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The stability of monochlorotriazinyl reactive dyes on cellulose films in aqueous alkaline solutions containing peroxide bleaching agents

Akimi Sugane[a], Aki Watanabe[a], Yasuyo Okada[a,*], Zenzo Morita[b]

[a]*School of Domestic Science, Otsuma Women's University, Sanban-cho, Chiyoda-ku, Tokyo 102-8357, Japan*
[b]*Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan*

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Abstract

The stability of seven reactive (one difluoromonochloropyrimidinyl and six monochlorotriazinyl) dyes on cellulose immersed in sodium peroxoborate (PB) solution (UK–TO solution) containing tetraacetylethylenediamine (TAED) was examined using cellulosic films at 60 °C. The extent of dye loss that occurred from the dyed cellulosic films which were immersed in the UK–TO solution without detergent correlated closely to the ratings obtained using the BS 1006 UK–TO wash test. The dye loss that occurred from the dyed cellophane films was attributed to three contributions, namely, alkaline hydrolysis of dye–fibre bonds, oxidative fading of the dye chromophore by peroxides and cellulose degradation accelerated by PB and TAED. The alkaline hydrolysis of the dye–fibre bond and the extent of cellulose degradation in the UK–TO solution were the main contributions to the dye loss; dye oxidation was a minor factor in the dye loss mechanism. The physical bonding of the dye molecules reinforced the covalent dye–fibre bond stability towards the UK–TO solution. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Monochlorotriazinyl reactive dye; Difluoromonochloropyrimidinyl reactive dye; Alkaline hydrolysis of dye–fibre bond; Sodium peroxoborate; Dye loss mechanism of reactive dyes from cellulose

1. Introduction

The stability of the chemical bonds formed between reactive dyes and cellulosic substrates to attack by peroxide solution was first investigated by Rattee et al. [1,2], who reported that the oxidation of triazine and pyrimidine nuclei by peroxide resulted in marked dye loss especially in the case of difluoromonochloropyrimidinyl (DFP) dyes. The catalytic action of metals in metal complex dyes to activate peroxide attack resulting in strength loss of cellulose fabrics has long been recognized [3]. With increasing use of oxidative bleaching agents in domestic laundry detergents, copper-complex azo reactive dyes have gradually disappeared from the market; the gradual lack of popularity of such dyes can also be attributed to their low colour fastness to light and perspiration. In Japan, a method for assessing the strength loss of cellulosic fabrics by peroxide bleaching agents was established in 1996 [4]. Thompson et al. [5–9] as well as Oakes et al. [10–18] have elucidated the mechanism of

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* Corresponding author. Tel.: +81-3-5275-5738; fax: +81-3-5275-6932.
E-mail address: yasuyo.okada@otsuma.ac.jp (Y. Okada).

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bleaching and the role of metals in the oxidation reaction of azo dyes and some model soil compounds in aqueous solutions of various bleaching agents.

Since the 1980s, reactive tendering has been recognized in the US to occur most frequently as a result of the commercial laundering of reactive-dyed cotton fabrics [19]. Yang and Hughes [19] attributed such tendering to the electron-withdrawing inductive effect of the reactive groups on the hydrolysis of the β-1,4-glucoside bonds of cellulose. The inductive effect of the reactive groups accelerates the acidic hydrolysis of the glucoside bonds during hot pressing conducted at low pH. No significant difference in the strength loss among undyed, vat- and direct-dyed cotton was found [19].

In Europe, studies [20–26] on the stability of cotton dyeing in home laundering have been carried out. Phillips et al. [20] examined the colour fading of cotton fabrics which had been dyed with more than 60 kinds of sulphur, direct, vat and reactive dyes and attributed the fading achieved during repeated washing with oxygen bleach-containing domestic laundry detergents to the oxidative fading of dyes by the action of the oxidizing agent. These authors also proposed a testing method to predict the colour fading of cotton fabrics after multi-cycle laundering with a bleach-containing domestic detergent. Phillips et al. subsequently [21,22] reported the results of an interlaboratory trial for testing the colour fading of cotton fabrics by activated oxygen bleach-containing detergent. This particular procedure was developed as a part of the test method for the colour fastness to domestic laundering oxidative bleach response, which has been established in the UK as BS 1006 UK–TO [26].

On the basis of this particular test method, Bradbury et al. [23], Collishaw et al. [24] and Phillips [25] proposed dye selection as a means of avoiding the fading of reactively-dyed cellulose garments. These workers stress the superiority of monochlorotriazinyl (MCT) dyes and attribute colour fading to light-induced and/or thermal oxidative hydrolysis. Recently, Gomes and Lima [27,28] as well as Winkler et al. [29] discussed the mechanism of dye loss of MCT reactive dyes on cotton fabrics in aqueous perborate solution.

In the BS 1006 UK–TO test method [26], phosphate-free ECE reference detergent is used, which consists of three parts, namely a base detergent powder, a peroxide bleaching agent (sodium peroxoborate tetrahydrate) (PB), and a bleach activator (tetraacetylethylenediamine (TAED)). The mechanisms of the reaction between dyes and bleaching agents, the activation by TAED, as well as the stabilizing, activating, and/or catalyzing by additives, if any, have not yet been completely elucidated.

In this work, three monoazo, two disazo, and two anthraquinone reactive dyes with MCT or DFP anchor were chosen, which have a wide spectrum of substantivity. However, as mentioned below, since the reverse reactions between the oxidizing agents in UK–TO solution have not been elucidated, reactive dyes which display high stability to oxidizing agents were selected, although two reference dyes were also used to check the contribution of oxidative fading. To elucidate what happens to reactive dyes on cotton in the UK–TO method [26], it is necessary to obtain details of the fading processes that occur. Although an attempt was made to analyse the differences in the fading behaviour of dyes on cellophane, the extent of dye loss or, in case of cellophane films, the relative fading by the original UK–TO method was too small to detect. Thus, the time of treatment was extended. Also, the extent of dye–fibre bond scission was examined by immersing the dyed films in an aqueous alkaline solution of higher pH than that used in the UK–TO method, because dye–fibre bond hydrolysis at the latter pH was too small to analyse. By taking into account the differences in the experimental conditions used, the contributions of dye–fibre bond scission and the oxidative fading of the chromophore to overall dye loss imparted by the UK–TO test method was determined.

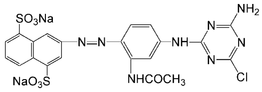
2. Experimental

2.1. Dyes and chemicals

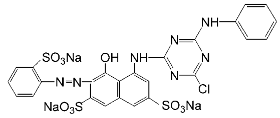
Six MCT dyes, supplied by Nippon Kayaku Co. Ltd., and a DFP dye, supplied by DyStar Japan

Ltd., were used. To compare the stability of seven dyes used with that of some reference dyes, C.I. Acid Orange 7 and a copper-complex azo dye, supplied by DyStar Japan Ltd., were also used. Their chemical structures are as follows:

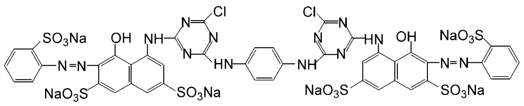
1) C.I. Reactive Yellow 3, C.I. 13245 (Yellow 3)



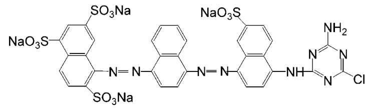
2) C.I. Reactive Red 3, C.I. 18159 (Red 3)



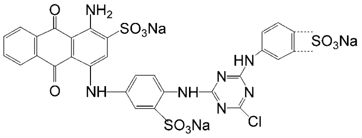
3) C.I. Reactive Red 120, C.I. 25810 (Red 120)



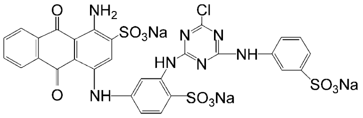
4) A disazo MCT dye (MCT Brown)



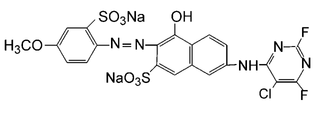
5) C.I. Reactive Blue 2, C.I. 61211 (Blue 2)



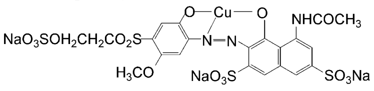
6) C.I. Reactive Blue 5, C.I. 61205:1 (Blue 5)



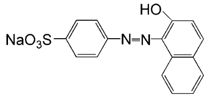
7) An azo DFP dye (Red DFP)



8) A Cu-complex dye (Blue-Cu)



9) C.I. Acid Orange 7, C.I. 15510 (Orange II)



Commercial dyes, supplied by DyStar Japan Ltd., were also used in Section 3.1 without any purification, which were the dyes with the same C.I. generic names as those used by Phillips et al. [20–22] and Collishaw et al. [23,24].

Chemicals other than bleaching agents were of reagent grade and were used without further purification.

2.2. Dyeing of cellulose film

Cellophane tapes cut from a cellophane sheet (No. 300, Futamura Kagaku Kogyo K.K.) were dyed, using an exhaustion method, with Red DFP at 60 °C and with the MCT dyes at 80 °C by adding sodium sulfate (100 g dm^{-3} except for C.I. Reactive Blue 5 (150 g dm^{-3})) dye fixation was then achieved using the alkali shock method (Na_2CO_3, 20 g dm^{-3}; Na_2SO_4, 100 g dm^{-3}) for 1 h at the same temperature. In the case of C.I. Reactive Red 3, an all-in method at pH 9.4 (80 °C) using phosphate solution containing Na_2SO_4 (100 g dm^{-3}) was used. The dyeing conditions such as dyeing time and the concentration of Na_2SO_4 used were adjusted so that the absorbance (abs) of dyed film at the λ_{max} had a value between 0.8 and 1.0. After dyeing, the dyed cellophane was thoroughly rinsed in boiling water to remove unfixed dye by renewing the water until it was no longer coloured.

2.3. Determination of dye loss from dyed cellophane film

The extent of dye loss that occurred from dyed cellulosic film was examined by measuring the absorption spectra of the films before and after various treatments for the prescribed time. After treatment, each piece of the sample was immediately rinsed in distilled water and dried between papers on which a weight was placed. The value of absorbance, A, at the λ_{max} of each dye was measured using a Ubest-50 spectrophotometer using a film holder (FLH-356) equipped with a double-folded paper sample holder, between which the film sample was placed. The extent of dye loss was estimated by the ratio, A/A_0, where A_0 was the original absorbance. The values of A_0 were measured at the $\lambda_{\max}$ of each dye.

2.3.1. Hydrolysis of dye–fibre in alkaline solution

A buffer solution (pH 10.56 at 60 °C, pH 11.0 at 25 °C) was prepared using a mixture (6:1) of 0.05 M Na_2HPO_4 and 0.05 M Na_3PO_4. Several pieces of the dyed cellophane films were immersed in the solution at 60 °C. Each piece of film was removed after a given time, rinsed immediately in water, and dried between papers on which a weight was placed. After drying, the absorbance of each film was measured by the same methods mentioned above.

2.3.2. Fading of dyes on cellulosic film under the UK–TO conditions

Dyed cellophane films were immersed in an aqueous solution containing non-phosphate ECE reference detergent at 60 °C for a given time as follows: PB ($NaBO_3 \cdot 4H_2O$) (12.0 g dm^{-3} (0.0780 M)), TAED (1.80 g dm^{-3} (0.0079 M)), sodium carbonate (1.18 g dm^{-3}), sodium silicate (0.34 g dm^{-3}), sodium sulfate (0.78 g dm^{-3}) and sodium dodecylbenzene sulfonate (DBS) (2.31 g dm^{-3}) were added to the solution (UK–TO solution). The recipe is based on BS 1006 UK–TO [26], but detergents, chelating agent, and detergent builders other than those mentioned above were removed. The preparation of the solution (usually 1.0 dm^3) was carried out by the UK–TO procedure (6.1 and 6.2 [26]) and the solution was divided into several portions. Section 3.2 discussed how the pH of the solution, changed with time. After removing the film from the solution, it was immediately washed in water, dried, and the absorption spectra of the dry films were determined as described above.

2.4. Decomposition of reactive dyes in UK–TO solution

The rates of fading for dyes were determined at 60 °C in UK–TO solution. Aliquots of the dye solution being tested were taken at specific times, acidified with phosphoric acid (0.05 mol dm^{-3}) solution of the same volume to terminate the reaction and the absorption spectrum of the sample was measured. No DBS was added to the solution, since surfactants have been confirmed to have no effect on the fading of dyes [30,31].

Chelating agents have been reported to strongly suppress the reaction of hydrogen peroxide (HP) with peracid anions by eliminating the effect of trace metal-ion catalysis [32,33]. In this work the solvent used was distilled water that had been passed through a mixed-bed ion-exchange resin. Since preliminary experiments showed a very small contribution of dye oxidation to total dye loss, no chelating agent was added to the solution.

The concentrations of dyes was adjusted so that absorbance at $\lambda_{\max}$ was in the range between 0.8 and 1.0. Since the dye concentration was of the order of 10^{-5} mol dm^{-3}, a decrease in alkalinity would be negligible.

2.5. Determination of the available concentrations of peroxides

According to the method of Swern [34], the concentration of HP, peracetic acid (PAA) and diacetyl peroxide were determined by titration with 0.1 N potassium permanganate and 0.1 N sodium thiosulfate at three rates: (1) titration of HP by potassium permanganate under strongly acidic and cooled conditions, (2) titration of PAA by sodium thiosulfate under cooled conditions, and (3) titration of diacetyl peroxide by sodium thiosulfate after heating the solution in a steam bath. The total concentration of peroxide was also determined by iodometry. The concentration of PAA was estimated from the difference between the total and the HP concentration by permanganate titration.

3. Results and discussion

3.1. Correlation between the relative fading of dyed cellophane and the grey scale ratings and ΔE values of dyed fabrics achieved using the UK–TO method*

Phillips et al. [20–22] used ΔE^* and Collishaw et al. [23,24] used grey scale ratings to determine the extent of dye loss from reactive cotton dyeing which occurred as a result of immersion in

UK–TO solution. In this study, the relative fading of dyed cellophane was used to describe and quantify the extent of dye loss. Initially, to determine the degree to which dyed cellophane could describe the extent of dye loss in the UK–TO solution, the correlation between the three methods: namely ΔE^*, grey scale ratings and the ratio of A/A_0 of dyed cellophane was examined for common commercial dyes.

3.1.1. Correlation between ΔE^* and the grey scale ratings

From the ΔE^* results (column F in Table 2) [20] and grey scale ratings of Collishaw et al. [23], and from BASF Technical Information [35], as well as those estimated from $\Delta E_{\mathrm{cmc}}(2{:}1)$ by Gomes [28], a correlation plot for twelve common dyes is shown in Fig. 1(a). From the values of $\Delta E_{\mathrm{cmc}}(2{:}1)$ achieved from the UK–TO test [28], the grey scale ratings were estimated using the relationship of the values of $\Delta E_{\mathrm{cmc}}(2{:}1)$, ΔE_{F}, and the ratings, listed in Table 3 of Ref. [36], for the dye of the same shade. For example, the ΔE^* value for 4% (o.w.f.) of dyeings of C.I. Reactive Black 5 [20] was plotted against the UK–TO ratings of 5 % (o.w.f.) dyeings [23]. Using the mean values of the ratings, the correlation coefficient, r, was calculated to be -0.910 ($P < 0.001$, $n = 13$). Some dyes such as C.I. Reactive Blue 221 and Blue 224 showed large deviation from the correlation curve. The ΔE^* values and the grey scale ratings for C.I. Reactive Black 5 were dependent upon the depth of shade (1.0, 4.0 and 5.0 % (o.w.f.)) but exhibited good correlation. The 1 % (o.w.f.) dyeings showed low colour fastness to the UK–TO test, while 4 and 5 % (o.w.f.) dyeings showed good colour fastness. Excluding C.I. Reactive Red 123 (rating 3), Blue 221 and Blue 224 (rating 2), which showed large deviations from the correlation curve, improved the correlation coefficient to $r = -0.969$ ($n = 12$, $P < 0.001$). This correlation may be used to estimate the validity of the cellophane method presented herein and also to select reactive dyes whose results can be compared to those of other workers [20–24].

3.1.2. Correlation between the values of A/A_0 and the UK–TO ratings

To analyse dye loss in detail, the values of A/A_0 should be determined as precisely as possible. For their tests, Phillips et al. [20–22] and Collishaw et al. [23,24] immersed the dyed cotton for 30 min at 60 °C. These conditions, however, yielded values too small for dye loss, $(1-A/A_0)$, using dyed cellophane. In order to obtain sufficient dye loss to analyse, longer immersion in UK–TO solution at 60 °C was necessary. From preliminary experiments, it was concluded that 24 and 48 h were suitable for determining the mechanism of dye loss in terms of A/A_0. Since the correlation between values of A/A_0 after 24 and 48 h was very good, both experimental conditions can be used. The correlation diagrams between the values of A/A_0 for 24 h and the UK–TO grey scale ratings [23,28,35] are shown Fig. 1(b) for fourteen common reactive dyes. In order to illustrate the similarity in the pattern in Fig. 1(a) and (b), the negative values of A/A_0 were plotted.

Since several dyes displayed large deviations [Fig. 1(a)], the correlation coefficient of Fig. 1(b) was calculated to be $r = -0.939$ ($n = 11$, $P < 0.001$) excluding C.I. Reactive Red 21 (rating 1), Red 123 (rating 3), Red 198, Blue 221, Blue 224 (ratings 1.5 and 2), whose plots are shown in parentheses.

Using cellophane films dyed with C.I. Reactive Black 5 at both intermediate and high concentrations ($A_0 = 1$ and 2) resulted in the same values of A/A_0, these being independent of concentration. This method is less sensitive to dye concentration, compared with the results of cotton dyeing by the UK–TO method. The UK–TO test on dyeings of C.I. Reactive Red 123 [20,28] gave similar results to the current cellophane method, while the method employed by the BASF group gave lower results [23]. The UK–TO test method applied to C.I. Reactive Blue 221[20] and Blue 224 [28,35] gave higher results than the cellophane method, while results on C.I. Reactive Red 21 [23] and Red 198 [23,35] showed the reverse result. Gomes reported that estimation using the UK–TO method was dependent upon the dyeing method employed [27,28]. Although no reasons for these deviations can be found, it seems reasonable to suggest that the dyeing methods, dyeing conditions and the type of substrate (such as cotton fabrics and cellophane film) have a considerable effect on the stability of the reactive dyeing when using the UK–TO solution.

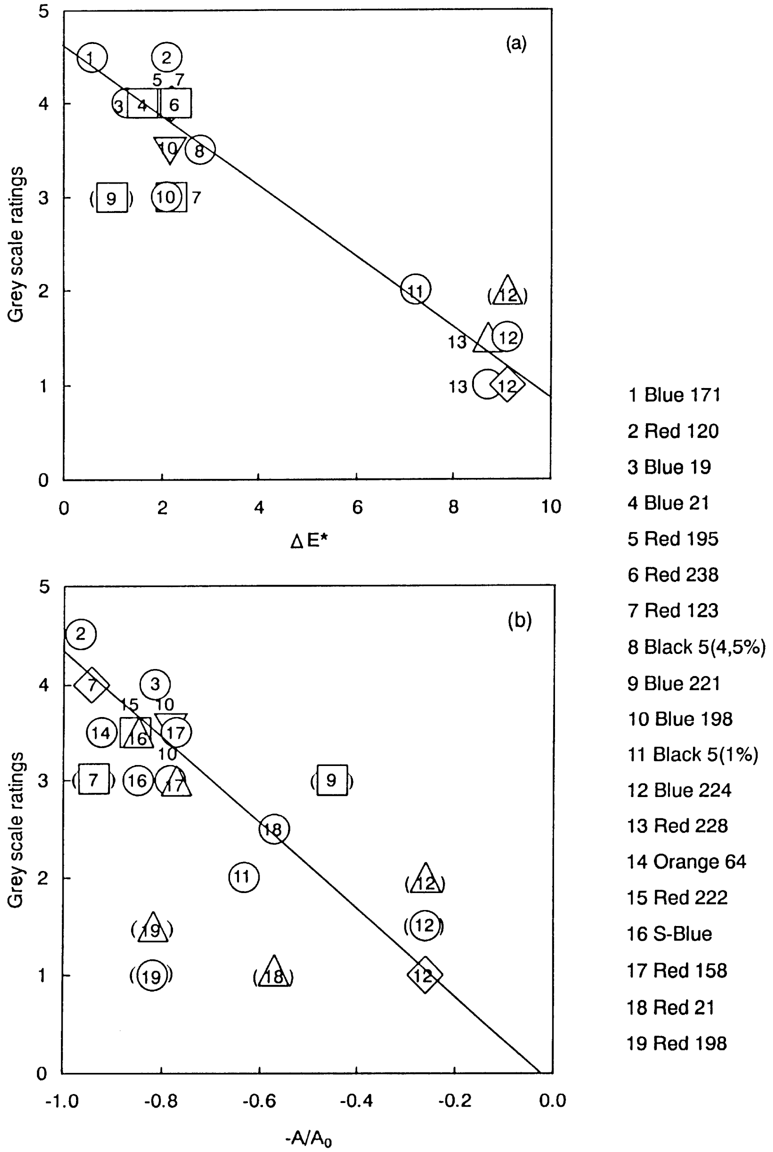


Fig. 1. (a) Relationship between the UK–TO grey scale ratings [23] and ΔE^* [20] for reactive cotton dyeings by the UK–TO method ($Y = 4.422 - 0.335X$, $r = -0.910$, $n = 13$). (Excluding plots shown in parentheses improved the coefficient $r = -0.969$; $Y = 4.705 - 0.384X$, $n = 12$.) (b) Relationship between the UK–TO grey scale ratings of reactive cotton dyeings [23,28,35] and the A/A_0-values of dyed cellophane immersed in UK–TO solution at 60°C for 24 h for reactive dyes. (Excluding plots shown in parentheses, the coefficient r was estimated as $r = -0.939$; $Y = -0.306 - 4.549X$, $n = 11$) (S-Blue = Sumifix Brilliant Blue GL).).

References	Symbols for the grey scale ratings		
	Individual ratings	Common ratings	
Bradbury et al. [23]	○	□	
BASF Tech. Info [35]	△		▽
Gomes [28]	◇		

Table 1

Contribution of alkaline dye–fibre bond hydrolysis, oxidative fading, and promotion effect to the dye loss from MCT and DFP dyeings of cellulosic film immersed in the UK–TO solution at 60 °C, estimated by A/A_0 at λ_{max}

Dye	Dye loss from film in the UK–TO soln (A_t)[a]		Dye–fibre bond hydrolysis at pH 10.56 (H_t)[b]		Oxidative fading in the UK–TO soln	Estimation of each contribution to the rate, *D*, of dye loss[c]	Promotion effect	
	Initial loss (*B*)	Rate (min^{-1}) (*D*)	Initial loss (*E*)	Rate (min^{-1}) (*F*)	Rate (min^{-1}) (*G*)		Rate, α[c] (min^{-1})	Initial loss $B-E$
Red DFP	0.028	3.1×10^{-5}	0	0	1.9×10^{-3}	$G/120$	1.5×10^{-5}	0.028
Red 120[d]	0.022	1.6×10^{-5}	0	1.3×10^{-5}	0.6×10^{-4}	$F/8+G/120$	1.4×10^{-5}	0.022
Yellow 3[d]	0.065	3.1×10^{-5}	0.040	8.6×10^{-5}	5.8×10^{-4}	$F/8+G/120$	1.6×10^{-5}	0.025
Brown	0.084	3.2×10^{-5}	0.050	8.9×10^{-5}	1.2×10^{-3}	$F/8+G/120$	1.4×10^{-5}	0.034
Blue 2[d]	0.050	2.8×10^{-5}	0.040	4.4×10^{-5}	$< 0.5\times10^{-5}$	$F/8$	1.3×10^{-5}	0.010
Blue 5[d]	0.040	4.2×10^{-5}	0.040	3.2×10^{-5}	2.8×10^{-3}	$F/8+G/120$	1.5×10^{-5}	0.0
Red 3[d]	–	–	0.015	1.1×10^{-4}	1.8×10^{-4}	–	–	–
Blue-Cu	0	7.5×10^{-2}	0.10	6.5×10^{-4}	8.7×10^{-1}	–	–	–
Orange II	–	–	–	–	5.2×10^{-2}	–	–	–

[a] $A_t=1-A/A_0=\mathrm{B}+(1-B)\{1-\exp(-Dt)\}$ (cf. Eq. (9); $B=C_0^1/C_0$; $1-B=C_0^2/\mathrm{C}_0$; $D=k_2$).

[b] $H_t=1-A/A_0=E+(1-E)\{1-\exp(-Ft)\}$ (cf. Eq. (9); $E=C_0^1/C_0$; $1-E=C_0^2/C_0$; $F=k_2$).

[c] $A_t=1-A/A_0=B+(1-B)\{1-\exp(-Dt)\}+1-\exp(-\alpha\mathrm{t})$ (cf. Eq. (11); $B=C_0^1/C_0$; $1-B=C_0^2/C_0$; $D=k_3$).

[d] C.I. Reactive generic name.

From these findings it was concluded that the results of A/A_0 obtained using the cellophane film method bear a close correlation to those obtained using the UK–TO method.

3.2. pH-variation and available HP in UK–TO solution

The nature of peroxoborate (PB) in aqueous solution has been studied by potentiometric titration [36], polarography [37], Raman spectroscopy [38], and ^{11}B NMR spectroscopy [39]. Alkaline PB solutions display an equilibrium involving the hydroperoxotrihydroxoborate anion [36–39]:

$$\mathrm{B(OH)_4^- + H_2O_2 \rightleftharpoons B(OH)_3(O_2H)^- + H_2O} \qquad (1)$$

$$K_1 = \frac{[\mathrm{B(OH)_3(O_2H)^-}]}{[\mathrm{B(OH)_4^-}][\mathrm{H_2O_2}]} \qquad (2)$$

The equilibrium constant, K_1, was determined as ca. 25 mol^{-1} dm^3 [36] or 20 mol^{-1} dm^3 [38] at 25 °C.

In acidic or neutral solutions, considering the ionization of boric acid, peroxoboric acid exists according to the following equilibrium:

$$\mathrm{B(OH)_3 + H_2O_2 \rightleftharpoons B(OH)_3(O_2H)^- + H^+} \qquad (3)$$

The dissociation constant, K_2, for Eq. (3) was determined to be $K_2=2\times10^{-8}$ [39].

In alkaline solution, taking the ionization of HP and water into consideration, the following equilibrium is derived:

$$\mathrm{B(OH)_4^- + O_2H^- \rightleftharpoons B(OH)_3(O_2H)^- + OH^-} \qquad (4)$$

$$K_3 = \frac{[\mathrm{B(OH)_3(O_2H)^-}][\mathrm{OH^-}]}{[\mathrm{B(OH)_4^-}][\mathrm{O_2H^-}]} = \frac{K_1 K_W}{K_{HP}} \qquad (5)$$

where K_{HP} and K_W are the acidic dissociation constants of HP and the ion product of water, respectively. When the ionic product of water at 40 °C is used, the value of K_3 is 0.328. Here, the total concentration [PB] of $[\mathrm{B(OH)_3(O_2H)^-}]$ and $[\mathrm{B(OH)_4^-}]$ can be kept constant. Under these conditions, since the mole fractions of tetrahydroxoborate and HP anions are the same, the sum of the concentrations, $[\mathrm{B(OH)_3(O_2H)^-}]+[\mathrm{HO_2^-}]$, is equal to the total concentration [PB]; the consumption of HP, therefore, corresponds to a decrease in the concentration of PB.

Table 2
Contribution of alkaline dye–fibre bond scission, oxidative fading, and promotion effect to the dye loss from cellulosic film immersed in the UK–TO solution at 60 °C for C.I. Reactive Red 3, estimated by $(A_0-A)/A_0$ at $\lambda_{\max}$

Dye	Dye loss from film in UK–TO soln ($A_{\rm R}$)[a]	Dye–fibre bond hydrolysis at pH 10.56 ($H_{\rm R}$)[b]	Contribution		
			Hydrolysis γ	Oxidation $\varepsilon \times 10^2$	Promotion rate (min^{-1}) $\alpha \times 10^5$
Red 3[c]	$A_{\rm R}(t)$	$H_{\rm R}(t)$	1.3_5[d]	1.2	1

[a] $A_{\rm R}(t)=(A_0-A)/A_0=(1/\gamma)H_{\rm R}(t)-\exp(-Gt/\varepsilon)-\exp(-\alpha t)+2$ [Eq. (12)]; $A_{\rm R}(t)$: fraction of dye loss from the substrate immersed in the UK–TO solution at time t for Red 3.

[b] $H_{\rm R}(t)=(A_0-A)/A_0$: fraction of dye on the substrate decreased by alkaline hydrolysis at time t for Red 3.

[c] C.I. Reactive generic name.

[d] Promotion of hydrolysis by a factor of 5.9.

The pH of an aqueous PB solution (1.0 g dm^{-3}) was reported to be 10.5 at 60 °C [28], which coincided with the value calculated using Eq. (5). Although the values of K_1 and $K_{\rm HP}$ at 25 °C as well as that of $K_{\rm W}$ at 60 °C were used, the effect of temperature on K_1 and $K_{\rm HP}$ may offset each, and the correct value of K_3 may be attained neglecting the effect of temperature on K_1 and $K_{\rm HP}$. Addition of TAED to UK–TO solution lowers the pH of aqueous PB solutions.

3.2.1. Variation in the concentration of PAA in UK–TO solution

The reaction of electrophiles and nucleophiles with oxidizing agents such as HP, PAA, hypochlorous acid and peracids, especially the reaction between HP and hypochlorous acid under alkaline conditions, are known to produce molecular singlet oxygen from the principle of spin conservation [40–44]. However, the yield of $^1O_2$ seems to fall abruptly with an increase in temperature. According to Evans and Upton [32,33] the reaction of HP with peracid anions is extremely sensitive to metal-ion catalysis and diethylenetriamine-*N*,*N*,*N*′,*N*″, *N*″-penta(methylphosphonic acid) (DETP) produces a dramatic decrease in reaction rate. The chelating agent, DETP, is always added to non-phosphate ECE reference detergent [26]. Studies involving HP and/or PAA have been carried out under defined conditions with or without addition of chelating agent such as ethylenediaminetetraacetic acid (EDTA) or DETP [32,33,45–56].

According to Davies and Deary [45], Jürges [46], and Hofmann et al. [47,48], in aqueous PB solution to which TAED or the other activators [49] have been added, 1 mol of TAED generates less than 2 mol of PAA via perhydrolysis by HP at pH > 8, where HP is generated from PB. If only perhydrolysis occurs, one mole of HP anion reacts with one mole of TAED or triacetylethylenediamine to generate one mole of peracetate anion. Besides perhydrolysis, hydrolysis also occurs generating acetic acid, depending upon the pH. The molar ratio of PAA to HP or PB varies over time in alkaline and neutral solutions [47–51]. The concentration of PAA reaches a maximum at a time dependent upon the temperature and pH of the solution. By perhydrolysis and hydrolysis, TAED is converted into diacetylethylenediamine via triacetylethylenediamine [45,46,51].

Judging from the experimental conditions used in these studies [45–51], the temperature (60 °C) and pH of the UK–TO solution seem to be too high and the concentration of TAED too low to allow the time necessary for PAA to be generated. Turner and Mathews [51] examined the concentration of PAA generated by the addition of TAED to aqueous HP solution at various pH values. Under the conditions of 60 °C, pH 8 and a molar ratio of TAED: HP = 1:2, the concentration of PAA started from zero and reached a maximum at 10 min after which it fell to half the maximum value after about 30 min; the concentration fell to almost zero after 90 min. At 40 °C, pH 10 and a molar ratio of 1:1 [48], the concentration of PAA reached a maximum within 10 min and then fell very slowly, while at 60 °C, pH 10, and molar ratio of 1:2 [47], PAA showed only a decrease in concentration and about 90% of it disappeared within 60 min. In this case, however, the concentration of HP decreased much more slowly. The decrease of peroxide, PAA and HP follows the reaction between dissociated and undissociated species of PAA and HP in which oxygen is generated [47–50,52,53]. Since the molar ratio of the UK–TO solution is 1:10 and the initial pH is ca. 10, PAA may show a reduction in concentration only at the higher temperature of 60 °C. The results of these studies show that the effects of chelating agents on the action of oxidizing agents remains unclear, although Evans and Upton [32,33] reported that the addition of DETP to HP solution minimized the rate of reaction for HP.

3.2.2. pH-variation of the UK–TO solution

Initially, the change in pH in the UK–TO solution over time was measured without immersing the cellulosic films, as shown in Fig. 2. TAED is known to generate PAA and acetic acid in aqueous peroxoborate solution along with a gradual decrease in pH [47,48,50,51]; in this experiment, the pH fell to 9.62 after 100 min, the value at pH coinciding with that of the original UK–TO solution (9.6 at 60 °C [28]). In the present study, the removal of some additives from the original recipes had little effect on pH (cf. Section 2.3.2). The pH decrease was then followed by a gradual increase, which may have been due to the progress of degradation of HP. HP is lost concurrently with the generation of oxygen in alkaline solution [52,53] and, as a result, the pH of the solution rises gradually, but the rise is very small and slow. According to Hauthal et al. [47], the concentration of PAA in aqueous PB solution to which TAED has been added becomes very low after about 2 h under conditions similar to UK–TO solution, due to the degradation of PAA by the reaction between them, in spite of the use of chelating agent EDTA.

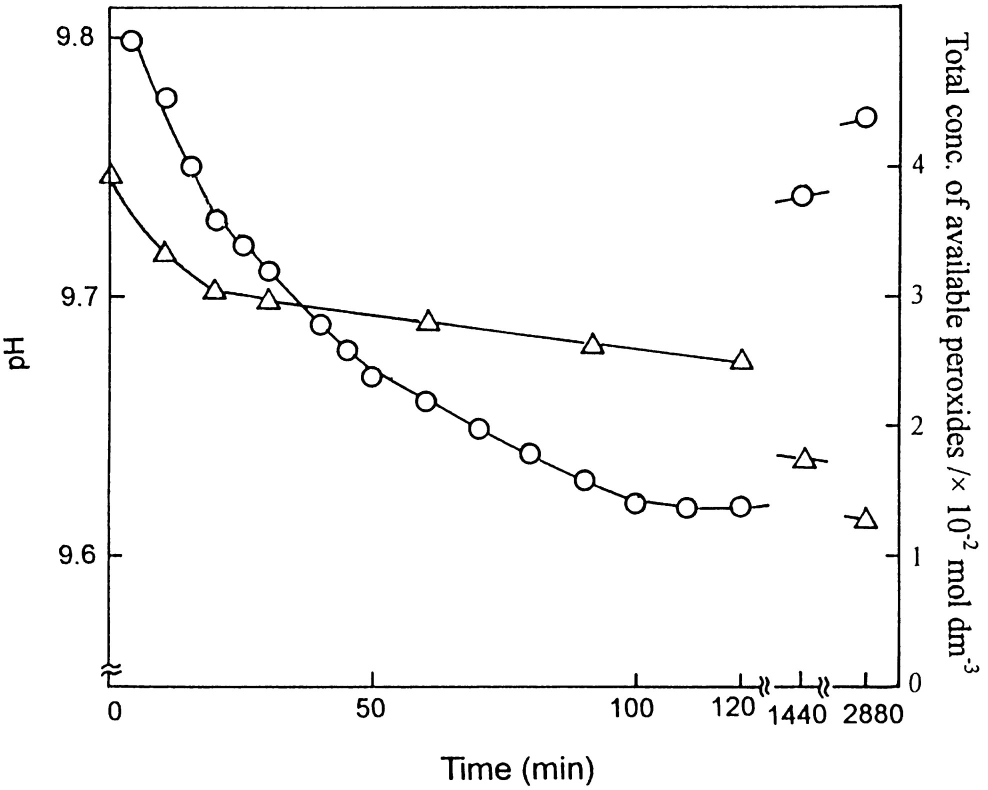


Fig. 2. Time course of changes in the pH (○) and total concentration (△) of available peroxides in the UK–TO solution at 60 °C.

The generation of PAA and acetic acid, which lowers the pH of the solution, and the degradation of HP and PAA, which causes an increase in pH, may occur simultaneously. As the generation of PAA and acetic acid ends, the pH of UK–TO solution starts to rise very slowly. This is one explanation for the pH-variation of UK–TO solution. The kinetics of reactions between various species and the effects of trace amounts of metal ions on these reactions remain to be examined, although these have been studied using model systems [8–14].

3.2.3. Available hydrogen peroxide in UK–TO solution

The pH-change of UK–TO solution, although it is small, has a direct effect on the rate of hydrolysis and on oxidative fading. Since only the HP anion (HO_2^-) acts as a nucleophile in oxidation by HP ($pK_a = 11.75$) [5–18,54] and undissociated PAA ($pK_a = 8.2$) as an electrophile in oxidation by PAA [17,54,55], the mole fraction of the effective species of these oxidizing agents may change with changing pH of UK–TO solution. Although the concentration of PAA is smaller than that of HP, the reactivity of the former is higher than that of the latter one. The overall effect is not clear. Judging from the pH variation of UK–TO solution which occurred mainly due to the effect of added TAED, an analysis of the effect of HP and PAA on dye loss may be difficult.

According to Eq. (4), the hydroperoxotrihydroxoborate anion acts as a reservoir of HP and only the HP anion of the same concentration as hydroxide anion is active in the alkaline PB solution. The pH values of PB solution at 60 °C were measured and the available peroxide concentration (HP+PAA) in UK–TO solution determined, as shown in Fig. 2. This figure shows a relatively rapid decrease initially and a subsequent slow down. The result of chemical analysis (cf. Section 2.5) showed that the initial rapid decrease corresponds to the disappearance of PAA, similar to previous reports [47–51] (cf. Section 3.2.1). The maximum molar ratio of PAA, PAA/(HP+PAA), is of the order of 0.1, which is the same magnitude as the ratio of TAED/PB; this is also the same as in previous reports [47–51]. Judging from the variations that are seen in the concentration of various components, the starting point of an experiments seems to be somewhat arbitrary, even though BS 1006 UK–TO sets forth a definite protocol for preparation. Variations in the concentration of the active components during preparation may be too large to disregard.

3.3. Hydrolysis of dye–fibre bond in aqueous alkaline solution

3.3.1. Bimodal behaviour of dye–fibre bond hydrolysis

The pH of the UK–TO solution is too low to obtain detailed hydrolytic behaviour of dye–fibre bonds and changes with time (Section 3.2.1). Dye loss due to alkaline hydrolysis of the dye–fibre bond was examined by immersing dyed cellophane in a phosphate buffer solution at 60 °C, pH 10.56, this being a pH higher than that of UK–TO solution. The absorption spectra of reactive dyes on cellulosic films immersed in an aqueous alkaline solution for different lengths of time were measured after neutralization. The spectra showed no shift in λ_{max} and the absorption decreased linearly over all wavelengths. The colouration of the alkaline solution increased gradually over time. These facts imply that only dye–fibre bond scission occurs without decomposition of dye chromophores. The plots of A/A_0 at λ_{max} as a function of the time of immersion for seven dyes examined are shown in Fig. 3. The order of the rates of bond-scission were as follows:

$$\begin{aligned}&\text{Red 3} > \text{Brown} \doteqdot \text{Yellow 3} \gg \text{Blue 2}\\&\gg \text{Blue5} \gg \text{Red 120} > \text{Red DFP}\end{aligned} \tag{6}$$

DFP dyes had the highest stability followed by bisMCT dye (Red 120) then the other MCT dyes.

Senn et al. [57,58] reported dye-fibre bond hydrolysis of reactive dyes with the same chromophore (e.g. C.I. Reactive Blue 19) but having different reactive groups over a wide range of pH. In their results, the rates of hydrolysis depended upon the reactive groups [57,58] as well as on the chromophore when the dyes had the same reactive group [59]. Rates were at a minimum at about pH 6, and were proportional to the concentration of hydroxide anion in the alkaline region and to the

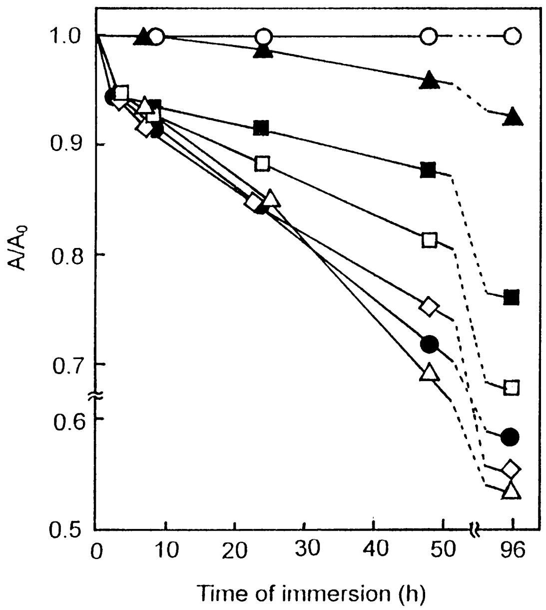


Fig. 3. Dye–fibre bond hydrolysis for C.I. Reactive Yellow 3 (◇), Red 3 (△), Red 120 (▲), Red DFP (○), Blue 2 (□), Blue 5 (■), and Brown (●) in alkaline solution at pH 10.56 and 60 °C.

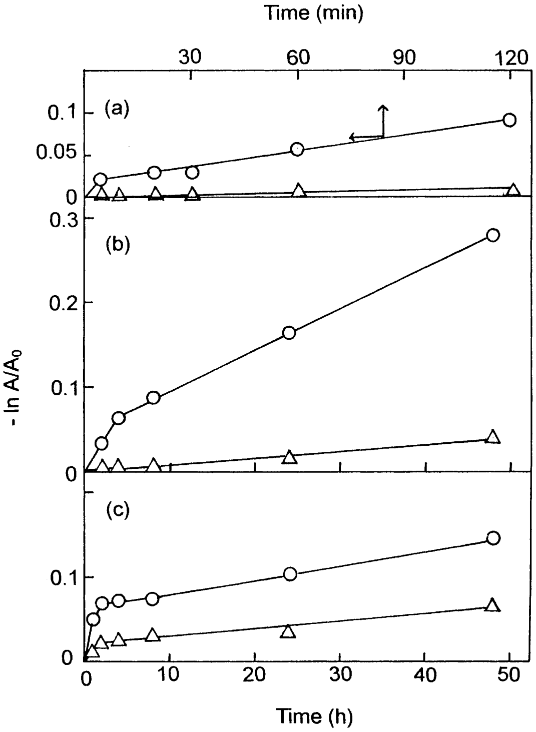


Fig. 4. (a) Oxidative fading of dyes in the UK–TO solution at 60 °C, (b) dye–fibre bond hydrolysis in alkaline solution at pH 10.56 and 60 °C and (c) dye loss from dyed cellophane films immersed in the UK–TO solution at 60 °C for C.I. Reactive Yellow 3 (○) and Red 120 (△).

concentration of hydronium ion with decreasing pH in the acidic region [57,58]. Since the value of the pH of the UK–TO solution is lower than the alkaline solution used for these studies, the UK–TO solution may result in a decrease in the rate of dye-fibre bond hydrolysis due to the difference in concentration of the hydroxide anion.

When the values of ln A/A_0 were plotted against time for C.I. Reactive Yellow 3 and Red 120, linear relationships were obtained as shown in Fig. 4. These relationships imply that hydrolysis obeys pseudofirst-order kinetics and resembles that of vinylsulfonyl (VS) dyes [59]. Except for C.I. Reactive Red 120 and Red DFP, the MCT dyes initially showed a large then slow dye loss with a constant rate of hydrolysis. In the analysis of dye loss mechanism for C.I. Reactive Red 3, on the other hand, the dye was treated by a different procedure from the other dyes (cf. Section 3.6.2). However, linearity between ln A/A_0 and t were not good.

3.3.2. Kinetics of dye–fibre bond hydrolysis

MCT dyes bound to cellulose undergo bimodal hydrolytic behaviour specific to such dyes. Compared to the concentrations of the corresponding components for VS dyes, the initial concentrations of MCT dyes with a faster rate of hydrolysis are lower, and the concentrations of dyes with a slower rate of hydrolysis are higher [59]. Like VS dyes, MCT dyes seem to bind with cellulose at least in a bimodal manner, one part loosely bound and the other part tightly bound. Thus, MCT dyes on a cellulosic substrate display bimodal hydrolytic behaviour when immersed in aqueous alkaline solution [59]. If the concentrations of dyes in a bimodal model are C_0^1 and C_0^2, their dye–fibre bonds are hydrolysed by pseudo-first order kinetics, like VS dyes [59], whose rate constants are k_1 and k_2 (min^{-1}), respectively. The hydrolysis of each component, i, is described by:

$$C^i = C_0^i\{1 - \exp(-k_i t)\} \qquad (7)$$

where t (min) denotes time.

Given the total initial concentration $C_0 = C_0^1 + C_0^2$, and the total concentration $C = C^1 + C^2$, the dye loss from the substrate is described by [59]:

$$\frac{C}{C_0} = \frac{C^1}{C_0}\left\{1 - \exp(-k_1 t)\right\} + \frac{C^2}{C_0}\left\{1 - \exp(-k_2 t)\right\} \quad (8)$$

Assuming that $C/C_0 = 1 - A/A_0$, one can obtain the duration of hydrolysis from the measurements of the absorbance of the cellulosic films immersed in alkaline solution.

Since dye loss occurred at a fast rate of hydrolysis and was completed within a few hours, the value of C_0^1/C_0 was small, i.e. at best 0.08 (cf. Table 1). This part of hydrolysis was regarded as the initial dye loss, a very fast rate of dye-fibre bond hydrolysis which was followed by a slow rate (k_2) of hydrolysis. Eq. (8) now becomes:

$$\frac{C}{C_0} = \frac{C_0^1}{C_0} + \frac{C_0^2}{C_0}\left\{1 - \exp(-k_2 t)\right\} \quad (9)$$

In this case, while the value of k_1 may not be infinite, no value of k_1 could be experimentally estimated due to the low value of C_0^1/C_0. Hereafter, this term is referred to as the initial dye loss. From then on, the duration of hydrolysis was determined by regarding the first term on the right hand side in Eq. (8) as constant. As mentioned below, analysis of dye loss from dyed films in UK–TO solution followed the same assumption (cf. Section 3.6).

The total hydrolysis for C.I. Reactive Red 120 and Red DFP is described by Eq. (9) as described above. The parameter of initial dye loss as E and for the rate of subsequent slow hydrolysis as F are listed in the forth and fifth columns of Table 1.

At first it was suspected that the initial dye loss might correspond to the unfixed dye adsorbed near the surface of the substrate. When the contribution by initial dye loss from the total loss was eliminated, the correlation between ΔE^* and A/A_0 shown in Fig. 1(b) deteriorated. The substantivity of dyes showed no correlation to the amounts of initial dye loss. Thus, it was concluded that initial dye loss is one of the essential properties of cellulosic reactive dyeings, and it correlates with the chemical structure of the chromophore. Contributing factors to bimodal dye loss behaviour may be: (1) the position of hydroxyl groups in the glucopyranose ring, (2) the chemical bonding with or without physical binding, (3) the bonding near or far from the chain end of cellulose, and/or (4) heterogeneous microstructure of cellulose. The former two may figure prominantli in the reactive dyeing of cellulose, while the other factors may act secondarily. Reactive dyes with large substantivity may physically adsorb on to the cellulose and bind chemically with it.

In fact, C.I. Reactive Red 120 and Red DFP, both with high substantivity, showed no initial loss, while the other dyes showed 4–5% (cf. Table 1). The rate of subsequent dye loss was the smallest for Red DFP and the second smallest for Red 120. The rates for other dyes seem to show no relation to substantivity. As with VS dyes [59], the bimodal character of hydrolytic behaviour and its relation to chemical structure remain to be solved for reactive dyes.

3.4. Oxidative fading of reactive dyes in UK–TO solution

As described below, the decomposition of the dye chromophore bound to cellulose in an aqueous peroxide solution was difficult to analyse, because dye–fibre bond hydrolysis occurred simultaneously at 60 °C. To start, the simplest case, the oxidation of commercial dyes, was examined in UK–TO solution. From the very moment that the dye solution is mixed with the UK–TO solution, both of which are twice as concentrated, the reaction of MCT and DFP groups in the dye to hydroxide ions as well as the oxidation reaction of chromophore with HP start. PAA generated from TAED may also react as an oxidizing agent (cf. Section 3.2). Since the concentration of dyes is much lower than that of the alkaline agent, a decrease in pH by the reaction may be regarded as negligible. The visible absorption spectra of dyes examined were similar in the alkaline aqueous solution, on dry and wet cellulosic films, and on films immersed in alkaline solution containing peroxoborate.

The absorption spectra of reactive dyes in the UK–TO solution were measured after neutralization. The variations in the spectra were observed as a function of reaction time. The absorption in the visible region gradually decreased showing no shift of $\lambda_{\max}$, implying the oxidative decomposition of the chromophore.

In order to examine the rates of decomposition, the values of $\ln A/A_0$ were plotted against the reaction time as illustrated in Fig. 4(a), giving a linear relationship implying pseudo-first order kinetics. The decomposition behaviour showed the typical pattern of initially fast and subsequently slow or almost negligible rates except for a few dyes. This may be common behaviour of dyes in aqueous oxide-bleach solution [6–9,15–17,54]. The quantity showing the fast rates varied with dyes. The order of the rates for the subsequently slower decomposition was as follows:

$$\text{Blue-Cu} \gg \text{Orange II} \gg \text{Blue 5} > \text{Red DFP} > \text{Brown} > \text{Yellow 3} > \text{Red 3} > \text{Red 120} > \text{Blue 2} \quad (10)$$

The values of the rates, obtained from the slope of the plots between $\ln A/A_0$ and t, are described by G, and are listed in the sixth column in Table 1. From the results, C.I. Reactive Blue 2 had the highest stability to peroxide bleaching agents among the dyes examined, while C.I. Reactive Blue 5 had low stability in spite of having the same aminoanthraquinone chromophore. It is notable that C.I. Reactive Yellow 3 with an o-acetoamido substituent had high stability to peroxide attack, comparable to C.I. Reactive Blue 2. In spite of the same chromophore, the rate of oxidation for C.I. Reactive Red 120 was a third of that for C.I. Reactive Red 3. Orange II examined as a reference had a rate constant of oxidation larger by two orders in magnitude than those of the common reactive dyes [17,55,56]. When the rate constant of oxidation for Orange II, listed in Table 1, was roughly converted into a second-order rate constant, the value for Orange II estimated in the present study was considerably larger than determined in previous studies, possibly an effect of catalytic action of trace metal ions. It was very clear in case the of Blue-Cu; this copper complex azo dye had an extremely large rate constant due to the catalytic action of copper atom. But, the common reactive dyes examined have had high stability to oxidative attacks in UK–TO solution in spite of the presence of trace metal ions.

Although, as mentioned above, the role of catalytic action of trace metal ions in the reaction of dyes with oxidizing agents, especially HP, has been emphasized [8–14,32,33], analyses of a complex system such as UK–TO solution in which many reactants as well as catalysts coexist remains to be examined. Differences in stability to oxidative attacks by HP and PAA among these dyes should be further examined.

3.5. Dye loss from dyed cellulosic films immersed in UK–TO solution

After the cellulosic films dyed with reactive dyes were immersed in UK–TO solution for the prescribed amount of time, the absorption spectra of dyes on the dry films were measured. Variations of spectra to the time of immersion were examined. Coloration of the aqueous solution was observed for most of the dyes, slight coloration of the UK–TO solution was observed after 1 h for C.I. Red 120, after 4 h for C.I. Reactive Yellow 3 and Red 8, after 8 h for Brown, and after 48 for C.I. Reactive Blue 5. No coloration was observed for Red DFP, Blue-Cu or C.I. Reactive Blue 2. Complete decomposition of chromophore occurred in solution in the case of Blue-Cu. None of the dyes examined showed a shift of $\lambda_{\max}$, implying the oxidative decomposition of chromophore and a decrease in the absorbance in the visible region. From the resemblance in the dye loss behaviour to that described previously (Section 3.3), it was concluded that dye-fibre bond scission due to alkaline hydrolysis played an important role in total dye loss, although some oxidative decomposition of dye chromophore might occur simultaneously.

In order to examine the rates of dye loss, the values of A/A_0 at $\lambda_{\max}$ for each dye were plotted against the time of immersion as shown in Fig. 5. The MCT and DFP dyes examined in general have strong resistance to oxidative attacks by prolonged immersion in an aqueous alkaline solution of

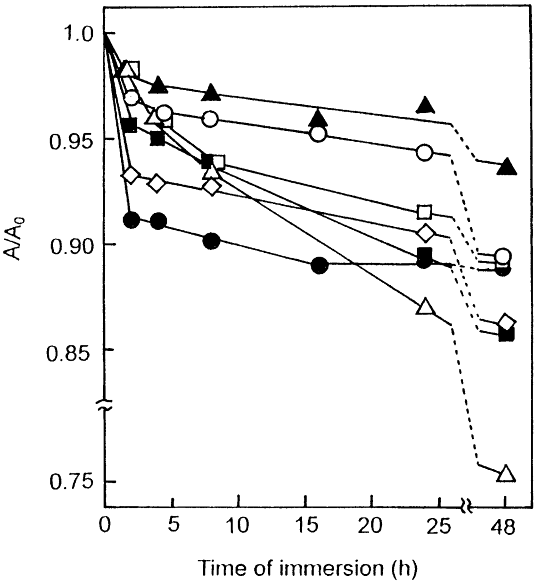


Fig. 5. Dye loss from cellophane films dyed with C.I. Reactive Yellow 3 (◇), Red 3 (△), Red 120 (▲), Red DFP (○), Blue 2 (□), Blue 5 (■), and Brown (●) in the UK–TO solution at 60 °C.

peroxide bleaching agent. C.I. Reactive Red 3 showed considerable dye loss after long immersion, although C.I. Reactive Red 120 with the same chromophore had the highest stability. Affinity of dyes to cellulose seems to contribute to the resistance to oxidative attacks.

MCT and DFP dyes can be used safely in repeated home laundering by peroxoborate containing detergent, when the dyes are carefully selected [23–25]. The results of the present study suggest that C.I. Reactive Red 3 and C.I. Reactive Blue 5 should perhaps be avoided when dyeing cotton garments that are washed with detergent containing oxide-bleach.

3.6. Mechanistic phenomenological analysis of dye loss under the UK–TO conditions

3.6.1. Analysis by pseudo-first order kinetics

As discussed above, at least two mechanisms contribute to dye loss from cellulosic substrate immersed in UK–TO solution. On the basis of the results described in Sections 3.3 and 3.4, total dye loss can be divided into two categories from dye–fibre bond hydrolysis, and from oxidative decomposition of the chromophore. The dye loss was analysed by the same procedure as dye–fibre bond hydrolysis by estimating the values of B and D so as to fit Eq. (9). The parameters for initial dye loss as B, and for the rate of subsequent slow dye loss as G, are listed in the second and third columns of Table 1.

3.6.1.1. Contribution of dye–fibre bond hydrolysis. Although the pH-values of UK–TO solution changed non-linearly with time, a mean value of pH within the first 2 h may be supposed to exist between 9.70 and 9.65. It increased to 9.74 after 24 h and to 9.77 after 48 h. The mean pH value within the first 24 h may also be regarded to be between 9.65 and 9.70. The mean value of pH for the lowest (9.62) and highest (9.74) values is 9.68 within 24 h, if the decrease in pH in the initial period is neglected. Dye–fibre bond hydrolysis was examined at pH 10.56, where the concentration of hydroxide ion was 3.5×10^{-3} mol dm^{-3} at 60 °C. The concentrations at pH 9.70 and 9.65 were 4.8×10^{-4} and 4.3×10^{-4} mol dm^{-3}, respectively. It was estimated, therefore, that the rate of alkaline dye–fibre bond hydrolysis in UK–TO solution was one eighth of the rate at pH 10.56. Thus, the dominator of F in the seventh column of Table 1 was determined to be eight (cf. Table 1).

3.6.1.2. Contribution of oxidative fading by bleaching agents. Red DFP underwent very little dye–fibre bond scission and C.I. Reactive Red 120 a small scission at pH 10.56 (cf. Fig. 3). The rate of dye loss in UK–TO solution for Red DFP ($3.1\times\ 10^{-5}$ min^{-1}) should be attributed to a mechanism other than the hydrolysis, while that for Red 120 (1.6×10^{-5} min^{-1}) might be in the similar situation (cf. Table 1). Oxidative decomposition (cf. Fig. 5) may be a principal factor in total dye loss. If the predominant mechanism other than the hydrolysis for both dyes is assumed to be the oxidative fading, the reduction factors of cellulosic substrate are 1/61 for Red DFP and 1/4 for Red 120. If the hypothesis that the larger the rates of oxidation in liquid phase, the larger the shielding effect by cellulose holds for all the dyes examined, there may be no third mechanism involved in dye loss. When a reduction factor for all the dyes was estimated, however, none was found. Thus an alternative mechanism to describe the dye loss other than hydrolysis was explored.

3.6.1.3. Contribution of cellulose degradation. In bleaching by HP, some degradation of cellulose occurs, depending upon the bleaching conditions [60–64]. It could be assumed that the rate of cellulose degradation in the UK–TO solution is around 1×10^{-5} min^{-1}, which corresponds to the value of α in Eq. (11). We tried to find a unified reduction factor for oxidative fading by adjusting the value of α so that the denominator of G in Table 1 becomes constant. It was found that this condition is satisfied when the factor is 1/120. These results are summarized in the seventh column in Table 1, and the rates of degradation are listed as α (min^{-1}) in the eighth column.

3.6.1.4. Kinetics of dye loss from cellulosic substrate in UK–TO solution. When dye loss is described by 1—A/A_0, the contribution of dye–fibre bond hydrolysis is given by Eq. (9), where the values of rate constants and concentrations are different from those in Section 3.3.2. As discussed above, the contribution of the oxidative fading as well as cellulose degradation must be taken into consideration. If their kinetics are assumed to be pseudo-first order, the kinetic equation of dye loss incorporating all the factors becomes:

$$\frac{C}{C_0}=\frac{C_0^1}{C_0}+\frac{C_0^2}{C_0}\left\{1-\exp(-k_3t)\right\}+1-\exp(-\alpha t) \qquad (11)$$

where k_3 (min^{-1}) is the sum of the pseudo-first order rate constants of dye-cellulose bond hydrolysis and oxidative decomposition of dye chromophore (i.e. $k_3=F/8+G/120$), and α (min^{-1}) the pseudo-first order rate constant described above. (From a mechanistic point of view, the pseudo-first order rate constants, k_3 and α, should contain a term for the concentration of reactants. Since the concentrations of HP or hydroxide ions in UK–TO solution decreased or changed, over the time course of experiment, this rate constant might not be actually constant. As discussed below (cf. Section 3.6.4), the rate constants were so small that the exponential term could be approximated by a straight line. Thus, even if the rate constant varied with time, the curvature of line would be very small, a linear approximation.)

3.6.1.5. Analysis and validity of the results. On the basis of the above analysis summarized in Table 1, the validity of the results was discussed. In general, since dye loss from cellulosic films immersed in UK–TO solution resembled the alkaline hydrolysis of dye–fibre bond in its time course, the predominant actor controlling dye loss was attributed to hydrolysis. Thus, the bimodal, initially fast and subsequently slow, behaviour of dye loss was the common feature for both processes, and could be described by the common Eq. (9). Promotion effects by PB and TAED may come into play in the initial dye loss, and are described by (B–E) in the last column of Table 1. Initial dye loss in the overall process of degradation, which is similar among all dyes is described by α listed in the second to last column. The former effect may be attributed to the action of PAA generated from TAED, while the latter process is due to the action of HP or PB. The details require further confirmation (cf. Section 3.6.3).

3.6.2. Analysis by $(A\text{-}A_0)/A_0$ versus time plots for C.I. Reactive Red 3

Dye–fibre bond hydrolysis in an aqueous alkaline solution and dye loss from cellulose immersed in the UK–TO solution for six dyes examined obeyed pseudo-first order kinetics, except for C.I. Reactive Red 3. The time course of dye loss in the UK–TO solution and of dye–fibre bond hydrolysis at pH 10.56 for C.I. Reactive Red 3 is illustrated as the relationship between $(A_0\text{-}A)/A_0$ and t in Fig. 6. The dye loss was described by the amount of dye lost because it was a large amount, while in the above discussion, this parameter was described by the amount of dye left on the substrate because dye loss was small. Thus, several different symbols are used in Eq. (12). Unlike the relation between slopes for A_t and H_t, the time courses of $A_\mathrm{R}(t)$ and $H_\mathrm{R}(t)$ for this dye resemble each other irrespective of difference in pH (cf. Table 1). The plots of

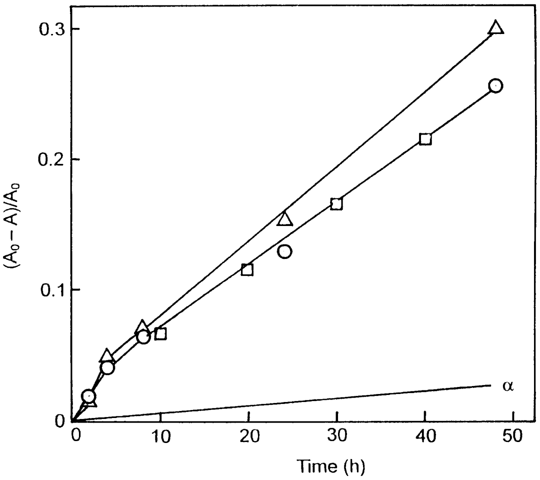


Fig. 6. Mechanism analysis of dye loss behaviour for C.I. Reactive Red 3 from cellophane films immersed in the UK–TO solution: alkaline dye–fibre bond hydrolysis (△) at pH 10.56 and 60 °C, dye loss (○) from cellophane immersed in the UK–TO solution, plots (□) of Eq. (12), and the contribution of cellulose degradation [1− exp(-αt)] (—) (cf. Table 2).

$H_R(t)$ lie in the neighbourhood of $A_R(t)$. As in the previous section, taking the effects of oxidative fading and cellulose degradation (α) into consideration, the time course of dye loss from substrate immersed in the UK–TO solution is described by:

$$A_R(t) = \frac{A_0 - A}{A_0} = \frac{H_R(t)}{\gamma} - \exp\left(-\frac{Gt}{\varepsilon}\right) - \exp(-\alpha t) + 2 \qquad (12)$$

The values of parameters were determined so as to fit Eq. (12) with the experimental time course $A_R(t)$ of dye loss. The results are listed in Table 2 and in Table 1 (G). The values for the contribution of oxidative fading (ϵ) and cellulose degradation (α) are the same as those estimated in Section 3.6.1 (cf. Table 1), while the values of γ for dye-fibre bond hydrolysis are considerably smaller. As shown below in Table 2, hydrolysis promotion was 6 times greater than that of the other six dyes. Since dye loss of C.I. Reactive Red 3 was very large, the effect of non-linear variation of HP and PAA in the concentration as well as that of pH variation may be apparent in a plot for this dye.

Thus, bond hydrolysis is promoted by immersing in the UK–TO solution. This may be referred to as oxidative hydrolysis, a term first used by Collishaw et al. [23,24]. The main reason why this dye having the least substantivity to cellulose among the dyes examined exhibits such promoted hydrolysis remains to be elucidated, although it may be attributable to the oxidation of hetero-aromatic reactive groups as proposed by Rattee et al. [1,2].

3.6.3. *Confirmation of bimodal mechanism by a second immersion*

As described above, the MCT dyes examined showed bimodal behaviour in dye–fibre bond scission by alkaline hydrolysis (cf. Section 3.3) as well as in the dye loss from substrate immersed in the UK–TO solution (cf. Sections 3.5 and 3.6). In the present study, it is supposed that this behaviour is due to the existence of a dye–fibre bond with both lower and higher bonding energies. TAED added to an aqueous PB solution causes the generation of PAA soon after its addition. The concentration of PAA may decrease gradually and monotonically under the UK–TO conditions (cf. Section 3.2), but the concentration of PAA must be zero before the addition of TAED. Thus, the effect of PAA, if any, on bimodal behaviour in dye loss may appear only at the time of immersion, since this is when concentration is the highest.

In order to confirm whether or not initial dye loss in the UK–TO solution could be attributed to PAA, the initial dye loss was in effect removed by immersing the original dyed film in the UK–TO solution for 2 h at 60 °C, the first immersion, then performing a second immersion. In the second immersion, C.I. Reactive Yellow 3, Blue 2, and Brown showed no initial dye loss. The dye loss behaviour was similar to that of C.I. Reactive Red 120, with very small rates. Thus, initial dye loss cannot be attributed predominantly to the effect of PAA but to the basic properties of reactive dyeings of cellulose.

3.6.4. *General feature of dye loss in the UK–TO solution*

Dye loss, A_t ($=1-A/A_0$), of six reactive dyes from cellulosic substrate immersed in the UK–TO solution, which can be approximated by a linear equation, is described by the following:

$$A_t = B + (1 - B)Dt + \alpha t \tag{13}$$

When $Dt \ll 1$ and $\alpha t \ll 1$, Eq. (13) is derived from Eq. (11) using different symbols (cf. Table 1). The values of B, initial loss, ranged from 0.022 to 0.084. These values may correspond to instances of smaller bonding energy such as dyes bound to end groups of cellulose chain or bound by some smaller physical binding force besides covalent bonding. This part for some dyes might be promoted by PAA generated from TAED. By comparing the values of B with those of E, the magnitude of initial loss in the UK–TO solution was equal to or a little larger than initial loss seen in alkaline hydrolysis for the same dyes at pH 10.56. The order of magnitude of dye loss by the two processes coincided well with each other (cf. Table 1) as follows:

$$\begin{aligned}&\text{Brown} > \text{Yellow 3} > \text{Blue 2} > \text{Blue 5}\\&> \text{Red DFP} > \text{Red 120}\end{aligned} \tag{14}$$

When the rates of dye loss, D, in the UK–TO solution were compared between dyes, on the other hand, dyes with a larger affinity to cellulose showed slower rates of dye loss as follows:

$$\begin{aligned}&\text{Red 3} \gg \text{Blue 5} \gg \text{Brown} \geqslant \text{Red DFP}\\&= \text{Yellow 3} > \text{Blue 2} \gg \text{Red120}\end{aligned} \tag{15}$$

Besides the chemical bond between dye and fibre, physical bonding seems to play an important role in the stability of reactive dyeings of cellulose immersed in the UK–TO solution. In the case of C.I. Reactive Red 3, a large promotion effect on the rate of dye loss in the UK–TO solution was observed, although the behaviour was the same as the other six dyes. It is note worthy that this dye has relatively low affinity to cellulose.

Besides alkaline hydrolysis of dye–fibre bond and oxidative decomposition of the dye chromophore, an oxidative degradation process whose rate, α, was common to all the reactive dyeings examined was confirmed to contribute to dye loss in the UK–TO solution.

According to Gommes and Lima [27,28], the rates of dye loss from reactive dyeings also depend upon dyeing methods. This observation may support the finding that dye–fibre bond hydrolysis was the dominant factor controlling the rates of dye loss in the UK–TO solution, since the degree of complete binding of bifunctional reactive dyes is known to correlate with dyeing methods [65,66].

4. Summary

The mechanism of dye loss from cellulosic reactive dyeings washed with non-phosphate detergent containing PB and TAED was analysed using dyed cellulosic films under conditions of the BS 1006 UK–TO method. The relative fading predicted by the cellophane film method corresponded well with the grey scale ratings of the corresponding dyes on cotton fabrics.

When cellulosic films dyed with one DFP and five MCT dyes were immersed in the UK–TO solution, initially fast and subsequently slow dye loss was observed. The initial dye loss and the rates of subsequent slow dye loss varied with the dyes; the higher the affinity of the dyes, the larger the magnitude of initial loss and the faster the rates of subsequent slow dye loss.

The mechanism of dye loss from dyed cellophane immersed in the UK–TO solution was attributed to the three factors: (1) alkaline dye–fibre bond hydrolysis, (2) oxidative degradation of cellulose, and (3) oxidative decomposition of dye chromophore. The contribution of hydrolysis of the dye–fibre bond to total dye loss was always larger than that due to the oxidative degradation of cellulose, as much as three times larger. The contribution of dye decomposition was the smallest of the three.

C.I. Reactive Red 3 having the lowest affinity, exhibited marked dye loss behaviour in the UK–TO solution, which was almost comparable to alkaline dye–fibre bond hydrolysis at pH 10.6; the contribution of the other factors being too small to estimate compared to the contribution of hydrolysis to total dye loss.

Besides the chemical bond between dyes and fibre, physical bonding plays an important role in the stability of the dye-fibre bond of cellulosic reactive dyeings immersed in the UK–TO solution at 60 °C.

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