Dyes and Pigments **22** (1993) 99–116

Formaldehyde-Induced Discoloration: Design of Formaldehyde-Fast Bisazo Dyes

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(Received 18 December 1992; accepted 20 January 1993)

ABSTRACT

Formaldehyde-induced discoloration of 1-amino-2,7-bisphenylazo-8-naphthol derivatives has been investigated. The results of this study indicate that electrophilic attack at the amino group by a $^{+}CH_2OH$ *ion initiates the discoloration, and that the resulting compound is heat- and light-sensitive, drastically causing further discoloration. Bulky and/or electron-withdrawing substituents can retard it; a 3-*SO_3Na *group, and a 2'-*$SO_2C_2H_4OSO_3Na$ *and a 2'-*SO_3Na *group on the 2-phenylazo group are useful in protecting the amino group. The blue dyes tested, including other chromogens, are resistant to formaldehyde. The visible absorption spectra of these dyes are also reported.*

1 INTRODUCTION

A variety of aftertreatments such as dye-fixing and resin-finishing have been devised over the last 100 years to improve wet- and washing-fastness of direct dyes on cellulosic fibres, and to impart dimensional stability, longer serviceability and easycare properties to these fibres.[1,2] Since the discovery of reactive dyes in 1954, such aftertreatments have been applied to these dyes. Whereas certain aftertreatments increase light-fastness of a few dyes, most aftertreatments decrease that of many dyes, particularly of blue dyes.[3–6]

Formaldehyde is always the focal point in discussing aftertreating agents. Great efforts have been made to lower the formaldehyde-evolution potential of the agents and to develop efficient formaldehyde-free agents.[2] However,

Dyes and Pigments 0143-7208/93/$06·00

formaldehyde-based agents are still very widely used, since they have several advantages, such as a low price, adequate reactivity and easy applicability. Because of consumer complaints about the discoloration of aftertreated dyed articles, deleterious effects on light-fastness and hue must be carefully considered in the selection of dyes.[7]

The present paper describes the adverse effects of aftertreatments on light-fastness and hue and the countermeasures against the disadvantages, from molecular-structural viewpoints. Since formaldehyde is an undesirable component of dye-fixing and resin-finishing agents, the discussion is limited to formaldehyde-involved reaction of dyes and formaldehyde-induced discoloration of resin-finished dyeings.

2 RESULTS AND DISCUSSION

2.1 Discoloration of resin-finished dyeings

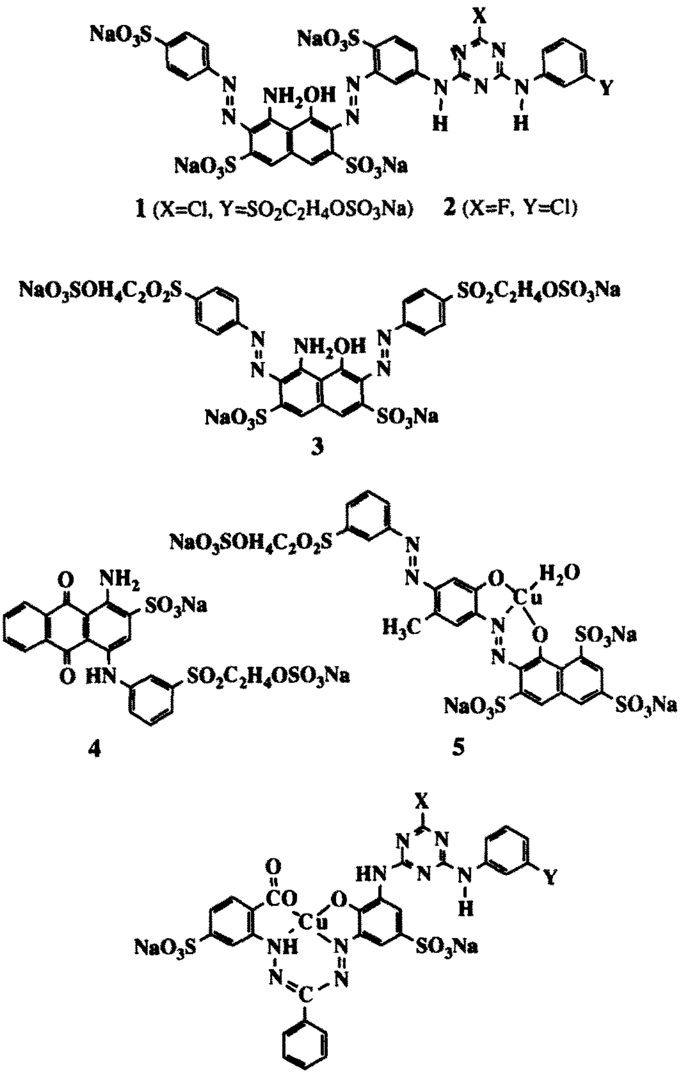
Figure 1 shows the reactive dyes (**1**–**7**) used, these having typical chromogens in the blue shade area. To evaluate the influence of formaldehyde contents in resin-finished dyeings from these dyes, two resin-finishing agents were used, i.e. dimethylol dihydroxyethyleneurea, as a low-formaldehyde reactant, and methylated methyloluron as a high-formaldehyde reactant.

Table 1 indicates that the discoloration of the dyeings depends not only on the substrates such as dyes and resin-finishing agents, but also on physicochemical factors such as heat and light; the higher the formaldehyde content, the larger is the colour change on resin-finishing and the lower is the heat-set- and light-fastness of resin-finishing dyeings. Thus, the discoloration is primarily based on three main processes:

(a) release of formaldehyde from resin-finished dyeings;
(b) reaction of dyes with formaldehyde; and
(c) thermo- or photochemical reaction of the resulting compounds

Of these, process (b) triggers the discoloration, because the dyes are fast to heat and light in the absence of formaldehyde.

Dyes **1**–**3** are more sensitive to heat and light in the presence of formaldehyde than dyes **5**–**7**; the former dyes drastically changed in color from navy blue to greenish blue in (b), and then to red in (c). This suggests that the amino group in dyes **1**–**3** participates in the discoloration. In contrast, the high stability of dye **4** is not surprising, since it is well documented that 1-aminoanthraquinone is approximately 10^5 times less basic than 1-aminonaphthalene.[8,9] Thus, the amino group in dye **4** is much more inactive than that in dyes **1**–**3**. Comparison of dye **1** with dye **2**, and **6**



1 (X=Cl, Y=$SO_2C_2H_4OSO_3Na$) **2** (X=F, Y=Cl)

3

4

5

6 (X=F, Y=SO_3Na) **7** (X=Cl, Y=$SO_2C_2H_4OSO_3Na$)

Fig. 1. Reactive dyes for cellulose having the major types of chromogens in shade from blue through navy blue to black: bisazos **1**–**3**, anthraquinone **4** and copper complexes of bisazo **5** and of formazans **6** and **7**.

with **7** shows that the discoloration is independent of their fibre-reactive groups.

Therefore, specific structural features are required in dyes **1**–**3** to render their chromogens resistant to formaldehyde. Since twice-coupled H-acid dyes such as these are the most important class of dyes in blue shade areas, the development of formaldehyde-fast dyes of this class is of great value.

TABLE 1

Discoloration of Dyes 1–7 on Cotton Caused by Resin-Finishing, Heat-Set or Light, and by Their Combination

Dye no.	*Resin-finishing agent*[a]	*Colour change by resin-finishing*[b]	*Fastness of (un)finished dyeings to:*		
			Heat-set[b]		*Light*[c]
			110°C, 10 min	*130°C, 20 min*	
1	A	4	3–4	2–3	5
	B	3	2–3	1	3–4
	C	—	(4–5)	(4–5)	(5)
2	A	4	3–4	2–3	5
	B	3	2–3	1	3–4
	C	—	(4–5)	(4–5)	(5)
3	A	4–5	4–5	4	5
	B	4	3–4	2–3	3–4
	C	—	(4–5)	(4–5)	(5)
4	A	4–5	5	4–5	≥5
	B	4	4–5	3–4	≥5
	C	—	(5)	(5)	(≥5)
5	A	4–5	4–5	4	≥5
	B	4	4	3–4	≥5
	C	—	(5)	(5)	(≥5)
6	A	4–5	4–5	4–5	≥5
	B	4	4–5	4	≥5
	C	—	(5)	(5)	(≥5)
7	A	4–5	4–5	4–5	≥5
	B	4	4–5	4	≥5
	C	—	(5)	(5)	(≥5)

[a] A. dimethylol dihydroxyethyleneurea; B, methylated methyloluron; C, not used.
[b] The degree is indicated by figure from 5 (no change) to 1 (much changed).
[c] By figure from 8 (no change) to 1 (much changed).

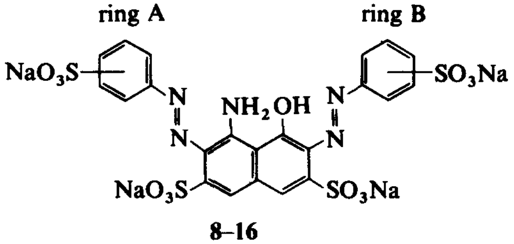
2.2 Reaction of model dyes with formaldehyde

Table 2 summarizes model dyes **8–18** tested and their visible absorption spectral data. These dyes comprise twice-coupled H-, K- and S-acids, and differ from each other in the number and position of SO_3Na groups.

Twice-coupled H-acid dyes **8–16** are characterized by a triple maximum at 589–603, 486–494 and 389–395 nm. In the first absorption band, which has the highest intensity, the SO_3Na group on ring A decreases the λ_{max} in the

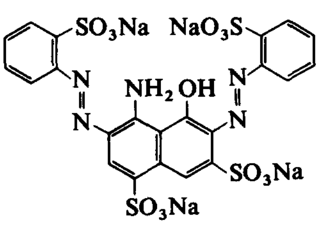
TABLE 2

Model Dyes Derived from H- (**8**–**16**), K- (**17**) and S-acids (**18**) and their Visible Absorption Spectral Data, λ_{max} in nm ($\varepsilon_{max} \times 10^{-4}$) in Water



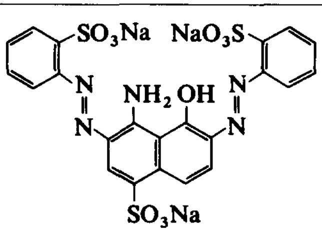
8–16

				Orientation of SO_3Na		
Ring A				*Ring B*		
		o		*m*		*p*
o	**8**	601 (4·36) 494 (1·21) 394 (1·29)	**9**	600 (4·58) 492 (1·27) 394 (1·28)	**10**	603 (4·65) 492 (1·30) 395 (1·32)
m	**11**	592 (4·52) 489 (1·24) 390 (1·32)	**12**	589 (4·68) 488 (1·27) 389 (1·27)	**13**	594 (4·84) 486 (1·32) 390 (1·32)
p	**14**	596 (4·76) 492 (1·25) 392 (1·40)	**15**	595 (4·86) 488 (1·27) 391 (1·29)	**16**	599 (5·08) 488 (1·34) 393 (1·44)



17

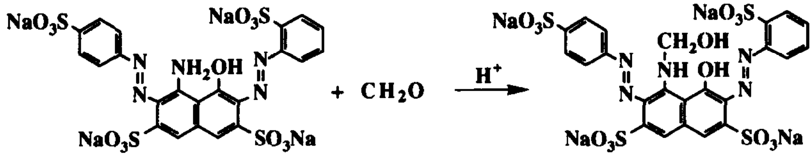
573 (4·24)
480 (1·29)
387 (1·18)



18

572 (4·21)
435 (1·10)
385 (1·15)

sequence $o > p > m$, in contrast to that on ring B, which has the sequence $p > o > m$. The different sequences are due to the presence of two azo-hydrazone equilibria in these dyes. The azo group linked to ring A exists predominantly in an azo form, whereas that linked to ring B is in a hydrazone form.[8] In fact, the SO_3Na group on ring B gives the same effect as that on the phenyl ring of phenylazo H-acid dyes coupled *ortho* to the hydroxy group.[10] The ε_{max} values decrease in the sequence $p > m > o$ for both SO_3Na groups. The SO_3Na groups on the naphthalene ring have almost no



14 **19**

Fig. 2. N-methylolation of dye **14**. An active species, $^{+}CH_2OH$, reacts selectively with the amino group.

influence on ε_{max} (dyes **8**, **17** and **18**); however, for λ_{max}, the 3-SO_3Na group on the amino-containing ring (dye **8**) results in a greater bathochromic shift than the 4-SO_3Na group (dyes **17** and **18**).

Formaldehyde reacts with dye **14** in aqueous acidic solutions to give compound **19** (Fig. 2), the structure of which was confirmed by ^1H= and ^{13}C= NMR spectra, and elemental analysis. Thus, formaldehyde undergoes N-methylolation, although it is believed that formaldehyde links together pairs of amino-substituted dye molecules by a methylene bridge.[1] In other words, this dye scavenges formaldehyde in the same manner as formaldehyde acceptors such as cyclic ureas, cyclic carboxylic acid amides and cyclic carbamates.[11-13] Unfortunately, the N-methylolation in dye **14** causes an

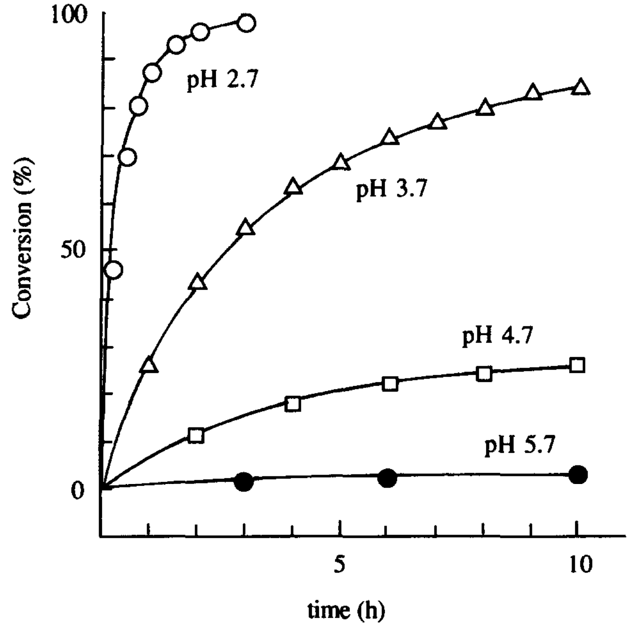


Fig. 3. pH-dependence on reaction of dye **14** with CH_2O in water. (40°C, dye concentration = 0·10M, CH_2O/dye **14** = 3·0 in molar ratio.)

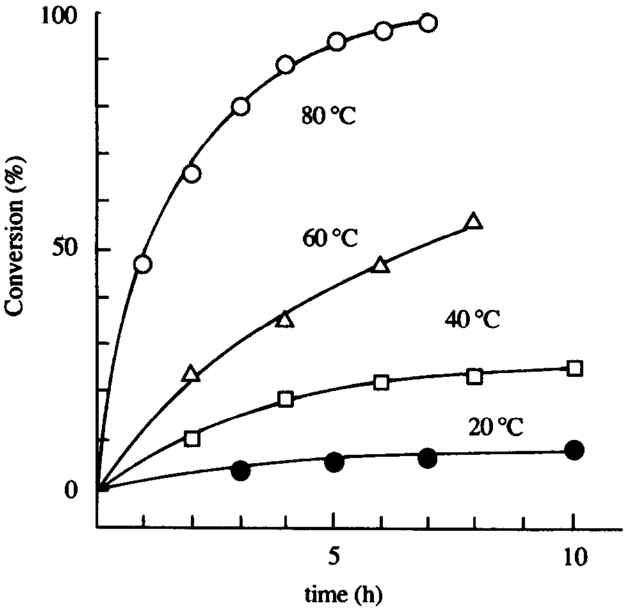


Fig. 4. Temperature-dependence on reaction of dye **14** with CH_2O in water. (pH 4·7, dye concentration = 0·10M, CH_2O/dye **14** = 3·0 in molar ratio.)

extreme color change (λ_{max} 596→653 nm), since the amino group (as an auxochrome) of this dye plays a vital role in giving a navy blue shade.

Figures 3 and 4 indicate that the pH and temperature of the reaction media affect a conversion of dye **14**; an increase in the conversion with lowering in pH is relatable to an increase in the active species, $^+CH_2OH$, with increase in the hydrogen ion concentration,[14] viz:

$$CH_2O + H_2O \rightleftharpoons CH_2(OH)_2$$
$$CH_2(OH)_2 + H^+ \rightleftharpoons {}^+CH_2OH + H_2O$$

Dye **14** is stable below 80°C, if formaldehyde is not present. Compound **19** is also stable to prolonged heating at 40°C, irrespective of the presence or absence of formaldehyde, but is unstable above 60°C, giving degradation products. Therefore, dye **14** can be converted by formaldehyde quantitatively into **19** at 40°C and pH 2·7–4·7.

On the basis of these results, the N-methylolation of the other model dyes was examined at 40°C and pH 4·7. Table 3 indicates that SO_3Na groups affect the conversion; in particular, the 3-SO_3Na group on the amino-containing ring (dyes **8–16**) markedly retards it, compared with the 4-SO_3Na group (dyes **17** and **18**). The *o*-SO_3Na group on ring A (dyes **8–10**) also retards it, compared with the *m*- and *p*-SO_3Na groups (dyes **11–13** and

TABLE 3
Reactivities of Dyes **8–18** with CH_2O and λ_{max} of N-methylolated Products

Dye no.	*Conversion (%)*[a]	λ_{max} *(nm)*
8	5	621
9	7	614
10	4	614
11	23	650
12	24	630
13	17	638
14	26	653
15	25	631
16	17	633
17	72	529
18	63	518

[a] After 10 h at 40°C, pH 4·7, dye concentration = 0·10 M and CH_2O/dye = 3·0 in molar ratio.

14–16, respectively). However, the *o*-SO_3Na group on ring B (dyes **11** and **14**) has no retarding ability.

The N-methylolation in dyes **8–16** causes a bathochromic shift (Tables 2 and 3); this relates to the colour change of their dyeings by resin-finishing. In particular, the *m*- and *p*-SO_3Na groups on ring A of dyes **11–16** significantly shift λ_{max}. The higher bathochromicity and reactivity in these dyes results in a larger discoloration than in dyes **8–10**. On the other hand, the N-methylolation in dyes **17** and **18** gave anomalous shifts.

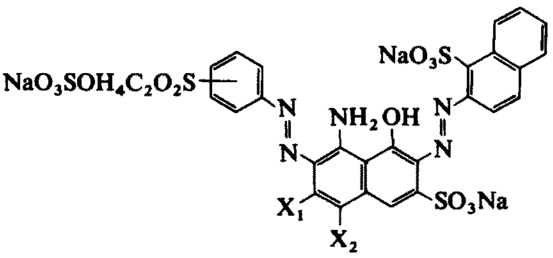
2.3 Reaction of reactive dyes with formaldehyde

Because of the retarding effect of the SO_3Na groups observed in the previous series when non-reactive dyes were used as model dyes, a further series of reactive dyes containing a $SO_2C_2H_4OSO_3Na$ group, one of the most widely used fibre-reactive groups, was examined under the same conditions. This group was stable to hydrolysis; the reaction of these dyes with formaldehyde can be followed using HPLC.

Table 4 shows that the *o*-$SO_2C_2H_4OSO_3Na$ group (dye **20**) is more effective in decreasing the conversion than the *o*-SO_3Na group (e.g. dye **8**). Such a tendency is also shown in the *m*- and *p*-positions, because of the strong electron-withdrawal of the substituent, analogous to a SO_2CH_3 group (σ_m 0·60, σ_p 0·72).[15] The combination of a steric and electronic effects explains the marked retarding ability of the *o*-$SO_2C_2H_4OSO_3Na$ group. The results for dyes **22** and **23** indicate, however, that the SO_3Na group in X_1

TABLE 4

Visible Absorption Spectral Data of Dyes **20**–**23** and their Reactivities with CH_2O



Dye no.	X_1	X_2	*Orientation of* $NaO_3SOH_4C_2O_2S$	λ_{max} *(nm)* ($\varepsilon_{max} \times 10^{-4}$)	*Conversion (%)*[a]
20	SO_3Na	H	*o*	625 (5·34)	1
21	SO_3Na	H	*m*	610 (5·23)	9
22	SO_3Na	H	*p*	619 (5·85)	8
23	H	SO_3Na	*p*	593 (4·56)	53

[a] After 10 h at 40°C, pH 4·7, dye concentration = 0·10 M and CH_2O/dye = 3·0 in molar ratio.

plays a much more important role in decreasing the conversion than the $SO_2C_2H_4OSO_3Na$ group in the *p*-position, and possibly in the *o*- and *m*-positions.

Table 5 summarizes the conversion of an additional series of reactive dyes employed under the same conditions. In this table, substituent R denotes a hetero-bifunctional reactive system comprising two different fibre-reactive groups, i.e. a *β*-sulphatoethylsulphone group and a monochlorotriazine group, as in Formula **I**.[16]

The conversion of dyes **1** and **24**–**27** is consistent with that of dyes **14**, **11**, **8**, **20** and **22**, respectively, having the same or similar chromogens (Tables 3 and

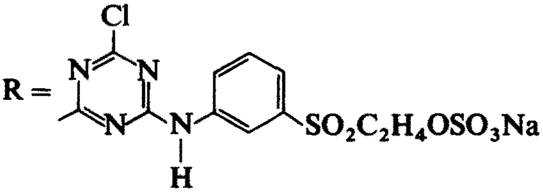


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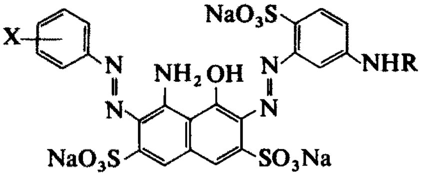
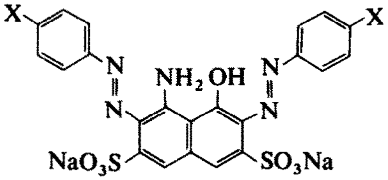
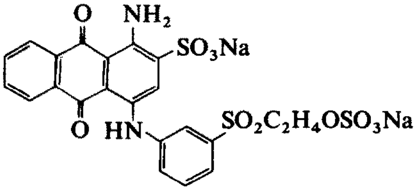
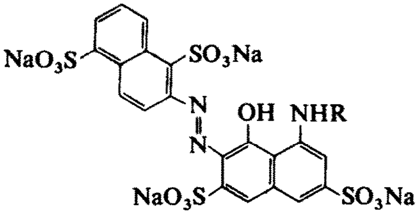
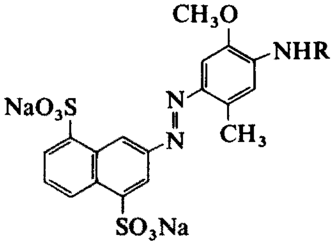
TABLE 5

Reactivities of Reactive Dyes with CH_2O

Structure[a]	*Dye no.*	*Conversion (%)*[b]
	**1** (X = *p*-SO_3Na)	27
	24 (X = *m*-SO_3Na)	25
	25 (X = *o*-SO_3Na)	4
	26 (X = *o*-$SO_2C_2H_4OSO_3Na$)	1
	27 (X = *p*-$SO_2C_2H_4OSO_3Na$)	12
	**3** (X = $SO_2C_2H_4OSO_3Na$)	11
	**4**	1
	**28**	<1
	**29**	<1

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[a] R, Hetero-bifunctional reactive system I.

[b] After 10 h at 40°C, pH 4·7, dye concentration = 0·10 M and CH_2O/dye = 3·0 in molar ratio.

TABLE 6
Formaldehyde-Fastness of Reactive Dyes on Cotton

Dye no.	*Formaldehyde-fastness*[a]
1	1
3	2
24	1
25	4
26	5
27	2

[a] The degree is indicated by figure from 5 (no change) to 1 (much changed).

4); it is little affected by the *m*-NHR (dyes **1** and **24–27**) and *p*-$SO_2C_2H_4OSO_3Na$ groups (dye **3**) on the phenylazo group adjacent to the hydroxy group. The conversion of dyes **1**, **3** and **4** in aqueous media bears a good relationship to the color change of these dyes on resin-finished cotton (Table 1).

The excellent formaldehyde resistance of dyes **28** and **29** indicates that the introduction of an electron-withdrawing group, such as a triazinyl group, into the amino group has a greater retarding effect than the steric and/or electronic protection of this amino group. Its applicability in designing formaldehyde-fast dyes is, however, limited to the yellow-red shade area, because of the resulting hypsochromicity.

The results of Table 6 are consistent with those of Table 5, in view of the retarding effects of the SO_3Na and $SO_2C_2H_4OSO_3Na$ groups. This means that these effects are apparent on cotton as well as in aqueous media.

2.4 Light stability of N-methylolated compound

To confirm the phenomenon that dyeings discolored by formaldehyde have markedly deteriorated light-fastness, the light stability of dye **14** and its N-methylolated compound **19** was examined. Since the experiment was carried out under sunlight irradiation, definite interpretations cannot be made on the absolute meanings of the numerical values shown in Tables 7 and 8; however, a comparison of the data is significant.

Table 7 indicates that N-methylolation leads to very light-sensitive compounds. It is surprising that such a slight structural change causes such a drastic decrease of light stability.

Table 8 indicates that the conversion of dye **19** is maximum at pH 4–6. This pH also accelerates the N-methylolation of twice-coupled H-acid dyes with lowering in pH. Although the pH of 4–6 gives rise to the lowest

TABLE 7

Conversion (%) of Dyes **14** and **19** by Sunlight[a]

Dye no.	*Irradiation time (h)*		
	2	*4*	*8*
14[b]	0	0	<1
19[b]	20	40	90
19[c]	0	<1	<1

[a] At 25–30°C, pH 4·2 and dye concentration = 3·7 × 10^{-5} M.
[b] Under sunlight irradiation.
[c] Under light-shading.

TABLE 8

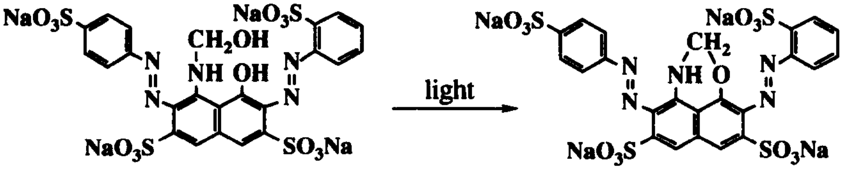
pH-Dependence on Conversion (%) of Dye **19** by Sunlight

Dye no.	*pH*[a]				
	1·5	*2·5*	*4·2*	*6·5*	*7·5*
19	17	28	40	37	30

[a] After 4 h at 25–30°C and dye concentration = 3·7 × 10^{-5} M.

formaldehyde-release from resin-finished cotton,[17] the released formaldehyde readily causes the N-methylolation of these dyes on cotton and the subsequent photoreaction at this pH. Therefore, pH plays an important role in all the discoloration processes, (a)–(c).

Dye **19** was converted on sunlight irradiation to a red compound having a λ_{max} of 525 nm; this is relatable to the color change of resin-finished dyeings caused by exposure to light. Figure 5 shows a presumed reaction scheme. The formation of a formal bond, as in compound **30**, has been reported for chromotropic acid (1,8-dihydroxy-3,6-naphthalenedisulphonic acid) in the earlier literature.[18]



19 **30**

Fig. 5. Presumed reaction scheme of dye **19** with light.

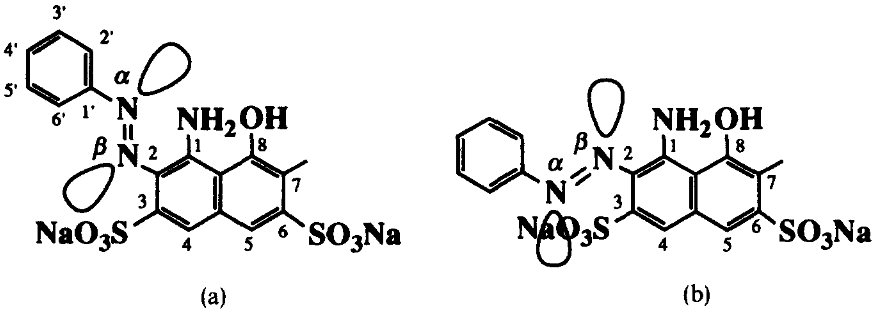


Fig. 6. Alternative conformations for the 2-phenylazo group in twice-coupled H-acid dyes (in which a 7-substituent is omitted). This group exists predominantly in conformation (a), because of minimizing the steric crowding between the 3-SO_3Na group and the lone pair orbital of the α-nitrogen atom.

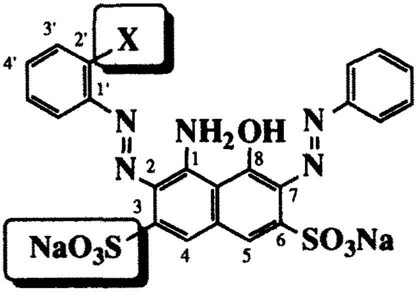
2.5 Design of formaldehyde-fast bisazo dyes

In the series of twice-coupled H-acid dyes, two planar conformations are possible for the 2-phenylazo group, as shown in Fig. 6. In conformation (b), there is steric hindrance between the 3-SO_3Na group and the lone pair orbital of the α-nitrogen atom. Such crowding can be relieved by rotation into conformation (a), in which the group would not exert much steric hindrance. Moreover, conformation (a) is stabilized by the strong intramolecular hydrogen-bonding between an NH_2 proton and the α-nitrogen atom, in addition to that between another NH_2 proton and the oxygen atom at the 8-position.

In contrast, the 2-phenylazo group in dyes, coupled to K-acid or S-acid can assume both conformations, in the absence of the steric hindrance caused by the 3-SO_3Na group. Conformation (b) is much less resistant to methylolation of the amino group than conformation (a), because twice-coupled K- and S-acid dyes are much more reactive with formaldehyde than twice-coupled H-acid dyes.

When a substituent on the 2-phenylazo group in conformation (a) is located *ortho* to the azo group, its preferred position will be 2'-, rather than 6'-, because of steric hindrance between a 6'-substituent and the lone pair orbital of the β-nitrogen atom. As a result, a 2'-substituent such as 2'-SO_3Na or 2'-$SO_2C_2H_4OSO_3Na$ gives an additional retarding effect based on steric factors, and which would not be expected for substituents at other positions.

The similarity of the retarding ability of SO_3Na and $SO_2C_2H_4OSO_3Na$ groups between two media, water and cotton, in which dyes with these groups are present, has already been described. Therefore, in designing formaldehyde-fast dyes based on 1-amino-2,7-bisphenylazo-8-naphthols, it is concluded, as shown in Fig. 7, that the introduction of an SO_3Na group into



$X = SO_3Na, SO_2C_2H_4OSO_3Na$

Fig. 7. Basic structure of formaldehyde-fast dyes derived from 1-amino-2,7-bisphenylazo-8-naphthol. The 3-SO_3Na group and substituent X effectively protect the amino group against electrophilic attack of $^{+}CH_2OH$.

the 3-position is essential in protecting the amino group against attack of a $^{+}CH_2OH$ ion, and that additional introduction of an SO_3Na or $SO_2C_2H_4OSO_3Na$ group into the 2′-position is preferable. The 3′- and 4′-positions are also effective only in the latter group. In contrast, SO_3Na groups on the 7-phenylazo group have little or no influence. It should be kept in mind that such 2′-substituents slightly decrease the ε_{max} of the corresponding dyes.

This formaldehyde-resistance-improving effect is maintained, even if the phenylazo groups at the 2- and 7-positions are replaced with naphthylazo groups. Additional SO_3Na groups can be introduced into suitable positions to increase water-solubilizing properties, to improve other fastness properties or to adjust substantivity to cellulose. An NHR group or its analogous reactive systems can also be introduced into the chromogens to design formaldehyde-fast reactive dyes. The role of an SO_3Na group in giving formaldehyde resistance will also be the same with other metal sulphonate groups such as an SO_3Li and SO_3K; the same situation pertains for an $SO_2C_2H_4OSO_3Na$ group.

3 EXPERIMENTAL

3.1 Materials

First-grade reagents or technical-grade ones were used for the syntheses. Special-grade reagents or their equivalents, and water purified by ion exchange, were used for analyses, dyeing and fastness tests, unless otherwise noted. The scoured and bleached unmercerized cotton knitted fabrics for dyeing were obtained from Nitto Boseki Co., Ltd.

3.2 Measurement

Visible absorption spectra were recorded on a Hitachi UV-Visible spectrophotometer model 228A, using water as solvent. ^{1}H- and ^{13}C-NMR spectra were recorded on a JOEL GX-270 spectrometer at 27°C, using DMSO-d_6 as solvent and TMS as internal standard. HPLC analyses were performed with a Shimadzu model LC-3A liquid chromatograph with a 4·0 mm (i.d.) × 250 mm Lichrosorb RP-18 column (Merck, reverse phase, 5 μm), using methanolic water solutions as eluent. The λ_{max} values of N-methylolated products separated in the column were measured using a Shimadzu model SPD-M6AS photodiode array UV-VIS detector connected to the HPLC system.

3.3 Synthesis

All dyes except **19** were synthesized following the previously reported method[19,20] or were obtained as commercial products. These dyes were purified by repeated recrystallization until chromatographically pure.

Dye **19** was synthesized as follows: a mixture of dye **14** (10·0 g) and formalin (37%, 3 g) in water (100 ml) was stirred for 3–4 h at 40°C, while adjusting the pH to 2·5–3·0. The crude product was salted out with sodium chloride and filtered. Residual inorganic salts in the cake were removed by mixing it with DMF and then filtering the mixture. Recrystallization was performed by adding acetone to the filtrate to give a green crystalline product. Elemental analysis, found (%): C 32·4, H 2·3, N 8·2. $C_{23}H_{15}N_5O_{14}S_4Na_4 . 2H_2O$ requires (%): C 32·8, H 2·3, N 8·3. ^{1}H-NMR, δ (ppm): 5·9 (2H, s, CH_2—O), 16·5 (1H, s, NH). ^{13}C-NMR, δ (ppm): 56·74 (CH_2—O). λ_{max} (nm) (ε_{max}): 653 (43 500), 426 (21 200).

3.4 Conversion

A 0·10M aqueous solution of each of dyes **1**, **3**, **4**, **8–18** and **20–29** was prepared, and was allowed to react with formalin (37%), 3·0mol based on the dye, while controlling at the given temperatures (control range ± 1°C) and pH values (control range ±0·2) under light-shading. The reaction was followed by the HPLC and the percentage of conversion of each dye at regular time intervals was calculated, with that of 0th h as a standard.

3.5 Light stability

A $3{\cdot}7 \times 10^{-5}$M aqueous solution (pH 4·2) of each of dyes **14** and **19** was prepared; solutions in a 1 cm quartz cell were exposed to sunlight at

25–30°C. Visible spectra were measured at 0, 2, 4 and 8 h. The percentage of change of extinction coefficient at each lapse time was calculated with that at 0th h as a standard. The same procedure was repeated using dye **19**, except that the pH was changed to 1·5, 2·5, 6·5 and 7·5, and the irradiation time to 4 h. The test on dye **19** was also carried out under light-shading.

3.6 Dyeing

Each dye **1–7** and **24–27** (0·1 g) was dissolved in water (200 ml). Sodium sulphate (10 g) and cotton (10 g) were added to the dye solution, which was then heated to 60°C. After 20 min with stirring, sodium carbonate (4·0 g) was added, and dyeing continued at the same temperature for 60 min. The dyed cotton was rinsed with cold water, then thoroughly washed with boiling water to remove unfixed dyes, and finally dried at 80°C. Of the respective controls for comparison, those giving dyeings of relatively high or low color depth were redyed so as to give dyeings having a similar color depth to each other.

3.7 Resin-finishing

Each dyeing from dyes **1–7** obtained as above was padded twice in an aqueous solution containing dimethylol dihydroxyethyleneurea (Sumitex Resin NS-11, 100 g/litre) (Sumitomo Chemical Co.) and a specific metal salt catalyst (Sumitex Accelerator X-80, 30 g/litre) to a wet pickup of *c*. 65%. The padded dyeings was dried at 90°C for 2 min and cured at 150°C for 3 min. Another aqueous solution containing methylated methyloluron (Sumitex Resin 800 K, 60 g/litre) and an organic amine salt catalyst (Sumitex Accelerator ACX, 6 g/litre) was also used for resin-finishing of each dyeing. The color change by resin-finishing was evaluated using the grey scale for color change.

3.8 Heat-set- and light-fastness

The heat-set-fastness test was carried out for the dyeings obtained in Section 3.6 and 3.7 at 110°C for 10 min and at 130°C for 20 min. The fastness was evaluated in the same manner as above. The light-fastness test was carried out for the same dyeings, according to JIS L 0842 (20 h).

3.9 Formaldehyde-fastness

The formaldehyde-fastness test was carried out for the dyeings obtained in Section 3.6, according to JIS L 0868.

4 CONCLUSION

In the blue dyes tested, 1-amino-2,7-bisphenylazo-8-naphthol derivatives are the most susceptible to formaldehyde. The formaldehyde-induced discoloration consists of two main reactions: N-methylolation of the amino group, and thermo- or photochemical reaction of the resulting compounds. Since the second reaction occurs very easily, it is essential to control the first reaction. Thus, the preferable countermeasures against the discoloration are as follows:

(a) use of formaldehyde-free resin-finishing agents;
(b) resin-finishing of dyeings under non-acidic conditions; or
(c) development of formaldehyde-fast dyes.

The 1-amino-2,7-bisphenylazo-8-naphthol derivatives can be rendered formaldehyde-resistant by a 3-SO_3Na group and by a 2′-SO_3Na or 2′-$SO_2C_2H_4OSO_3Na$ group on the 2-phenylazo group. The results are applicable to the design of formaldehyde-fast dyes in navy blue to black shade areas.

ACKNOWLEDGEMENTS

The author is indebted to Mr K. Otake for his cooperation of this project and to Mr N. Iwata for the NMR spectral measurements.

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