in water.

Using this hypothesis, we show how fading behaviours of vat dyes on cellulosic and nylon substrates can be explained in this paper. Besides vat dyes, this hypothesis may be applied to the photofading of various kinds of dyes on dry cellulosic substrate as well as the other textiles, as some proofs of reactive dyes imply [17–19], since there are no reason why vat dyes are discriminated from reactive dyes in the photofading mechanism. The photo-reduction of the other dyes than vat dyes, however, may be difficult to discover the concrete proofs of the simultaneous occurrence on exposure under aerobic conditions, because the other dyes exhibit little colour change by the reduction except for disperse dyes with nitro groups.

3.5.1. Fading of thioindigoid dyes

Thioingoid dyes are used as only the substitutes for anthraquinone dyes to make up a loss in the shade despite of the lower lightfastness, although thioindigoid dyes have still higher lightfastness than indigoid dyes except for on wool [46]. High photostability of indigo derivatives was explained by a fast internal conversion from the lowest excited singlet state, which was brought about by proton transfer from nitrogen to oxygen in the excited state due to the hydrogen bond [55–60]. In spite of these reports, thioindigoid dyes used have larger quantum yields of T_1 states than annelated anthraquinone dyes have, and indigoid dyes have lower lightfastness than the thioindigoid dyes on cellulose [46]. The energy gap law of internal conversion [61,62] may explain better these situations than the deactivation promoted by the hydrogen bond [55–60].

Indigoid and thioindigoid dyes exist preferentially as trans-tautomer of higher stability than the cis-tautomer of lower one, though they exist as their mixtures in some cases [57,60]. These dyes were reported to be faded via singlet oxygen mechanism [63,64].

The present study proves as well that the lightfastness on dry cotton fabric can be attributed to the photo-oxidative fading. Thioindigoid dyes also suffer photo-reductive fading on exposure under anaerobic conditions. The extent of photofading of the dyes on cotton fabric could be explained by an extension of the fading of vat dyes, the same mechanism of photofading. This may show also that anthraquinone vat dyes suffer oxidative fading on cellulose.

3.5.2. Fading and photochemical properties of anthraquinone dyes

The absorption spectra of the annelated quinones can be accounted for by the summation of the spectral absorption maxima of quinone chromophore arising from the two aryl-carbonyl subunits and those of benzenoid chromophores [65–67], although the spectroscopy of annelated quinones still remains to be argued. The values of extinction coefficients of colour band of vat dyes are smaller than those of azo dyes by a factor larger than 3, while those of UV and/or near-UV bands are very large and reached up to 1.5×10^5 [68].

The photo-chemically aggressive properties of anthraquinone vat dyes such as oxidative and reductive fading, catalytic fading, tendering by light and dyeing depend solely on the highly localized $T_1(n\pi^*)$ states concerned with carbonyl groups [27,28,69,70], while the useful and excellent properties resulting in its colour and the protecting properties depend on the $S_1(\pi\pi^*)$ states concerned with benzenoid chromophore. The excited triplet

$T_1(n\pi^*)$ states of only carbonyl groups act a role in the photosensitization by the energy transfer to dioxygen to give $^1O_2$, as well as the hydrogen abstraction from substrate [27,28,69,70]. The $n\pi^*$ absorption exists at the wavelength shorter than ca. 500 nm and $\log \varepsilon\phi 3$ [65–72]. Carbonyl groups in yellow and orange dyes absorb light energy to reach the $T_1(n\pi^*)$ states via the singlet excited state. Since the groups in blue, green and olive dyes are masked or shielded behind the strong $\pi\pi^*$ absorption of the corresponding colour band, they have a small probability to reach the $T_1(n\pi^*)$ states. The former dyes show active phototendering property but the latter ones, although the essential reason of phototendering remains to be argued. The blue and green dyes are observed as a result to have very small values of *f*. Besides phototendering, the other photofading behaviours of vat dyes such as photo-reduction can be also explained by the property of carbonyl groups [27,28,69,70].

3.5.3. Protective action of anthraquinone vat dyes

As being shown by the rates of fading of Pyr-Yellow photosensitized by vat dyes in the 8th column of Table 4, the ratios of the rates with and without a yellow filter were in a narrow range. But the differences which may describe the photosensitization by light of wavelengths <470 nm, listed in the last column of Table 4, were in the following order:

$$\begin{aligned}&\text{Orange 5} > \text{Red 1} > \text{Orange 2} > \text{Red 10} >\\ &\text{Red 23} > \text{Blue 20} > \text{Green 3} \div \text{Blue 4} \div \text{Green 1}\end{aligned} \tag{6}$$

Little shielding effect was observed for blue and green dyes. C.I. Vat Blue 20 has an intermediate property considerably different from the groups, weak and no tenderers or orange/red and blue/green groups. The excited singlet $S_1(\pi\pi^*)$ states of these three annelated anthraquinone dyes (Blue 4, Green 1 and green 3) are inferred to be almost deactivated by internal conversion. Baugh et al. [25,26] reported firstly this fact by light of wavelengths shorter than and longer than 300 nm. By this study, the boundary should be extended to 460 nm, and further to all the $\pi\pi^*$ absorption or to the colour band of annelated anthraquinone dyes. Thus, the dyes of non-tenderer have a property of filter or a coloured UV absorber, which prevents tendering dyes from absorbing the UV and near-UV light (otherwise the $\pi\pi^*$ absorption by aromatics and the $n\pi^*$ one by the carbonyl groups cause tendering and/or catalytic fading), and improves the lightfastness of the dyes used in admixture. Dörr et al. [27,28] also assigned visible absorption bands of dyes accepted as inactive tenderers as $\pi\pi^*$ absorption and found weak longest-wavelength $n\pi^*$ bands only in the spectra of the dyes generally accepted as active tenderers, although carbonyl groups must exist all the vat dyes because they act as solublizing groups in the vatting process.

3.5.4. Phototendering

1. *Tendering by vat dyes on dry cellulose*: Although the mechanism of phototendering has not yet been settled [7], it is assumed in the present paper that the first step of phototendering and tendering by dyeing is attributed to photo-reduction, in which vat dyes abstract hydrogen from cellulosic substrate by the $T_1(n\pi^*)$ states of carbonyl groups. The photo-reduction or the repetition of photo-reduction and re-oxidation in the inner part of the substrate may make a starting point from which the oxidative degradation of cellulose substrate begins at portions nearest to the photo-reduced dyes on exposure in air. Since little diffusion of vat dyes may occur in dry cellulose, the vat dyes may repeat the reduction/oxidation during irradiation. If tendering of the first step is due to this mechanism, the tendering should occur in the inner part closer to the surface of substrate, because no photo-reduction of many dyes occurs on cellulose under aerobic conditions, but under anaerobic conditions or in the presence of substrates under aerobic conditions (cf. 3.4). It is well known that the photo-reduction by hydrogen abstraction results in the radical formation in cellulose and dye [4,11,30,31,73–76]. In the presence of oxygen, a photo-oxidative degradation of cellulose occurs via radical mechanism by a result of photo-reduction of vat dyes, where cellulose radicals have been reconfirmed by ESR spectroscopy. The addition of oxidizing agents such as molecular oxygen and

hydrogen peroxide to the radical may be the second step to the fibre degradation, and as a result a photo-oxidative degradation of cellulose occurs.

2. *Tendering by leuco-compounds adsorbed on cellulose during dyeing*: Baumgarte and Wegerle [7] called this phenomenon "damage by dyeing," while IG group [32] called it "tendering by dyeing" and wrote an attention: "protect alkaline unoxidised vat dyeings from direct sunlight." This severe tendering was observed by the action of light and air upon cellulosic substrate adsorbed with the sodium salt of leuco-compounds (V–ONa) in vat dyeing for short time [77–80]. This 'tendering by dyeing' is markedly reduced in the case of the exposure of vat acids (V–OH) on wet cellulosic substrate.

There are three observations of tendering by following different conditions (approximate duration in which the tendering occurred is shown in the parentheses):

T1	By vat dyes (V=O) in the oxidized state (some months)
T2	By alkaline V–ONa in the reduced state (some ten minutes)
T3	Little tendering by V–OH in the reduced state (longer time than T2)

In case of T2, the simultaneous photo-oxidative fading of the re-oxidized species, which should occur at the wet fibre surface in vat dyeing, may occur depending upon the extent which the V–ONa are oxidized in air. Since no ideal T3 tendering may exist under aerobic conditions, i.e., in air, large increase in the time of exposure may be required to obtain some tendering.

These three observations depending upon the different conditions may explain the following three hypotheses of the mechanisms for tendering:

M1	Photo-reduction
M2	Preferential photo-oxidation from the surface of polymer substrate
M3	Photo-reduction in the inner part of polymer substrate

Relationships between the three observations T1–T3 and the mechanisms M1–M3 can be explained as follows:

1. The above discussions suggest that vat dyes on dry cellulose suffer photo-oxidative fading and the simultaneous occurrence of photo-reduction. This fact indicates M2 and M3, since the oxidation occurs under aerobic conditions and the reduction under anaerobic ones.
2. The T2 phototendering occurs drastically even by a short time of exposure to direct sunlight, compared with T1 by exposing V=O in the inner part of fibre substrate behind a layer of oxidized vat dyes in dry cellulose, which make the inner part anaerobic, a filter effect by V=O. Thus, the dramatic increase in the rate of T2 tendering, compared with that of T1 may also indicate M2 and M3.
3. Since the thermally reduced conditions (i.e. alkaline dithionite solution) prepare the anaerobic conditions, photo-reduction M1 may occur even in the superficial part of fiber substrate in air.
4. Since the acid dissociation constants of the $T_1(n\pi^*)$ states of carbonyl groups become even several orders smaller than those of the ground state [51,72,81–85], the carbonyl groups in the $T_1(n\pi^*)$ states may abstract hydrogen from cellulose even though the groups exist in the dissociated state ($\mathrm{V-O^-} \rightarrow \mathrm{V-\dot{O}H^-}$, a formation of leuco anion radical). Since the T2 tendering, the abstraction by the carbonyl groups dissociated, occurs preferentially in the superficial part of substrate by the direct exposure of light, the abstraction or the start of substrate degradation may increase dramatically compared with T1 on dry cellulose caused by long indirect exposure. Under alkaline conditions, immediately after the excited states are deactivated to the ground states, a hydrogen atom is released. Continuing the exposure, the repetition of abstraction-release processes may result in severer tendering than T1, since the re-oxidation in T1 may occur slowly due to the restricted supply of oxygen.
5. The fact that, when the alkaline vat dyeings were neutralized or acidified, smaller

tendering was observed than that of alkaline dyeings, i.e. the rate of T3 < the rate of T2 [77,80] indicates M1, since no V–OH may perform the hydrogen abstraction by light absorption. An increase in the extinction coefficients of carbonyl groups by the ionization with alkaline reducing agent in the dyeing process may further contribute to the promotion of tendering. This is observed by the marked colour variation by the ionization of V–ONa.

6. Since, in the case of T2, there is little filter layer of vat dyes, the photo-reduction occurs from the surface of fibre. It may proceed drastically, compared with the photo-reduction in the inner part by the indirect exposure.

The $T_1(n\pi^*)$ states of carbonyl and azo groups abstract one and more than one hydrogen atom, respectively, since they result in V–OH and the corresponding amines via hydrazines. Simply considering, azo groups should have stronger degradation effects on polymer substrate than carbonyl groups, but the reality is reverse. The reverse may be explained by the repeated abstraction by carbonyl groups via re-oxidation, but azo groups. Above discussions show that the observations on the phototendering by vat dyes can be consistently explained by the mechanisms or the hypotheses introduced in the present study.

3.5.5. *Catalytic fading*

Existence of catalytic fading in mixture-dyed vat dyes is another one of the definite proofs of singlet oxygen mechanism in photofading. In the present study, the aggressive character is described by the values of f, while the subjective one, a response to the external photo-oxidative stress, by the values of k_0. Although, as being mentioned above, vat dyes on dry cellulose should perform simultaneously the oxidative and reductive photochemical reactions in air, no one has explained the mechanisms systematically. Many chemists have reported the results from either point of view: phototendering of cellulose (cf. 3.5.4) or catalytic fading of vat dyes [7,49,53] except for a few [77,86].

Müller [49] reported a comprehensive paper on catalytic fading, in which he determined the apparent lightfastness (grades 1–5) of each dye on cotton fabric dyed with all the binary combinations of ten strong to mild tenderers (yellow, orange and red dyes) and eight non-tenderers (blue, green and olive dyes). For example, in the mixture dyeing with C.I. Vat Green 3, all the tendering dyes showed the highest lightfastness of a grade of 5, while in the dyeing with C.I. Vat Green 1, Red 10 showed a grade of 1, Yellow 1 a grade of 4, and Yellow 2 a grade of 2, respectively. He estimated the protecting property as the mean values of the grades of tendering dyes, although the mean values as well as the grades of individual dyes depended on the relative concentrations of component dyes. The results, however, indicated that the non-tendering dyes had strong protecting effect on the tendering dyes, the extent of which depended on the combinations of component dyes. The order of protecting property obtained from the 1:1 mixture dyeings was as follows [49]:

$$\text{Green 3} > \text{Green 11} > \text{Blue 4} > \text{Blue 14} > \text{Green 1} > \text{Blue 6} > \text{Green 2} \qquad (7)$$

These qualitative arguments of the fading of tendering dyes may be semi-quantitatively described by both the parameters of the component dyes. When the photofading behaviour of vat dyeings in admixture with the combination of dyes, either one of which has the protective action, however, cannot be described by the two×two parameters. In this case, the values of f of active dyes may be considerably lowered by the partner dye. Moreover, since dyes exist heterogeneously in substrates, usually the concentrations nearer to the surface are a little higher than those in the inner part, and the photo-oxidative fading occurs preferentially from the surface, the mutual effects by mixture-dyed components is too complicated to describe quantitatively.

Since some vat dyes cause catalytic fading of partner dyes, they may also sensitise the degradation of cellulose. If the mechanism contributes predominantly to the photodegradation, the same degradation must be experienced by reactive-dyed cellulose, because the quantum yields to generate

$^1O_2$ of some reactive dyes range among those of mild tenderers. Since no such reports have been so far found, the contribution of photosensitised degradation of cellulose by this mechanism may be minor, compared with the photo-reduction mechanism.

Light has four kinds of aggressive effects on vat-dyed cellulosic substrate in air: (1) phototendering of cellulose, (2) phototendering of cellulose sensitized by vat dyes, (3) catalytic fading of vat dyes (mixture dyeing), and (4) photofading of vat dyes (single dyeing). In terms of protective properties of vat dyes, the aggressive effects (1)–(3) are discussed below.

3.5.6. Protective properties of vat dyes

The protective property against catalytic fading may be explained by the shielding effects of ππ* absorption bands with large extinction coefficients of the non-tendering dyes on the nπ* absorption bands of the partner dyes, which cause tendering by photo-reduction, depending on the combination of partner dyes. When the ππ* absorption of the partner dye sensitises also the singlet oxygen generation (see below), shielding such ππ* bands results in protective effects. These are mutual effects between different kinds of molecules, while the effect mentioned above (3.5.4) is the one between the same kinds of molecules. Then, since the effects holds in the tendering, the phototendering of cellulose mixture-dyed with non-tendering dyes becomes smaller than that of the single dyeing of tenderer, as verified by Fiebig et al. [41,84]. The magnitude of protecting property was C.I. Vat Blue 4 > Blue 20.

1. *Protection of cellulose photodegradation*: Baumgarte and Wegerle [7] classified vat dyes into protecting and tendering dyes, and the catalytic action of the dyes into active and susceptible properties as listed in Table 1. They seemed to regard these protecting and tendering properties as a conflicting one, and described the protecting property as a plus number and the tendering one as a minus number, respectively.

The shorter the wavelengths of UV light, the stronger the tendering action of cellulose [74–76]. Shielding the active wavelengths of light by a non-tendering dye may result in the protection of cellulose from degradation. The protective action may be attributed to the prevention of light absorption in far UV region responsible for the aggressive action, besides nπ* absorption bands in the visible region. Since UV light <290 nm is not required to be taken into consideration, the larger absorption around 300 nm may act efficiently as UV absorber against cellulose degradation. This viewpoint may anticipate the protection property from the absorption spectra of seven anthraquinone vat dyes, which were so dyed that the absorbance is in the range between 0.8 and 1.0 at $\lambda_{\max}$, illustrated in Fig. 7 as follows:

$$\text{Red } 10 > \text{Blue } 4 > \text{Green } 3 > \text{Orange } 2 > \text{Blue } 20 > \text{Green } 1 > \text{Red } 23 \quad (8)$$

Eliminating the tendering dyes, this order describes very well the estimation by Baumgarte and Wegerle [7]. A larger absorption band around 300 nm with the $\lambda_{\max}$ of longer wavelength is effective to the coloured UV absorber against cellulose photodegradation, although the protection effect depends also on the dyeing depth.

2. *Protection of vat dye-induced phototendering*: There are two kinds of intramolecular and intermolecular protection mechanisms against the

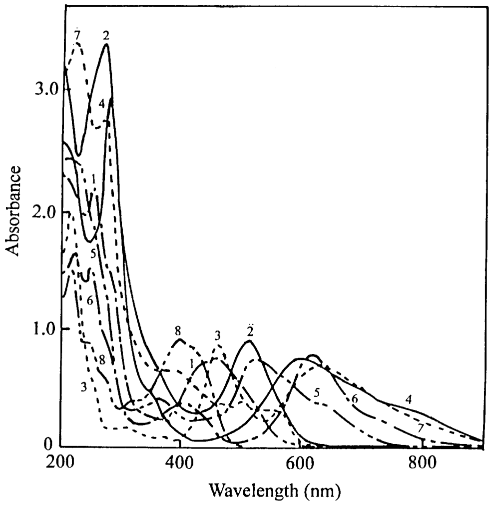


Fig. 7. Absorption spectra of seven anthraquinone vat dyes and Pyr-Yellow on dry cellophane: (1) C.I. Vat Orange 2; (2) C.I. Vat Red 10; (3) C.I. Vat Red 23; (4) C.I. Vat Blue 4; (5) C.I. Vat Blue 20; (6) C.I. Vat Green 1; (7) C.I. Vat Green 3; and (8) Pyr-Yellow.

photo-reduction of vat dyes. The former mechanism may hold in non-tendering vat dyes. In order to suppress the photo-reduction of tenderers, shielding the nπ* absorption bands of tenderers may be effective by the strong absorption bands of non-tenderers. If the nπ* bands of carbonyl groups in vat dyes have a similar wavelengths and intensity of absorption, the effectiveness of the shielding by a dye may be inversely proportional to the tendering activity of the dye. The quantum yields to the $T_1(n\pi^*)$ states, whose magnitude is given by the order (5), are roughly inversely proportional to the effectiveness. This was only partially proved by Fiebig et al. [41,84].

3. *Protection of catalytic fading by partner dye*: As being mentioned above (3.5.5), the quantum yields (f) to generate $^1O_2$ of individual dyes are proved to be due not only to the $T_1(n\pi^*)$ states of the carbonyl groups but also to the other $T_1(\pi\pi^*)$ states, since orange and red dyes used showed a considerable decrease in the photosensitivity by use of yellow filter (cf. Table 4), a contribution of UV absorption to the sensitivity. The results by Müller [49] may be analysed from the same method as above in terms of the superposition of absorption spectra as follows:

1. C.I. Vat Red 10 has a strong absorption band around 300 nm ($\lambda_{max} = 267$ nm) and a main colour band ($\lambda_{max} = 510$ nm), both of which may be active in the photosensitivity. Superposition of the absorption spectrum of Red 10 on that of Green 3 ($\lambda_{max} = 266.5$ nm) is considerably larger than on that on Green 1 ($\lambda_{max} = 249.5$ nm). Probably the minimum overlap with Green 1 in the spectrum may explain the difference in the extent of catalytic fading very well, since the photo-aggressive properties of Red 10 appears as it has.
2. C.I. Vat Green 1 has two colour bands ($\lambda_{max} = 620$ and 405 nm), a UV band with double peaks <290 nm and no absorption around 500 nm. Thus, it has no latent ability of UV absorber and little ability of suppressing the nπ* absorption. This dye itself is a non-tenderer but has no ability to protect Red 10.
3. C.I. Vat Green 3 has a broad colour band ($\lambda_{max} = 626$ nm) and a strong UV band of double peaks ($\lambda_{max} = 267$ and 223 nm), and broad absorption over visible to near UV region. Thus, it has high latent ability as UV absorber and high ability to suppress the nπ* absorption. This dye is a non-tenderer, an excellent UV absorber and has a high ability to protect fibre substrate from tendering or photo-reduction by various vat dyes.
4. C.I. Vat Blue 4 has a colour band ($\lambda_{max} = 601.5$ nm) and a strong UV band ($\lambda_{max} = 276$ nm), but no absorption over 380–500 nm. Thus, it has a high latent ability as UV absorber and little ability to suppress the nπ* absorption of partner vat dyes. This dye is a non-tenderer and an excellent UV absorber but a smaller ability to suppress the nπ* absorption than Green 3 has.
5. Descriptions (2)–(4) explain also the relations of three dyes in the order (7).
6. From the viewpoint of absorption spectrum, C.I. Vat Red 10 looks like UV absorber. But since the UV band is active as the sensitiser, this dye has no protecting ability.

Protecting properties of vat dyes may depend upon the position and strength of absorption and the mutual superposition or the shielding by absorption spectrum. As mentioned above, the spectral analysis of vat dyes on cellulosic substrate may explain the experimental observations in catalytic fading [49], the degradation of cellulose, and phototendering.

4. Summary

4.1. Photofading on water-swollen cellophane films under aerobic and anaerobic conditions (cf. 3.1–3.4)

The photofading of non- and mildly-tendering vat dyes on water-swollen cellophane films was examined under aerobic and anaerobic conditions to elucidate the mechanism of the fading on dry cotton substrate. Under the conditions, either photo-oxidation or reduction was confirmed to occur. Comparing the results of photofading on the films under aerobic and anaerobic conditions with the lightfastness on dry cotton fabrics, which oxidative or reductive fading occurred on dry cellulose was analysed. The following conclusions were obtained:

1. Lightfastness of vat dyes is determined by the photo-oxidation, the grades being primarily depended on the photosensitivity (f).
2. The ease (k_0) with which vat dyes are photo-oxidized is smaller than that of usual reactive dyes.
3. Lightfastness of vat dyes is proportional to log ($f\ k_0$). The vat dyes with the highest fastness possess the very small values of both the parameters.
4. The excited singlet states of anthraquinone vat dyes with non-tendering property by the absorption of UV and near UV regions are deactivated almost completely by internal conversion, or $S_1(\pi^*)$ states of vat dyes have a very low probability to transfer to $T_1(\pi^*)$ states.
5. The photo-reduction of vat dyes does not progress, although the acid leuco-compounds are often and easily formed under anaerobic conditions. The leuco-compounds are often completely re-oxidized to the original oxidized dyes, reversible photo-reduction.
6. No progress of photo-reduction or reversibility is another reason of the highest photo-stability.
7. The photosensitivity (f) of vat dyes examined is similar to or smaller than that of reactive dyes with high light fatness.

4.2. Fading mechanism, catalytic fading, phototendering and protective properties of vat dyes (cf. 3.5)

Utilizing the results of the present study and those of phototendering and catalytic fading so far reported, the fading mechanism and photochemical properties of vat dyes on cellulose were discussed. At the same time, the reason why vat dyes have the highest lightfastness on cellulose was pursued. The following conclusions were obtained:

1. Catalytic fading is caused by photo-oxidation, but shielding the $\pi\pi^*$ and $n\pi^*$ bands of yellow to red dyes by the $\pi\pi^*$ bands of blue to green dyes have considerable effects to prevent the catalytic fading. Overlapping of absorption spectra of component dyes explains the extent of the effects.
2. The aggressive properties of vat dyes are attributed to photo-sensitisation, caused by energy transfer from $T_1(n\pi^*)$ and $T_1(\pi\pi^*)$ states to molecular oxygen, as well as to photo-reduction, caused by the hydrogen abstraction by carbonyl groups in the $T_1(n\pi^*)$ states from fibre substrate. Vat dyes of strong tenderer in many cases with yellow and orange hue possess high quantum yield to generate the $T_1(n\pi^*)$ and $T_1(\pi\pi^*)$ states. In annelated anthraquinone vat dyes of non-tenderer in many cases with blue, green or olive hue, the strong absorption of colour bands shields carbonyl groups from the $n\pi^*$ absorption.
3. Photo-oxidation occurs preferentially from the surface of dry cellulosic substrate in air.
4. Photo-reduction observed on dry cellulose by long exposure in air occurs in the inner parts of the polymer substrate, and the hydrogen abstraction promotes the degradation of cellulose.
5. Since the photo-reduction of leuco-compounds on cellulose immersed in alkaline dithionite solution occurs from the surface of substrate, the tendering action dramatically rises, resulting in marked degradation even by lightening of sunlight for short period of time (tendering by dyeing).
6. Acidifying the alkaline vat dyeings to form the vat acids decreases the tendering on exposure. It supports terms (3)–(5).
7. Since wool is a good quencher of singlet oxygen and the photo-reduction is reversible, vat dyes show excellent lightfastness on wool.

8. The positions and strengths of absorption bands and the superposition of the bands can explain many photochemical properties of vat dyes.
9. Anthraquinone vat dyes with blue, navy blue, green and olive hues are ideal chromophore, whose properties are non-photosensitive, non-tendering and protective, those so far manufactured with yellow to red hue are non-ideal one, and those with violet hue are boundary.
10. The molecular extinction coefficients of color band of vat dyes are smaller than those of usual azo reactive dyes.

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