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Color variations of anthraquinone and azo reactive dyes on cellulose caused by nitrogen oxides under wet conditions

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Abstract

The effects of nitric acid and nitrous acid on the color variations of aminoanthraquinone and azo dyes on cellulose film were examined. The immersion of dyed films in an acidic aqueous nitrite solution led to color variations caused by the diazotization of the amino groups in the anthraquinone and azo reactive dyes examined in addition to the dye–fiber bond scission by acid hydrolysis. When the dyed films immersed in an acidic nitrite solution were exposed to light, the photodecomposition of the diazotized dyes occurred to generate the corresponding phenols via dediazotization, together with the products generated by the photofading of the original dye. No nitrosation of the imino groups was observed for many reactive dyes with imino groups. The color fastness of reactive dyes to nitrogen oxide is primarily attributed to the irreversible color change caused by the apparently direct transformation of amino groups into hydroxyl ones through these processes. Dyes that show larger color changes at higher rates possess lower color fastness to nitrogen oxide.

Keywords: Color fastness to nitrogen oxide; Aminoanthraquinone dye; Azo dye; Reactive dye; Diazotization; Dediazotization

1. Introduction

NO_x is the main component of air pollutants, and its primary source is the exhaust gas from vehicle traffic [1,2]. Most of the NO_x is emitted as NO, which is then oxidized to NO_2 in the atmosphere [2]. At the high temperatures of combustion, some N_2 is converted to NO in the presence of O_2 and, in general, the higher the combustion temperature, the more NO_x is produced even indoors in places such as dyeing factories. It has been recognized that nitrogen oxide pollutants affect the dyes on textiles [3–13]. Without referring to any literature, Giles et al. [3,4] have reviewed the history and details of the burnt gas-fume fading of wool dyeing studied by a research team of the dye-manufacturing firm Meister, Lucius and Bruning (MLB) in the early 20th century. Especially aminoanthraquinone (AAQ) dyes were confirmed to suffer 'burnt-gas-fume fading' on cellulose acetate in the 1930s [3,4]. According to Giles et al. [3,4], Rowe and Chamberlain [5], who made a systematic study of the gas-fume fading of cellulose acetate rayon dyed with many AAQ dyes, independently reached a conclusion similar to that of the MLB team. The MLB team [3,4] and Rowe and Chamberlain [5] suggested that free or substituted amino groups in the dye became either diazotized or nitrosated in the fading. The reactions, which may occur in fading or color variation, are as follows [3,4]:

(a) With primary amino groups in the dye:

$$R{-}NH_2 + HNO_2 \rightarrow R{-}N_2^+OH^- + H_2O \qquad (1)$$

(b) With secondary amino groups:

$$R{-}NH{-}R' + HNO_2 \rightarrow R{-}N(NO){-}R' + H_2O \qquad (2)$$

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Unlike photofading, in which the decomposition of azo groups or main nuclei occurs, the reaction of the primary or secondary amino substituent in the dye is an irreversible color change and no treatment can return the dye to the original shade. Inhibitors, which are designed to react preferentially with nitrogen oxide on fiber, can retard but not prevent it. The SDC [6] was the first to establish a testing method for testing color fastness to gas fading in 1948. Intensive studies on this subject were thereafter reported mainly in the 1950s [7–12].

Dyes with amino substituents may fade on any fiber, but, in practice, fading is most noticeable on cellulose acetates and polyester fibers, less so on wool [3,4]. Salvin et al. [7] reported the phenomenon of gas fading caused by nitrogen dioxide and discussed the reaction mechanism in relation to the nature of the fabrics and the chemical structure of the dyes and inhibitors involved. Cellulose acetate absorbs nitrogen dioxide at a high rate, and the concentration of nitrous oxide increased with decreasing acetyl values. The effects of humidity and acid gases were also noted [3,4,7,8]. Myles and Reiss [9] investigated in detail the adsorption of nitrogen dioxide on cellulose acetate. Couper [10] investigated the fading of 1,4-bis(methylamino)anthraquinone on cellulose acetate caused by light and gas fumes and analyzed the products extracted from the textiles chromatographically. Both causes of fading yielded similar products, although the proportions were different; the products included *N*-dealkylation products and hydroxyl groups through hydrolysis, but no nitroso groups were formed. Asquith and Campbell [11] carried out a similar study using nitrodiphenylamine dyes and suggested the formation of nitrosation and oxidation products. The proper selection of dyes and inhibitors solved the problems of gas-fume fading. Gas-fume fading on wool was also reported [12,13]. Then, the ISO [14,15] and JIS [16] stipulated the testing methods appropriate for testing color fastness to nitrogen oxides.

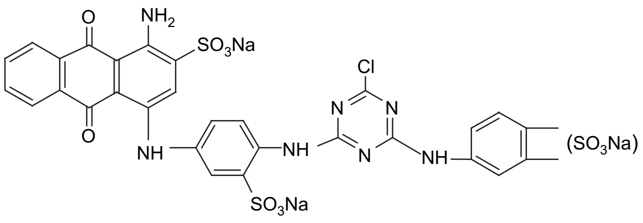
In the present study, the fading behavior of anthraquinone and azo reactive dyes containing amino groups on cellulose caused by nitrogen oxides dissolved in water was examined under wet conditions, to elucidate the possible color changes in reactive dyes on cellulose due to the nitrogen oxides in the atmosphere. Color change due to the diazotization of the amino groups in AAQ and azo reactive dyes in the dark was confirmed by the presence of the coupling reaction. The light irradiation effects on dyed cellulose films immersed in an acidic nitrite solution, or on the photodecomposition of diazotized dyes as well as the original ones, were examined.

2. Experimental

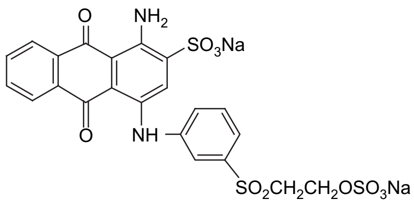
2.1. Dyes used

Seven reactive dyes and an azoic coupling component, supplied by Nippon Kayaku Co., Ltd. and DyStar Japan Ltd., were used. Their chemical structures, C.I. generic names, C.I. constitution numbers, if available, and abbreviations, shown in parentheses, are as follows:

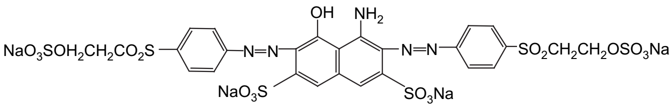
(1) C.I. Reactive Blue 2, C.I. 61211 (Blue 2)



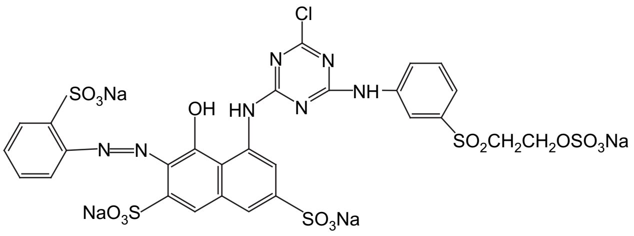
(2) C.I. Reactive Blue 19, C.I. 61200 (Blue 19)



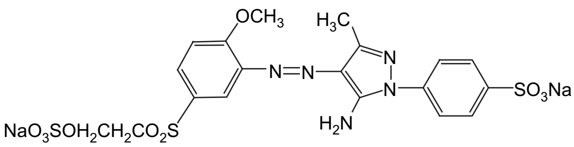
(3) C.I. Reactive Black 5, C.I. 20505 (Black 5)



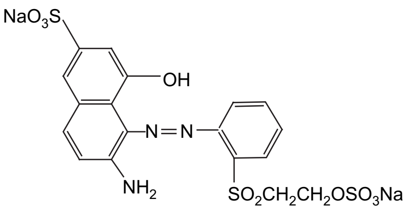
(4) C.I. Reactive Red 194, C.I. 18214 (Red 194)



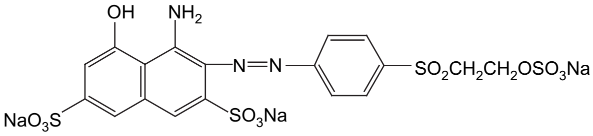
(5) An aminopyrazolinyl azo dye (Yellow)



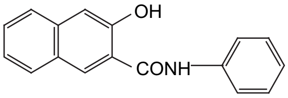
(6) A red azo dye (Red gVS)



(7) A VS monoazo dye from H-acid (Red H)



(8) C.I. Azoic Coupling Component 2, C.I. 37505, Naphthol AS



The color fastnesses to nitrogen oxides of the anthraquinone and azo dyes used are listed in Table 1.

2.2. *Dyeing of cellulose films*

The cellophane sheets used (Futamura Kagaku Kogyo K.K., #300) were cut into rectangles 4.0 cm wide and 20 cm long and scoured with distilled water for 3 h. The films were dyed by the alkali-shock method at 50 °C for the vinylsulfonyl (VS) dyes and at 80 °C for the monochlorotriazinyl (MCT) dyes so as to obtain an optical density between 0.8 and 1.0 (after washing) at λ_{max}. After fixation, the dyed films were washed thoroughly with boiling water to remove the unfixed dye.

2.3. *Testing methods and measurement of the absorption spectra*

The absorption spectra of the dyed films before and after various treatments were measured using a Ubest-50 recording spectrophotometer (Jasco Corp.). The rates of dye loss and the color variations were determined based on the ratio of absorbance $(A_0 - A)/A_0$ (A_0: absorbance of the original sample; A: that after the corresponding treatment) at the appropriate wavelength (usually λ_{max}).

Nitrogen oxides dissolved in water generate HNO_3 and HNO_2 in aqueous solution. In the preliminary experiments, we determined that the concentrations of the acidic aqueous nitrite solution, which cause the color variation due to the diazotization of the amino groups in the dyes on the cellulose substrate immersed in the solution, are of the order of 10^{-3} mol dm^{-3}. In the present study, therefore, the effects of nitric acid (HNO_3, 9.68×10^{-4} mol dm^{-3}, pH 3.05 at 25 °C) and an aqueous sodium nitrite solution ($NaNO_2$, 9.70×10^{-4} mol dm^{-3}, pH 3.37 (adjusted by HCl) at 25 °C) on the color variations of reactive dyes on cellulose films were examined.

Table 1
Color fastness of reactive dyes to nitrogen oxides and ozone on cotton fabrics estimated by JIS L 0855

C.I. Reactive	Color fastness to nitrogen oxides
Blue 2	1
Blue 19	3
Black 5	5
Red 194	5

In order to confirm whether the reactive dyes were diazotized or not, the reactive dyes on the cellulose films were diazotized by immersing the films in an aqueous sodium nitrite solution (7.91×10^{-4} mol dm^{-3}, pH 1.19 (adjusted by HCl) at 25 °C) for 30 min. After diazotization, the films were immersed in a Naphthol AS (1.0 g dm^{-3}) − NaOH (0.1 mol dm^{-3}) solution for 30 min to allow coupling.

When necessary after the diazotization, the cellulose films were exposed to a carbon arc using a fadeometer, in accordance with the previous paper [17].

3. Results and discussion

3.1. *Influence of nitric acid*

3.1.1. *Acid hydrolysis of the dye–fiber bond*

Cellulose films dyed with C.I. Reactive Red 194, Blue 2, Blue 19 and Black 5 were immersed in an aqueous nitric acid solution (9.68×10^{-4} mol dm^{-3}; pH 3.05 at 25 °C) under three conditions: in the dark at 25 and 60 °C and under exposure to a carbon arc (ca. 50 °C). The changes in the absorbance at λ_{max} are shown in Fig. 1(a)–(c) as the relationship between $(A_0{-}A)/A_0$ and the treatment time. As in the case of the MCT reactive dyes on cellulose immersed in an aqueous solution containing peroxide bleaching agents [18], the dye loss profiles were approximately described by the following equation:

$$\frac{A_0 - A}{A_0} = \frac{A_0^1}{A_0} + \frac{A_0^2}{A_0}\{1 - \exp(-k_2 t)\} \tag{3}$$

Here, A_0^1/A_0 and A_0^2/A_0 are the proportions of the initially fast hydrolyzed component and those of slowly hydrolyzed component, respectively, where the latter rate of hydrolysis is k_2 (min^{-1}) and $A_0^1 + A_0^2 = A_0$. The values of the parameters from the dye loss profiles in Fig. 1 are summarized in Table 2. At 25 °C, the rates of acid hydrolysis were in the following order:

$$\text{Blue 2} \gg \text{Red 194} > \text{Blue 19} > \text{Black 5} \tag{4}$$

Dye–fiber bond scission was observed at pH 3 and 25 °C in the dark for C.I. Reactive Blue 2, while little scission was observed for C.I. Reactive Red 194, Blue 19 and Black 5, indicating the high stability of VS dye–fiber bonds at ambient temperature. The absorption spectra of the dyed films immersed in an aqueous solution at pH 3 in the dark showed a linear decrease in absorbance over the whole range from 190 to 750 nm. The dye–fiber bond scission was concluded to occur due to the immersion in the dark. In the case of C.I. Reactive Blue 2, two kinds of bond scission, fast and slow, occurred

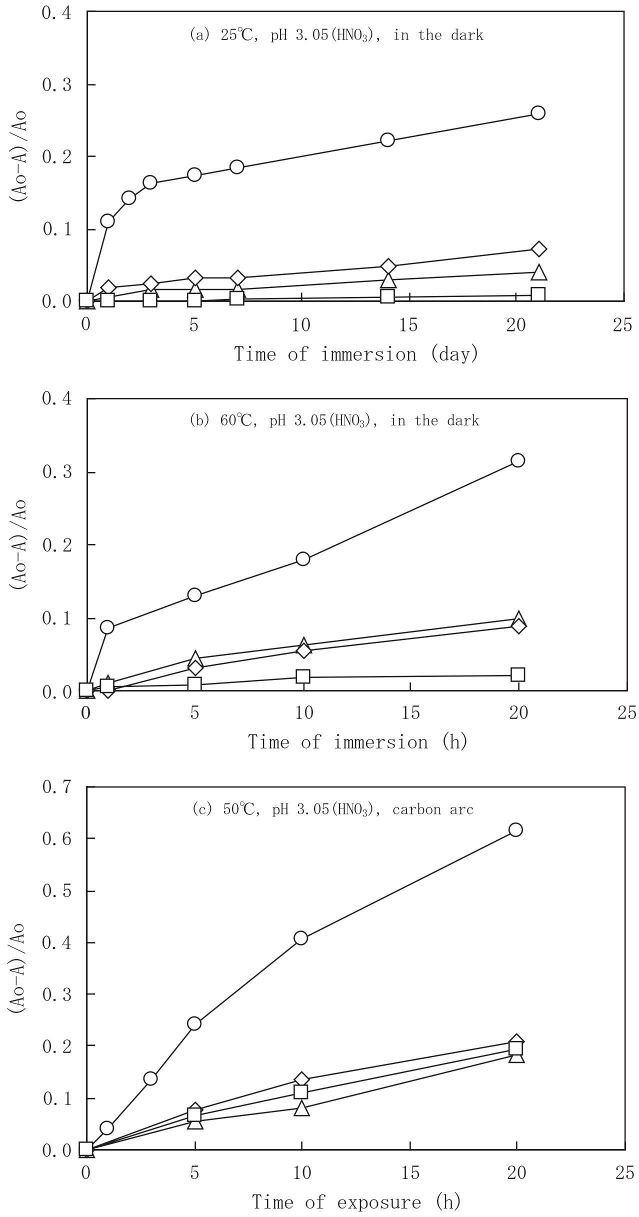


Fig. 1. Relationship between $(A_0 - A)/A_0$ at λ_{max} for C.I. Reactive Blue 2 (○), Blue 19 (△), Red 194 (◇) and Black 5 (□) on cellophane and the immersion time in an aqueous nitric acid solution (9.68×10^{-4} mol dm^{-3}) at pH 3.05 (a) at 25 °C in the dark, (b) at 60 °C in the dark, and (c) at 50 °C on exposure of the dyed film to a carbon arc using a fadeometer. The absorption spectra for the dyes over the whole range from 190 to 750 nm decreased proportionally.

simultaneously. About 10% of C.I. Reactive Blue 2 underwent fast scission, while 90% underwent slow scission. This two-step scission behavior was found in the alkaline hydrolysis of VS cellulose dyeings [19]. The other VS dyes examined showed no such stepwise behavior at pH 3. Senn and Zollinger [20,21] reported that the dye–fiber bonds of MCT dyes had a lower stability than those of VS dyes in the acidic region. Stepwise bond scission may occur in dyes with relatively weak dye–fiber bonds. This may be due to the position of the hydroxyl groups in the glucose ring of cellulose. In other words, dye–fiber bonds where the contribution of chemical bonding is large (and the total stability is relatively low) may exhibit stepwise dye-loss behavior in the acid region for MCT dyes and in the alkaline region for VS dyes [19] and MCT dyes [18], while bonds where the contribution of physical bonding is large (and the total stability of dye–fiber bond becomes high) may have no stepwise dye-loss behavior or no stepwise dye loss may be noticed. If cellulose fabrics dyed with reactive dyes become wet with acid rain and are left as they are, fading caused by bond scission is conceivable, although it depends on the reactive groups and the structure of the dyes involved.

3.1.2. Effect of temperature

At 60 °C, the order of the acid hydrolysis rate for the dye–fiber bond was as follows (cf. Table 2):

$$\text{Blue 2} \gg \text{Blue 19} \gtrsim \text{Red 194} \gg \text{Black 5} \tag{5}$$

C.I. Reactive Blue 2 exhibited a very fast rate, while Blue 19 and Red 194 a similar, small rate and Black 5 a very slow rate. An increase in temperature up to 60 °C caused the rate of hydrolysis for Red 194 and Black 5 to raise by a factor of 40, for Blue 2 by a factor of 50, and for Blue 19 by a factor of 70. The increase in temperature markedly lowered the stability and raised the rate of hydrolysis at the dye–fiber bonds. C.I. Reactive Blue 19 exhibited the largest relative increase in the rate of hydrolysis, while Red 194 and Black 5, which have the high affinity to cellulose, showed a small relative increase in the rate as a result of the rise in temperature, implying the high stability of the dye–fiber bond for the latter two dyes even at high temperatures.

3.1.3. Effect of light and temperature

When the dyed films immersed in an aqueous acidic solution at pH 3 were exposed to a carbon arc using a fadeometer, the apparent increases in the dye loss were about 100-fold for Blue 19 and Red 194, about 200-fold for Blue 2 and larger than 1000-fold for Black 5, as rapid as the increase in the dark at 25 °C, when roughly analyzed using Eq. (3) (the results of the calculations are listed in Table 2; cf. also Fig. 1(a) and (c)).

On exposing the dyed films to a carbon arc using a fadeometer, the temperature of the solution was raised to 50 °C. In

Table 2
Analyses of dye loss for reactive dyes on cellophane immersed in aqueous nitric acid solutions of pH 3.05 by use of Eq. (3)

C.I. Reactive	25 °C, in the dark			60 °C, in the dark			50 °C, carbon arc		
	A_0^1/A_0	A_0^2/A_0	k_2 (min^{-1})	A_0^1/A_0	A_0^2/A_0	k_2 (min^{-1})	A_0^1/A_0	A_0^2/A_0	k_2 (min^{-1})
Blue 2	0.15	0.85	3.5×10^{-6}	0.08	0.92	$1.8_7 \times 10^{-4}$	0.12	0.88	6.0×10^{-4}
Blue 19	0	1.0	1.5×10^{-6}	0	1.0	$1.1_0 \times 10^{-4}$	0	1.0	$1.6_7 \times 10^{-4}$
Black 5	0.0035	0.9965	$1.1_5 \times 10^{-7}$	0.0035	0.9965	4.3×10^{-6}	0.0035	0.9965	1.8×10^{-4}
Red 194	0.02	0.98	1.5×10^{-6}	0.02	0.98	5.9×10^{-5}	0.02	0.98	1.8×10^{-4}

order to separate the temperature effect from the total dye loss, we added a term for photofading to Eq. (3), as follows:

$$\frac{A_0 - A}{A_0} = \frac{A_0^1}{A_0} + \frac{A_0^2}{A_0}\{1 - \exp(-k_2 t)\} + \frac{A_0^3}{A_0}\{1 - \exp(-k_3 t)\} \qquad (6)$$

where k_2 (min^{-1}) is the same as for Eq. (3) and k_3 (min^{-1}) the rate of photofading, respectively. Since fast hydrolysis occurred during the initial period of immersion, the proportion A_0^3, which was caused by the photofading, may be regarded as equal to the proportion A_0^2, which was caused by the slow hydrolysis. The rates of hydrolysis at 50 °C were assumed to be 5/7 of the rates at 60 °C for each dye. The profiles of dye loss were analyzed using Eq. (6), and the parameters obtained are listed in Table 3 (cf. Fig. 1(c)).

On exposing the dyed films immersed in the acidic aqueous solution to light, the dye loss increased. In addition to the temperature effect, therefore, light irradiation promoted further dye loss. Since the temperature effects on the rate of photofading are usually small, the effects on the total dye loss may be attributed to the change in the rate of dye–fiber bond scission. The apparent promotion of dye loss (in quantity) by light in water at pH 3 was the largest for C.I. Reactive Blue 2, although a similar promotion was observed for the other dyes (Table 3 and Fig. 1(c)). The estimated contributions of photofading (estimated by k_3 in Eq. (6)) to the total dye loss (estimated by k_2 in Eq. (2)) were in the following order at 50 °C: Black 5 (almost 100%) > Red 194 (90%) > Blue 2 (80%) > Blue 19 (50%). Although the dye–fiber bond stability for Black 5 and Red 194 is high, light irradiation lowered the stability considerably, resulting phenomenologically in the disappearance of the excellent dye–fiber bond stability for Black 5. Compared with the photofading at neutral pH under wet conditions, the rate for Black 5 seemed to be promoted considerably [22].

The reason why Blue 2 and Black 5 showed the largest promotion and the other dyes exhibited these phenomena was not examined further. But wet dyed fabrics may suffer considerable dye loss on exposure to sunlight in an environment containing nitrogen oxides or when becoming wet with acid rain.

3.2. *Diazotization of reactive dyes with amino groups on cellulose substrates*

Rowe and Chamberlain [5] suggested that the gas-fume fading of many acetate dyes on cellulose acetate rayon is due to the diazotization of the amino groups in the dyes or to the nitrosation of secondary amino groups such as methyl- and phenylamino groups. Salvin et al. [7,23] found that a completely faded AAQ dye, Celanthren Blue FFS, showed fluorescence under UV radiation and acid–base change in aqueous sodium carbonate (0.1%). They inferred from these phenomena that oxidative hydrolysis occurs to give hydroxyanthraquinone. It has been recognized that pollutant nitrogen oxides affect the dyes on textiles. Reactive dyes with amino and/or imino groups on cellulose substrates may suffer color variation due to diazotization, depending upon conditions such as the concentration of nitrite and the pH of the solution, besides the chemical structure of the dye itself. (Although Salvin et al. [7,23] and Rowe and Chamberlain [5] inferred the nitrosation of the imino groups, no reaction of the imino groups was confirmed in our present study (cf. Section 3.2.4).) The concentrations of nitrogen dioxide and water on textiles may be determined based on their concentrations in the atmosphere and the adsorptivity of such acidic gases on cellulose substrates and their additives, including the dyes.

Table 3
Analyses of dye loss for reactive dyes on cellophane on exposure to a carbon arc in aqueous nitric acid solutions of pH 3.05 by use of Eq. (6) (cf. Fig. 1(c) and Table 2)

C.I. Reactive	Acid hydrolysis			Fading in acidic solution	
	A_0^1/A_0	A_0^2/A_0	k_2 (min^{-1})	A_0^3/A_0	k_3 (min^{-1})
Blue 2	0.12	0.88	$1.3_4 \times 10^{-4}$	0.88	4.7×10^{-4}
Blue 19	0	1.0	7.9×10^{-5}	1.0	8.8×10^{-5}
Black 5	0	1.0	3.1×10^{-6}	1.0	1.8×10^{-4}
Red 194	0	1.0	4.2×10^{-5}	1.0	1.6×10^{-4}

3.2.1. *Immersion of dyed films into an aqueous nitrous solution at pH 3 in the dark*

The absorption spectra of the AAQ and reactive azo dyes on cellulose films before and after immersion in an aqueous nitrite solution at pH 3.37 in the dark are given in Fig. 2(a) for C.I. Reactive Blue 2 and Fig. 2(b) for C.I. Reactive Blue 19. The 1-amino groups of C.I. Reactive Blue 2 and Blue 19 were gradually diazotized. The diazotization was demonstrated by the coupling reaction with Naphthol AS (cf. Fig. 4). The diazotization of C.I. Reactive Blue 19 (Fig. 2(b), Spectra 1 → 2, 3, 4) occurred more slowly than that of C.I. Reactive Blue 2 (Fig. 2(a), Spectra 1 → 2, 3). The diazotization of C.I. Reactive Blue 2 was completed in 2 h (cf. Fig. 3(b)), while that of C.I. Reactive Blue 19 proceeded slowly, becoming complete in 1 day. (No spectra for Blue 2 immersed for 2 and 26 h are given since there were only slight deviations from Spectra 3.) Practically, there seemed to be little diazotization in C.I. Reactive Black 5 under these diazotization conditions as far as we could see with the naked eye. (But diazotization did in fact occur (cf. Section 3.2.3).)

The time course of the spectral variation due to the diazotization in the acidic nitrous acid solution (pH 3.37) in the dark is given in Fig. 3 as the relationship between $(A_0 - A)/A_0$ at $\lambda_{\max}$ and the immersion time. The diazotization rate of C.I. Reactive Blue 2 was faster and the magnitude of the color change was greater than those for Blue 19 (Fig. 3(b)). The diazotization rate and magnitude of the color change for C.I. Reactive Black 5 were smaller than those for the two blue dyes (Fig. 3(a)). (At pH 3.37, Black 5 was partially diazotized (about 10%) within 1 h (cf. Fig. 3(b)), but the reaction did not proceed further (cf. Fig. 3(a)).) As explained below, it is notable that the absorption spectra of the diazonium salts were not the spectra of the final products generated by nitrogen oxides, as assessed by the ISO and JIS methods [14–16]. But the rates of change caused by diazotization for $(A_0 - A)/A_0$ at $\lambda_{\max}$ were closely related to the rating of color fastness to nitrogen oxides, as shown in Table 1.

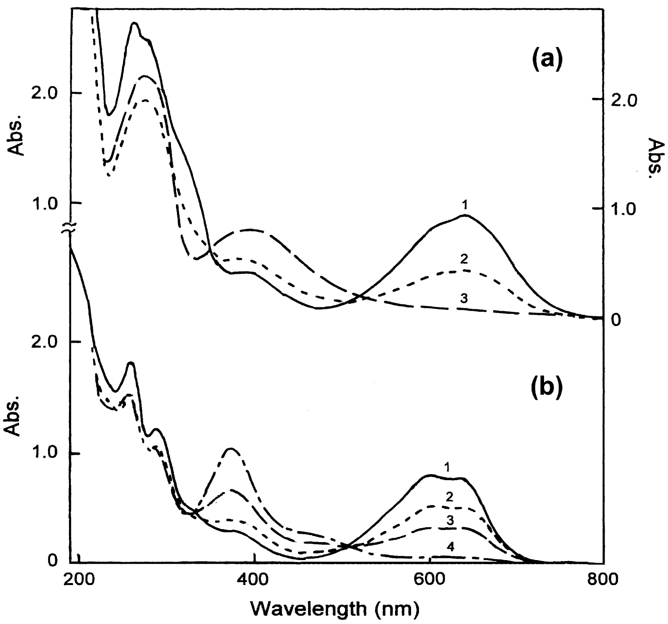


Fig. 2. Absorption spectra of (a) C.I. Reactive Blue 2 and (b) C.I. Reactive Blue 19 on cellophane immersed in an acidic aqueous nitrite solution ($NaNO_2$ 9.70×10^{-4} mol dm^{-3}) at pH 3.37 in the dark: (1) original (before immersion), (2) immersion for 30 min, (3) for 1 h and (4) for 24 h.

3.2.2. Diazotization of C.I. Reactive Blue 2 and Blue 19

In order to further confirm these phenomena, stronger diazotization conditions than those applied above and the coupling reaction of the diazotized dyes with Naphthol AS were used. The results are shown in Fig. 4(a) and (b). The diazotization of the two anthraquinone dyes occurred with a decrease of the main absorption band and an increase of the absorption band at the λ_{max} value of 370–400 nm (Spectra 2 in Fig. 4(a) and (b)); this means a color variation from blue to yellow. The coupling reaction of the diazotized compounds occurred with a decrease of the main absorption band for diazonium compounds and an increase of the absorption band at a λ_{max} value of 510–520 nm; this means a color variation from yellow to pale red. The spectral variation shows that diazotization and the coupling reaction with Naphthol AS occurred (No nitrosation reaction of imino groups was confirmed to occur for Blue 2 and Blue 19, since no dye chromophore was stripped by immersing the dyed cellophane in the acidic aqueous nitrite solution.).

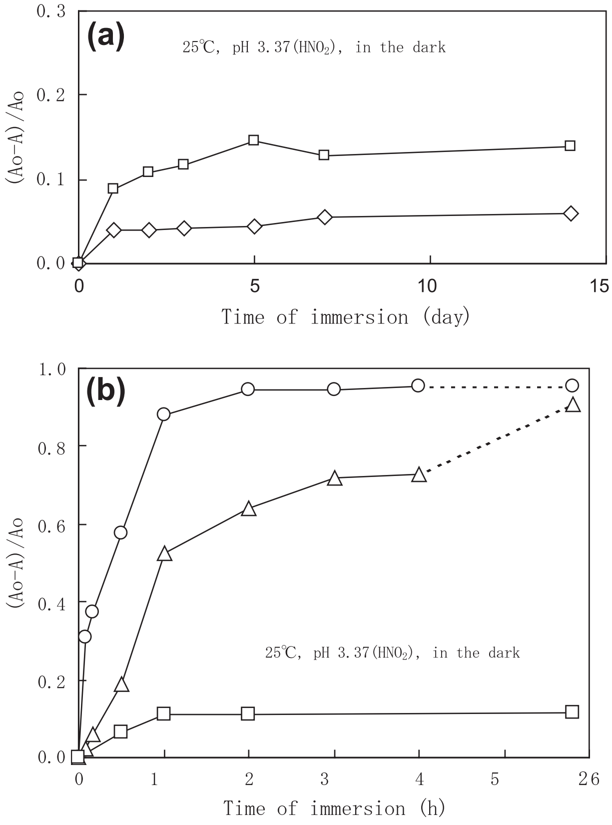


Fig. 3. Relationship between $(A_0 - A)/A_0$ at λ_{max} for reactive dyes on cellophane and the immersion time in an acidic aqueous nitrite solution (9.70×10^{-4} mol dm^{-3}) at pH 3.37 and 25 °C in the dark: (a) C.I. Reactive Red 194 (◇) and Black 5 (□), and (b) C.I. Reactive Blue 2 (○), Blue 19 (△) and Black 5 (□).

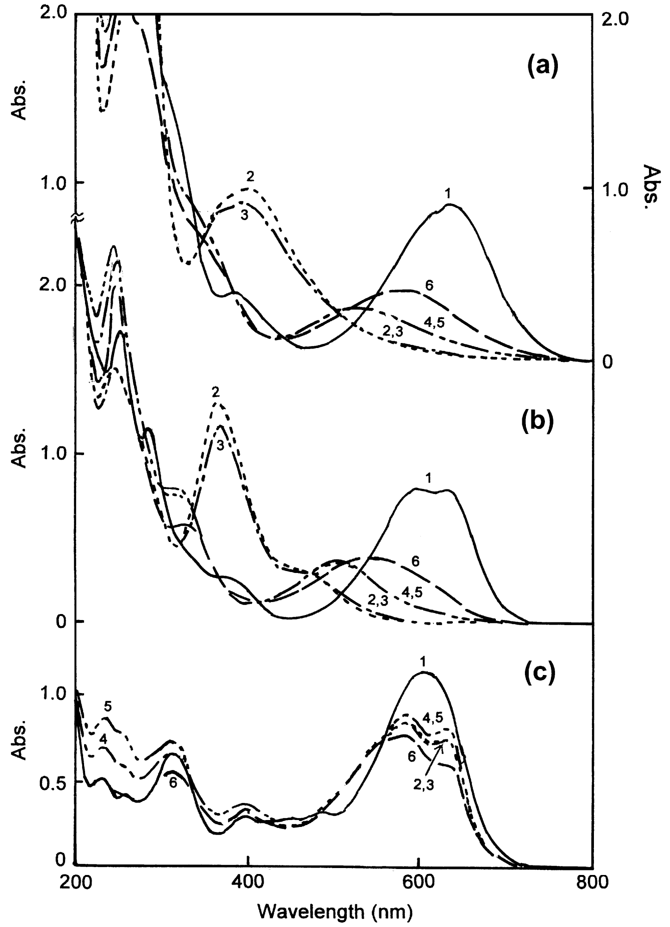


Fig. 4. Absorption spectra of (a) C.I. Reactive Blue 2, (b) C.I. Reactive Blue 19, and (c) C.I. Reactive Black 5 on cellophane: (1) original, (2) after diazotization ($NaNO_2$ 7.91×10^{-4} mol dm^{-3} in 0.24 M HCl (pH 1.19) for 30 min), (3) after diazotization (30 min) and boiling (30 min), (4) after diazotization (30 min) and coupling with Naphthol AS (1.0 g dm^{-3} in 0.1 M NaOH), (5) after diazotization (30 min), boiling (30 min) and then coupling with Naphthol AS, and (6) after diazotization (30 min) and exposure to a carbon arc (30 min).

In order to clarify these situations, the effect of the pH on the rates of color change caused by the diazotization of C.I. Reactive Blue 2 on cellophane film was examined, as shown in Fig. 5. At pH > 5, little or no diazotization of Blue 2 occurred. At pH 4, on the other hand, the effects of the HNO_2 concentration on the diazotization rate of C.I. Reactive Blue 2 and Blue 19 on cellophane film were also examined, as shown in Fig. 6. The diazotization rates of the two dyes on cellophane increased with increasing HNO_2 concentration, as expected. But at HNO_2 concentrations of less than 0.1 mM, little or no diazotization of C.I. Reactive Blue 2 and Blue 19 occurred. If the environmental conditions are below the HNO_2 concentration limit and above the pH limit, the reactive dyes with free amino groups may suffer no color variation as a result of diazotization.

3.2.3. Diazotization of C.I. Reactive Black 5, pyrazolinylazo dye and azo dyes from γ-acid

Reactive azo dyes possess higher color fastness to gas fading (cf. Table 1) than reactive AAQ dyes. Azo dyes, such as C.I. Reactive Black 5 and Pyr-Yellow, seemed to undergo no diazotization on cellulose substrates immersed in an aqueous nitrite solution (1.0×10^{-3} mol dm^{-3}) at pH 3.4, while AAQ dyes showed a marked spectral variation caused by diazotization. We examined whether or not the azo dyes with primary amino groups undergo diazotization under the same strong conditions described in the previous section. The absorption spectra before and after the treatments are shown in Fig. 4(c) for C.I. Reactive Black 5 and Fig. 7(a) for Pyr-Yellow. Although the spectral variations are less marked than those for the AAQ dyes, the formation of diazonium compounds and the coupling reaction with Naphthol AS can be inferred from the spectral variations; new azo compounds with different absorption spectra from those of the original dyes were formed. In order to confirm the diazotization of C.I. Reactive Black 5 and the coupling with Naphthol AS, Red H with half the structure of Black 5, in which a *p*-VS-phenylazo group was introduced at the *o*-position of the amino group, on cellulose film was subjected to the same reaction conditions. The absorption spectra for Red H are given in Fig. 7(b). There are large variations in the spectra, implying the occurrence of diazotization and coupling. The 8-amino groups in the H-acid undergo diazotization and subsequently coupling, depending upon the reaction conditions.

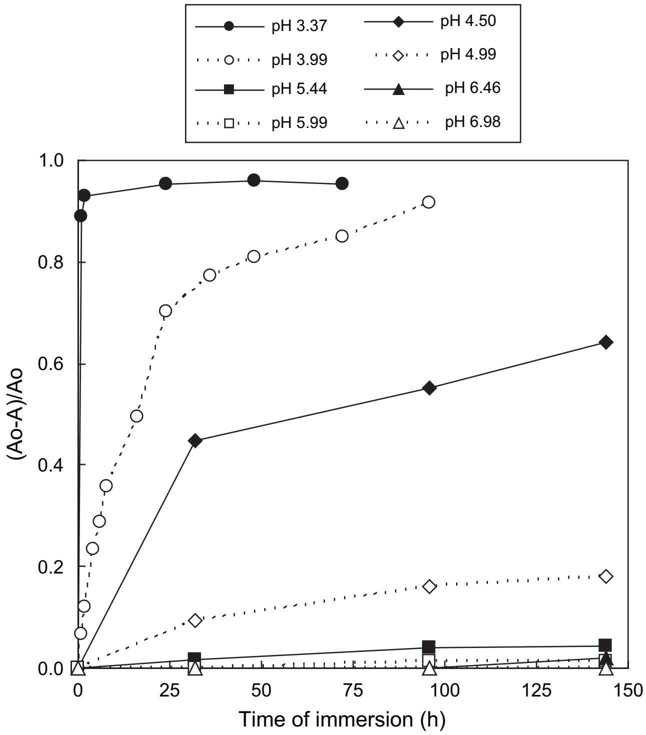


Fig. 5. Effect of the pH on the rates ($(A_0 - A)/A_0$ at λ_{max}) of diazotization for C.I. Reactive Blue 2 on cellophane immersed in an aqueous nitrite solution ($NaNO_2$ 9.70×10^{-4} mol dm^{-3}) of various pHs at 25 °C in the dark. (The pHs were adjusted using Clark–Lubs buffer.)

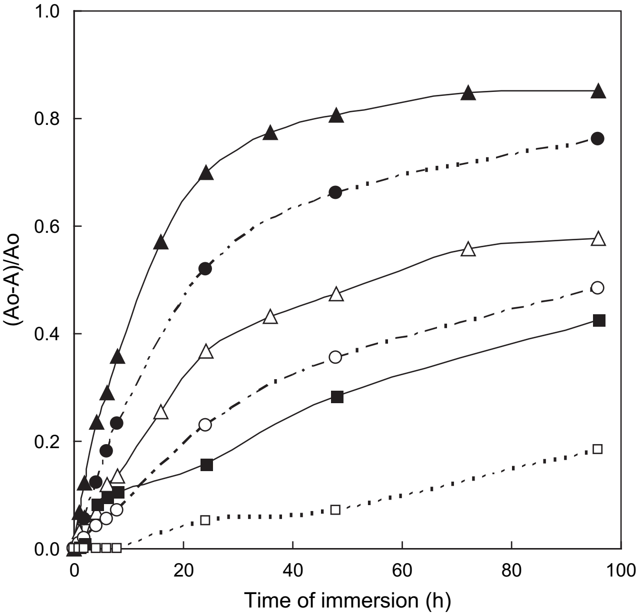


Fig. 6. Effects of the concentration of sodium nitrite on the rates ($(A_0 - A)/A_0$ at λ_{max}) of diazotization for C.I. Reactive Blue 2 (closed symbols) and Blue 19 (open symbols) on cellophane immersed in a sodium nitrite solution ($NaNO_2$: ▲,△: 9.70×10^{-4} mol dm^{-3}; ●,○: 4.85×10^{-4} mol dm^{-3}; ■,□: 9.70×10^{-5} mol dm^{-3}) at 25 °C and pH 3.99 in the dark. (The pH of the solution was adjusted using potassium hydrogen phthalate–HCl buffer.).

In order to confirm whether or not the amino group of γ-acid undergoes the same reactions, Red gVS on cellulose film was also subjected to the same reaction conditions. The absorption spectra (Fig. 7(c)) show the occurrence of the reactions. The free amino groups in the reactive dyes bound with cellulose underwent diazotization depending upon the conditions, although the rates and extent of the color change varied with the chemical structure and the reaction conditions of diazotization.

3.2.4. Immersion of C.I. Reactive Red 194 on cellophane in an acidic aqueous nitrite solution

No diazotization of C.I. Reactive Red 194 without an amino group but with imino groups was observed even under such strong conditions. Thus, this dye on cellulose showed only a slow dye–fiber bond scission in the acidic aqueous nitrite solution, as shown in Fig. 1(a), and in nitrous acid at pH 3

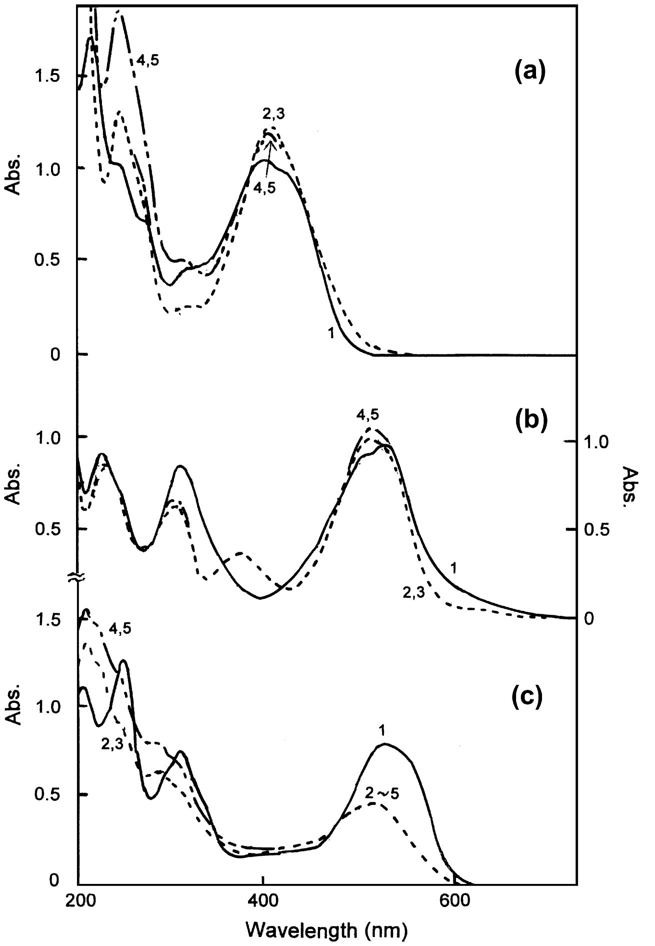


Fig. 7. Absorption spectra of (a) Pyr-Yellow, (b) Red H and (c) Red gVS on cellophane: (1) original, (2) after diazotization ($NaNO_2$ 7.91×10^{-4} mol dm^{-3} in 0.24 M HCl (pH 1.19) for 30 min), (3) after diazotization (30 min) and boiling (30 min), (4) after diazotization (30 min) and coupling with Naphthol AS (1.0 g dm^{-3} in 0.1 M NaOH), and (5) after diazotization (30 min), boiling (30 min) and then coupling with Naphthol AS.

in the dark, as shown in Fig. 3(a). The fact that the imino groups in reactive dyes on cellulose have no potential to undergo diazotization and nitrosation reactions was confirmed by the fact that no spectral change and no coupling reaction after diazotization occurred at pH 1. (No reaction of the imino groups is also confirmed in the diazotization reaction of Blue 2 and Blue 19 (cf. Section 3.2.2).)

3.3. Stability of diazonium compounds generated on cellulose

In these reactions, the diazonium compounds on cellulose were found to be highly stable. After the AAQ dyes were diazotized, the dyed films were boiled for 30 min. But almost no spectral variation was observed, as shown in Fig. 4 (Spectra 2 → 3) for C.I. Reactive Blue 2, Blue 19 and Black 5. The stability against the boiling treatment was confirmed by the fact that the same coupling to Naphthol AS (Spectra 4 → 5 in Fig. 4) occurred. The diazonium salt of C.I. Reactive Blue 2 and C.I. Reactive Blue 19 on cellulose may become very stable due to the salt formation between the adjacent sulfonic acid and the diazonium cation in the dye molecules. Even after the diazotized dyes on cellulose and in solution were boiled, they engaged in coupling reactions with some coupling components.

Even in the case of azo reactive dyes without adjacent sulfonic acids, the diazonium salt of C.I. Reactive Black 5 on cellulose was very stable. After the diazotized dyes on cellulose are boiled, coupling with various coupling components can occur. This fact was confirmed by the coupling of the diazotized dyes with Naphthol AS (Spectra 3 → 4 or 5), as shown in Figs. 4 and 7. The drying of cellulose films containing diazonium salts had no effect on the stability. The essential processes of a series of these reactions accompanied by irreversible color variations in reactive dyes on cellulose are summarized in Scheme 1.

3.3.1. Stability of diazonium compounds generated in an aqueous solution

In order to elucidate the reason for the high stability of diazonium salts of the active commercial versions of three dyes, C.I. Reactive Blue 2, Blue 19, and Black 5, on cellulose films, and to determine whether or not the diazonium salts are highly stable only on cellulose, we performed diazotization, boiling and coupling to Naphthol AS in an aqueous solution, in that order.

The high stability of the diazonium salts of the two AAQ dyes was confirmed by the spectral change due to the diazotization and coupling reactions after the boiling of the diazonium compounds. The chemical structures of the diazonium salts of C.I. Reactive Blue 2 and Blue 19 did not have a very good stabilization mechanism, so they decomposed during boiling in the aqueous solution. They suffered the same color change in the solution as on cellulose during the successive reactions, in spite of the boiling midway.

In case of C.I. Reactive Black 5, the diazonium compound suffered dediazotization by boiling to generate a product with the absorption spectrum (Fig. 4(c)) similar to but partially different from that of photodecomposition product of diazonium salt, which was confirmed by the facts that no coupling with Naphthol AS occurred after the boiling. But without boiling the coupling reaction was confirmed to occur.

Thus, it is inferred that there may be two kinds of stabilizing mechanism for the diazonium compounds of the examined reactive dyes on cellulose. For C.I. Reactive Blue 2 and Blue 19, the mechanism is effective on cellulose and in aqueous solutions, while for C.I. Reactive Black 5, the mechanism is effective only on cellulose. The first mechanism is inferred to be the salt formation between the diazonium cation and the adjacent sulfonic acid anion in the molecule. It holds only for the two AAQ dyes, and not for C.I. Reactive Black 5. A similar mechanism on cellulose may be the salt formation between the diazonium cation and the carboxyl anion in the molecule.

However, the high stability of the diazonium compounds of reactive dyes on cellulose is useless, because the transformation to the diazonium compounds is irreversible and these compounds cannot return to the original dye. Diazotization under light causes rapid photodecomposition without the formation of diazonium compounds.

1. Diazotization of aromatic amines on cellulose: e.g., C.I. Reactive Blue 2

$$R-NH_2 + HNO_2 + HNO_3 \rightarrow R-N\equiv N^+ NO_3^-$$

2. Reaction and properties of diazonium salts on cellulose
  a) High stability on cellulose at high temperatures (in the dark)
  b) Coupling reaction to the azoic coupling component (spectral changes caused by the formation of azo compounds):

$$\rightarrow R-N=N-R'$$

  c) Photodecomposition caused by light through dediazotization accompanied by small to drastic spectral variations (the formation of aromatic phenols as the main products):

$$\xrightarrow{\text{light}} R-OH \text{ (main products)} + N_2$$

3. Irreversible color variations caused by nitrogen oxides in reactive dyes with amino groups
  a) This phenomenon is attributed to the irreversible color change caused by the transformation of the amino groups into hydroxyl groups through photo-dediazotization after diazotization by an aqueous nitrous acid.
  b) The larger and the easier the color change, the lower the color fastness to nitrogen oxides.
  c) Azo dyes, whose free amino groups undergo such photo-dediazotization but exhibit only a small or slight color change (e.g., C.I. Reactive Black 5), are estimated to have high color fastness to nitrogen oxides.
  d) Imino groups in the dye molecules (such as dyes derived from N-triazinyl-H-acids, e.g., C.I. Reactive Red 194) cause neither diazotization nor nitrosation.

Scheme 1. Essential processes of irreversible color variation caused by nitrogen oxides in reactive dyes on cellulose.

3.4. Low stability of diazonium compounds on cellulose against light

The effect of light on the diazonium compounds of dyes on cellulose film was examined by exposing them to a carbon arc. The absorption spectra of the exposed samples are Spectra 6 shown in Fig. 4; as can be seen, there was a marked spectral change (Spectra 2, 3 → 6).

In the case of azo dyes that undergo no diazotization, besides the dye–fiber bond scission caused by acid hydrolysis, the photofading of the dyes on cellulose immersed in an acidic aqueous solution occurred (cf. Fig. 1(c)).

3.4.1. Photodecomposition products of the AAQ dyes and Black 5

Drastic spectral changes were observed in the diazonium salts on cellophane films of C.I. Reactive Blue 2 and Blue 19, as shown in Fig. 4 (Spectra 6). In the case of C.I. Reactive Black 5, the spectral changes caused by diazotization were also marked, but no apparent change in hue was noticed, since the diazotization occurred partially at $pH \geq 3$ (cf. Fig. 4(c), Spectra 6). The absorption spectra for the diazonium salts (Spectra 2 and 3) changed into Spectra 6. Exposure of the diazonium salts of C.I. Reactive Blue 2 (Fig. 4(a)) and Blue 19 (Fig. 4(b)) on cellulose film to light led to their decomposition and the generation of new violet-colored products. C.I. Reactive Black 5 (Fig. 4(c)) showed a small but definite change in the absorption spectrum as a result of the exposure. Three dyes were confirmed to undergo no coupling with Naphthol AS, implying the decomposition of the diazonium salts.

The thermal or photo-elimination of N_2 from azo compounds, which occurs during the decomposition of the reaction intermediates, has been clarified as dediazotization [24–29]. This process is utilized in imaging technology [26–28] and as an initiator of radical reactions [30]. It has also been investigated theoretically using the MO method [31]. Depending on the experimental conditions, diazo compounds undergo several reactions such as the hydro-replacement of a diazo group by hydrogen, the hydroxy-formation of phenol, and halogeno- and cyano-dediazotization [26,29].

The photodecomposition products of the diazonium salts of C.I. Reactive Blue 2 and Blue 19 resembled the products of coupling with Naphthol AS in the absorption spectra. But the former spectra showed a red shift of the visible main absorption band and weaker absorption in the UV region below 300 nm, as compared with the latter spectra. Salvin et al. have identified the end product of AAQ dyes as hydroxyanthraquinone [7,23]. By immersing the diazonium salts on cellulose film in a dilute sodium hydroxide solution, 1-hydroxyanthraquinone derivatives may be formed through hydroxyl-dediazotization. The photodecomposition products of the two anthraquinone dyes examined were identified as 1-hyrdroxy derivatives by comparing the absorption spectra (Spectra 6 in Fig. 4(a) and (b)).

The generation of 1-hydroxyanthraquinone derivatives via the diazotization of 1-AAQ dyes was pursued based on the absorption spectra of the diazonium salts. No diazonium salt, however, was indicated by the spectra, implying very high rates of photodegradation of the diazonium salts via dediazotization [24–29].

A series of these reactions for reactive dyes on cellulose, including the color variations caused by dediazotization, are summarized in Scheme 1. These color variations are completely irreversible and the rates and extent of the color change were determined by the chemical structure of the dyes, although they also depended upon the environmental conditions.

Azo dyes with free amino groups may undergo diazotization followed by dediazotization, resulting in the substitution of hydroxy groups for amino ones. When azo dyes with such amino groups exhibit small color changes resulting in high color fastness to nitrogen oxides, the performance properties of the modified dyes may become inferior to those of the original ones. Typical of this scenario were azo dyes derived from H-acids, which are frequently utilized in reactive diazo dyes with a navy or black color. Fortunately, azo dyes derived from *N*-acyl-H-acids or containing imino groups, many of which are utilized in red dyes, did not suffer such diazotization.

4. Summary

The effects of nitric and nitrous acids, generated by dissolving nitrogen dioxide in water, on the color variations of the AAQ reactive dyes C.I. Reactive Blue 2 and Blue 19, whose ratings of color fastness to nitrogen oxides are 1 and 3, respectively, and of azo dyes with high color fastness were examined using cellulose film. The effects of acidic nitrite solutions on the color variations of C.I. Reactive Blue 2 and Blue 19 on cellulose were examined under wet conditions. The color variation caused by diazotization was confirmed by the coupling reaction of the diazotized dyes on cellulose with Naphthol AS in an aqueous alkaline solution. Even after boiling the diazotized compounds on cellulose and in solution, the same coupling to Naphthol AS was observed, and the diazotized compounds on cellulose were highly stable in the dark. Bond scission between C.I. Reactive Blue 2 and cellulose was observed at pH 3, but not for C.I. Reactive Blue 19 and the other azo VS dyes. Acidic nitrite solutions caused the diazotization of the amino groups of the AAQ and azo reactive dyes.

The diazonium salts of C.I. Reactive Blue 2, Blue 19 and Black 5 on cellulose were very stable due to the salt formation between the adjacent sulfonic acid in the dye molecules. Even after boiling the diazotized dyes on cellulose, the dyes underwent coupling with some coupling components.

The diazonium salts of C.I. Reactive Black 5 and Red H (half the structure of Black 5), which are dyes that have no sulfonic acid group adjacent to the amino groups, on cellulose were also very stable. After boiling the diazotized dyes on cellulose, coupling with some coupling components occurred.

The irreversible color change caused by nitrogen oxide can be attributed to the reaction scheme summarized in Scheme 1: the diazotization of the free amino groups in the dye molecule is followed by the photo-hydroxy-dediazotization of the diazonium salts. The color fastness to nitrogen oxide depends upon the color change or the color difference due to the transformation of the amino groups into hydroxy ones in the dye through photo-dediazotization, although the rates of diazotization vary with the dye. In addition to the irreversible color variation caused by the diazotization, dye loss caused by dye–fiber bond scission through acid hydrolysis and/or photofading in acidic solutions occurs depending upon the environmental conditions.

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