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Design of Chlorine-fast Reactive Dyes. Part 1: The Role of Sulphonate Groups and Optimization of their Positions in an Arylazonaphthol System

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ABSTRACT

The effect on colour fastness to chlorinated water caused by incorporating a sodium sulphonate (SO_3Na) group into the structure of reactive dyes based on arylazonaphthol has been investigated. The results of this study indicate that the SO_3Na group can play a vital role in increasing the colour fastness of these dyes on cotton, and it is effective to arrange this group on each of the aryl and naphthol rings so that the azo group is surrounded from both sides. The most likely explanation for the effect lies in the ability of the two SO_3Na groups to sterically protect the —NH—N= group of the hydrazone form which predominates in the arylazonaphthol system. A CO_2Na group on the aryl ring exerts the same effect. The colour fastness is further affected by the position of an N-substituted amino group on the naphthol ring. The visible absorption spectra of these dyes are also described.

1 INTRODUCTION

A sulphonate (SO_3^-) group is used extensively in dye chemistry for its ability to increase water-solubilising properties, to adjust substantivity to

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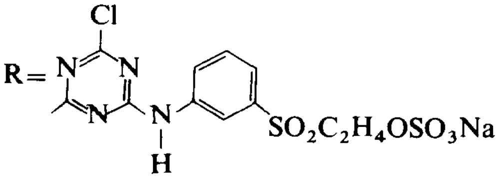
cellulose, to lower mutagenicity and to act as a good leaving group in nucleophilic substitutions. A further approach, in which the sulphonate group plays a role in improving fastness properties, thereby facilitating the design of new, high-fastness dyes is commercially valuable.

The sulphonate group located *ortho* to the azo group of acid dyes retards their oxidative decomposition by active chlorine (Cl^+) in an aqueous medium;[1] however there are various limitations in terms of hue, dyeing characteristics, fastness properties etc., in applying this result to the development of reactive dyes for practical use.[2] A few reactive dyes have been examined in an aqueous medium[3] and on cellulose.[4] There are still many unknown aspects about the role that the sulphonate group plays in improving the colour fastness to chlorinated water (hereafter called chlorine fastness) of reactive dyes fixed to cellulose by covalent bonding.

Chlorine fastness problems can be caused by the action of a small amount of active chlorine which may be present, for example, in tap-water and in swimming-bath water, and similar problems arise from chlorine-based bleaching agents used in laundering; therefore the demand for chlorine-fast reactive dyes has dramatically increased, particularly in Japan. To improve the poor chlorine fastness of reactive dyeings and printings, some aftertreatment fixatives have been developed and commercialized;[2,5–8] however such agents are not yet complete in their performance. Reactive dyes which have intrinsic high chlorine fastness are still required.

The purpose of the present investigation was to assess the relationship between the position of a sodium sulphonate (SO_3Na) group, the most widely used salt of a sulphonic acid group, and chlorine fastness in the reactive dyes based on arylazonaphthol in order to clarify the influence of this group on the chlorine fastness, and thence to design chlorine-fast reactive dyes. Because of the limited commercial availability of the 4-arylazo-1-naphthol system, the arylazonaphthol system examined was limited to the 2-arylazo-1-naphthol and 1-arylazo-2-naphthol systems having more than one SO_3Na group, and an NHR group, where R is a hetero-bifunctional reactive system comprising two different fibre-reactive groups, namely a β-sulphatoethylsulphone group and a monochlorotriazine group as in formula (**I**).[9]



(**I**)

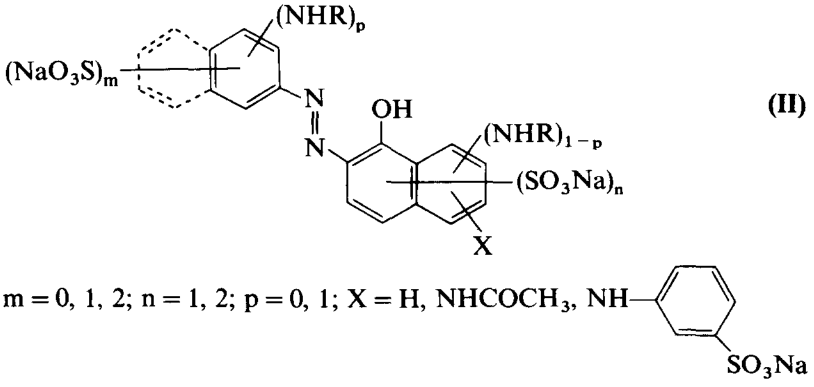
Test methods for chlorine fastness of dyed cotton are specified in JIS L 0884 (effective chlorine 5 mg/dm^3), AATCC 105 (5 mg/dm^3), ATTS (10 mg/dm^3) and ISO 105-E03 (20 mg/dm^3); in all cases sodium hypochlorite is used as an oxidizing agent to generate active chlorine. The ISO method was adopted here for testing under the most severe condition.

2 RESULTS AND DISCUSSION

2.1 2-Arylazo-1-naphthol system

The 2-arylazo-1-naphthol system examined comprised a series of hetero-bifunctional reactive dyes as shown by formula (**II**) (Fig. 1). All dyes contain more than one SO_3Na group on the aryl (phenyl or naphthyl) and/or naphthol rings, and the NHR group on either ring. The formula is abbreviated hereafter to Rd—N=N—Rc for convenience: Rd and Rc represent the residues of a diazo component (Rd—NH_2) and of a coupling component (Rc—H), respectively. Each dye was prepared by diazotizing Rd—NH_2 and coupling the resulting diazonium salt to Rc—H.

Table 1 summarizes the visible absorption spectral data for 50 hetero-bifunctional reactive dyes **1A–10E** (p = 0, X = H in formula (**II**)), derived from ten arylamines (Rd—NH_2) and five aminonaphtholsulphonic acids (precursors of Rc—H), i.e. H-acid (8-amino-1-naphthol-3,6-disulphonic acid), K-acid (8-amino-1-naphthol-3,5-disulphonic acid), sulpho J-acid (6-amino-1-naphthol-3,5-disulphonic acid), J-acid (6-amino-1-naphthol-3-sulphonic acid) and γ-acid (7-amino-1-naphthol-3-sulphonic acid).

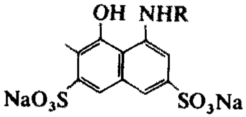
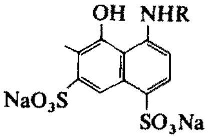
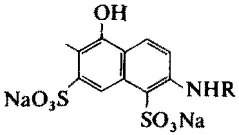
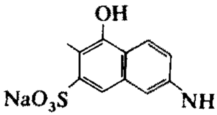
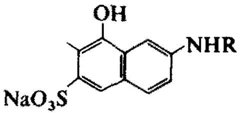
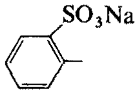
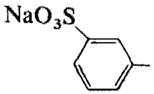
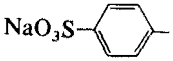
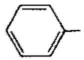
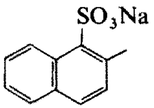


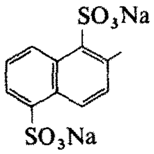
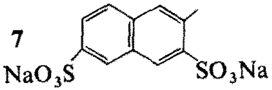
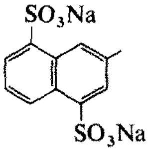
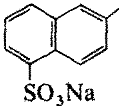
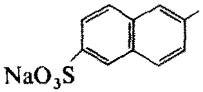
(**II**)

Fig. 1. Hetero-bifunctional reactive dyes based on 2-arylazo-1-naphthol. The formula is shown as an azo form with no implications concerning the equilibrium position and is abbreviated to Rd—N=N—Rc for convenience, where Rd and Rc represent the residues of a diazo component and of a coupling component, respectively. R is a hetero-bifunctional reactive system (I).

TABLE 1

Visible Absorption Spectral Data, λ_{max} in nm and (ε_{max} in $dm^3/(mol\ .\ cm) \times 10^{-4}$) for Dyes **1A–10E** (Rd—N=N—Rc) in Water

Rd \ *Rc*		A	B	C	D	E
						
1		514 (3·26) 534 (3·29)	509 (2·99) 522s (2·91)	484 (3·03)	483 (3·20)	394 (1·06) 500 (2·01)
2		513 (3·61) 531 (3·65)	508 (3·16) 524s (3·05)	482 (3·12)	482 (3·21)	392 (1·17) 502 (2·03)
3		517 (3·77) 534 (3·80)	512 (3·35) 529s (3·25)	486 (3·51)	487 (3·45)	396 (1·38) 504 (2·39)
4		516 (3·06) 540 (3·09)	512 (2·95) 532s (2·87)	489 (3·05)	490 (2·90)	396 (0·98) 509 (1·90)
5		522 (3·71) 548 (3·84)	517 (3·79) 539 (3·74)	494 (3·89)	495 (3·86)	399 (1·05) 509 (2·43)

6		518 (3·92) 543 (4·09)	513 (3·84) 535 (3·80)	489 (3·96)	487 (4·22)	381 (1·36) 504 (2·89)
7		525 (4·02) 550 (4·13)	524 (3·97) 541s (3·77)	502 (3·95)	500 (4·01)	411 (1·02) 513 (3·14)
8		531 (4·14) 548 (4·09)	519 (3·80) 542 (3·74)	496 (3·87)	494 (4·15)	405 (1·27) 515 (2·69)
9		527 (3·96) 553 (3·96)	520 (3·71) 549s (3·54)	499 (3·86)	497 (3·55)	406 (1·03) 517 (2·56)
10		529 (4·20) 554 (4·18)	524 (3·92) 549s (3·76)	502 (4·08)	506 (3·77)	412 (1·10) 520 (2·76)

The data on **1A–3A** are cited from Ref. 10.
R = hetero-bifunctional reactive system (I), s = shoulder.

The λ_{max} in the 480–550 nm region and the ε_{max} in the 30 000–40 000 region of dyes **1X–10X** (X = **A–D**) suggest that these dyes exist predominantly in the hydrazone form, in view of previous studies.[11] Doubt concerning the predominance of the hydrazone form in dyes **1E–10E** arises because of a double maximum, *c.* 100 nm apart and a much lower ε_{max} than that of dyes **1X–10X** (X = **A–D**). This difference, however, relates to the fact that only γ-acid has not found widespread commercial use as a coupling component in reactive dyes.

The NHR and SO_3Na groups in Rc affect the λ_{max} and ε_{max} of these dyes as auxochromes; the former group drastically decreases them in the sequence 8- > 7- > 6- and 8- ≈ 6- > 7-, respectively; the latter group slightly, both in the sequence 6- > 5-. Thus, the H-acid dye series (**1A–10A**) containing both the 8-NHR and 6-SO_3Na groups has the deepest and strongest red colour in all the dye series, and shows remarkable bathochromic (*c.* 50 nm) and hyperchromic shifts (1·1–1·3 times), compared with the corresponding 2-arylazo-1-naphthol-3,6-disulphonic acid dyes (e.g. λ_{max} 486 nm, ε_{max} 26 600 when the aryl is 2'-sulphophenyl).[1] In contrast, the 6-NHR group in Rc gives almost the same λ_{max} but a much higher ε_{max}, compared with a 2-(2'-sulphophenylazo)-1-naphthol-3-sulphonic acid dye (λ_{max} 485 nm, ε_{max} 21 600 as a result of our observation).

The SO_3Na group on the phenyl ring in Rd causes the small hypsochromic and hyperchromic shifts, irrespective of Rc, in the sequence

$$\text{H} < p\text{-SO}_3\text{Na} < o\text{-SO}_3\text{Na} < m\text{-SO}_3\text{Na, and}$$
$$\text{H} < o\text{-SO}_3\text{Na} < m\text{-SO}_3\text{Na} < p\text{-SO}_3\text{Na, respectively.}$$

The naphthyl ring in Rd gives more bathochromic and hyperchromic bands than the phenyl ring. The SO_3Na group on the naphthyl ring shortens λ_{max}, irrespective of Rc, in the sequence 6'- > 5'- > 1'-; 6'-substituted dyes (**10A–10E**) are the most bathochromic in the naphthylazo series, and 1',5'-disubstituted dyes (**6A–6E**) the most hypsochromic, both with a higher ε_{max} than 1'- or 5'-substituted dyes (**5A–5E** and **9A–9E**).

Table 2 shows a representative example of chlorine fastness of cotton dyed with six reactive dyes at different dyeing concentrations. Very few or no changes in the chlorine fastness of each dye were observed in the 0·5–1·5% o.w.f. range; this fastness depends primarily on the dye structures under the test condition employed, because of the presence of an excess of active chlorine over the dyes fixed to cotton.

Additionally, it must be mentioned that all the dyes only faded; no phenomena such as swealing and bleeding were observable. This suggests that active chlorine cleaves exclusively the chromogen of these dyes, and not the dye–fibre bond. The high dye–fibre bond stability is not surprising,

TABLE 2

Relationship between Dyeing Concentration and Chlorine Fastness of Dyes on Cotton[a]

Dye No.	*Dyeing concentration (% o.w.f.)*		
	0·5	*1·0*	*1·5*
1E	2–3	2–3	2–3
4B	1	1	1–2
5C	3	3	3
6A	4–5	4–5	4–5
7D	3–4	3–4	3–4
9A	1	1	1

[a] ISO 105 E-03: effective chlorine 20 mg/dm^3, 25°C, 4 h.

since it is well documented that a fibre-reactive group of the hetero-bifunctional reactive system (**I**), i.e. β-sulphatoethylsulphone, essentially imparts a stable dye–fibre bond formation.[9,12] The SO_3Na group bonded to a chromogen is also stable to active chlorine.[13] Therefore, the relationship between the position of this SO_3Na group and the chlorine fastness can be exactly assessed. The test for dyes **1A–10E**, including the six reactive dyes, was carried out on each dyeing obtained at 1% o.w.f. and the results are given in Table 3.

Table 3 illustrates that the chlorine fastness of dyes **1X–10X** (**X** = **A–E**) decreases in the following order in each **X**, as expressed by Rd (**1–10**): **6** $\geq$ **1** $\geq$ **5** $\approx$ **7** $\gg$ **2** = **3** = **4** = **8** = **9** = **10**. This order indicates that the

TABLE 3

Chlorine Fastness of Dyes **1A–10E** (Rd—N=N—Rc)[a]

Rc / *Rd*	*Chlorine fastness*				
	A	**B**	**C**	**D**	**E**
1	4	4	4	4	2–3
2	1	1	1	1	1
3	1	1	1	1	1
4	1	1	1	1	1
5	4	4	3	3	2
6	4–5	4	4	4	2–3
7	3–4	3–4	3–4	3–4	2
8	1	1	1	1	1
9	1	1	1	1	1
10	1	1	1	1	1

[a] Rd (**1–10**) and Rc (**A–E**) are the same as those shown in Table 1.

chlorine fastness depends strongly on the position of the SO_3Na group in Rd, irrespective of Rc; dyes **NA–NE** (N = **1** and **5–7**) containing the SO_3Na group adjacent to the azo group of each dye are much faster than dyes **NA–NE** (N = **2**, **3** and **8–10**) not containing this group and dyes **4A–4E** containing no SO_3Na groups in Rd. The most striking feature in the 2-arylazo-1-naphthol system is the extremely beneficial effect of the SO_3Na group at the 2'-position on the phenyl ring (dyes **1A–1E**), and at the 1'- and 3'-positions on the naphthyl ring (dyes **NA–NE** (N = **5–7**)). Additionally, the 5'-SO_3Na group on the latter ring is slightly effective so far as the 1'-SO_3Na group exists (dyes **6A** and **6C–6E**). The others in Rd are totally insignificant. The role of the SO_3Na group in chlorine fastness will also be the same as for other metal sulphonate groups such as an SO_3Li and SO_3K.

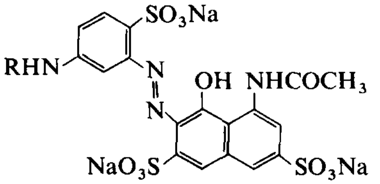
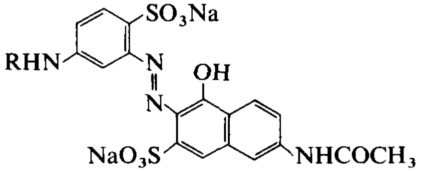
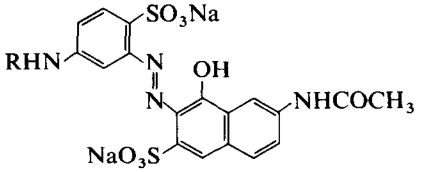
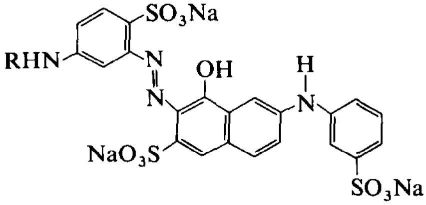
Gregory and Stead have reported that the half-life of the oxidative decomposition of 2-arylazo-1-naphthol-3,6-disulphonic acid dyes caused by active chlorine in an aqueous medium varies with the aryl groups used.[1] The resistance of these dyes to oxidative decomposition becomes weak in the following order as expressed by Rd (**1–7**) in the same manner as above (no data on **8–10**): **6** $\gg$ **1** $\gg$ **5** $\approx$ **3** $>$ **2** $\gg$ **4** $>$ **7**. This order, however, does not indicate the clear dependence of the resistance on the position of an SO_3Na group in Rd. In particular, their findings that the 3'-position in **7** does not contribute to the resistance, because of it not being the true *ortho* position, and the *para* position in **3** contributes to it as well as the 1'-position in **5**, differ from our results. The difference has not been clarified, but it may be true that there is a large error when the rate of oxidative decomposition fluctuates widely in the evaluation method with the half-life, as pointed out by Sudoh and Iijima.[3] Whether this is true or not, the resistance of the 2-arylazo-1-naphthol system is governed by the SO_3Na group in the aryl group more strongly on cotton than in an aqueous medium.

Again, Table 3 indicates that the chlorine fastness of dyes **1A–10E** depends also on the position of the NHR group in Rc. It decreases in the order of the 8-, 6- and 7-positions, without changing the order of the chlorine fastness on Rd mentioned above. In other words, it depends on the aminonaphtholsulphonic acids used, the order being as follows:

$$\text{H-acid} \approx \text{K-acid} \geq \text{sulpho J-acid} = \text{J-acid} \geq \gamma\text{-acid}$$

Because of the structure–fastness relationship observed in the previous series when the 1-naphthol-3-sulphonic acids with the NHR group were used as a coupling component, a further series of reactive dyes containing this group in a diazo component was examined (aryl = phenyl, m = 1,

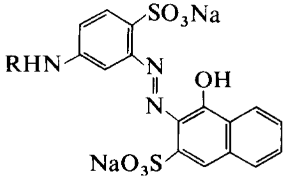
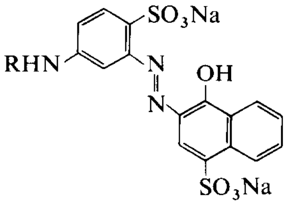
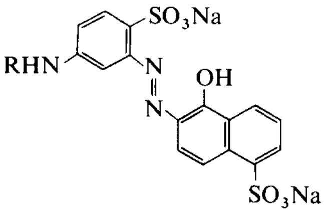
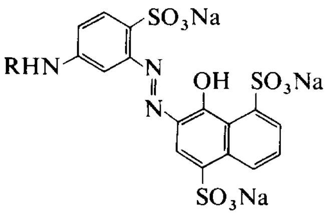
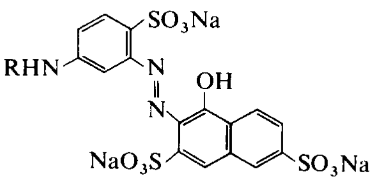
TABLE 4
Chlorine Fastness of Reactive Dyes 'Containing NHR in Diazo Component Residue

Dye No.	*Structure*	λ_{max} *(nm)* ($\varepsilon_{max} \times 10^{-4}$)	*Chlorine fastness*
11		510 (2·84) 526 (2·82)	3–4
12		484 (2·78)	3–4
13		389 (0·91) 499 (2·06)	2
14		447 (1·48) 533 (1·37)	1–2

R = hetero-bifunctional reactive system (I).

p = 1 in formula (II)). Table 4 shows that the chlorine fastness of dyes **13** and **14** derived from γ-acid is inferior to that of dyes **11** and **12** derived from H-acid and J-acid, respectively. This tendency, including the behaviour of the λ_{max} and ε_{max}, is the same as that of the previous series, irrespective of whether the NHR group is present in the coupling or diazo component residue. The poor improving effect of the γ-acid dye series seems to be related to the absorption spectra being of a different type to the others. In this case, the chlorine fastness is still practically insufficient, even if the SO_3Na group in the diazo component residue adjoins the azo group.

TABLE 5
Effect of SO_3Na-position in Coupling Component Residue on Chlorine Fastness

Dye No.	*Structure*	λ_{max} *(nm)* ($\varepsilon_{max} \times 10^{-4}$)	*Chlorine fastness*
15		487 (2·34)	3–4
16		494 (2·16)	1
17		505 (1·87)	1
18		492 (2·33)	1
19		491 (2·43)	3–4

R = hetero-bifunctional reactive system (I).

Comparing dyes **15** and **19** with dyes **16–18** in Table 5, the 3-SO_3Na group in the coupling component residue is also indispensable to maintain high chlorine fastness. The effects of the other SO_3Na groups in this residue are insignificant. In general, an SO_3Na group is introduced into the 3-position of 1-naphthols so that coupling solely *ortho* to the hydroxy group is achieved. It is interesting that this SO_3Na group plays a further role in improving the chlorine fastness of the dyes derived from the resulting 1-naphthol-3-sulphonic acids.

2.2 1-Arylazo-2-naphthol system

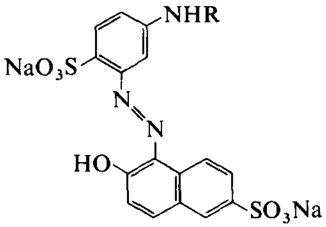
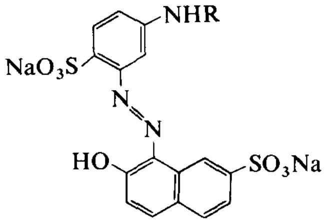
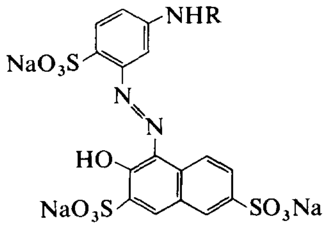
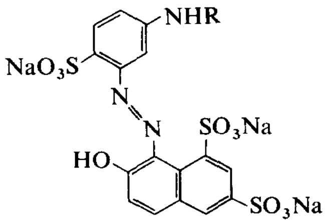
The 2-naphtholsulphonic acids available as coupling components of the 1-arylazo-2-naphthol system are limited to 2-naphthol mono- or disulphonic acids without amino groups; therefore the 1-arylazo-2-naphthol system examined comprised several hetero-bifunctional reactive dyes based on 1-phenylazo-2-naphthol containing the NHR group on the phenyl ring and two or three SO_3Na groups on the phenyl and naphthol rings.

In contrast to the 3-SO_3Na group in the 2-arylazo-1-naphthol system, the 8-SO_3Na group in the 1-phenylazo-2-naphthol system (Table 6) plays an important role in increasing the chlorine fastness (dye **23**). The other positions on the naphthol ring are of little significance (dyes **20–22**). The 2'-SO_3Na group in the phenyl ring is concluded to make a large contribution to maintaining high chlorine fastness by analogy with the 2-arylazo-1-naphthol system. It is reasonable that, in both these systems, the two SO_3Na groups solely adjacent to the azo group contribute to increasing chlorine fastness. The lower ε_{max} of the 1-phenylazo-2-naphthol system compared to the 2-phenylazo-1-naphthol isomers (Table 5) decreases the availability of the former system as a colourant; this factor is consistent with this system being unacceptable for providing commercial reactive dyestuffs.

2.3 Design of chlorine-fast reactive dyes

Table 7 gives further evidence, from [^{15}N]NMR, that arylazonaphthol dyes exist predominantly in the hydrazone form.[14,15] Considering that the position of substituent X in formula (III) has little or no influence on the chemical shifts $\delta(N^1)$–$\delta(N^4)$ (Table 7) and the λ_{max} (Table 1) of dyes **1A–3A**, and that the oxidative decomposition of the acid dyes caused by active chlorine initiates at the —NH—N= group of their hydrazone forms,[1] the effect of SO_3Na groups on chlorine fastness is mainly steric rather than electronic. In fact, the chlorine fastness of all the dyes tested is in good agreement with the presence or absence of the two SO_3Na

TABLE 6
Chlorine Fastness of Reactive Dyes of 1-Phenylazo-2-naphthol Series

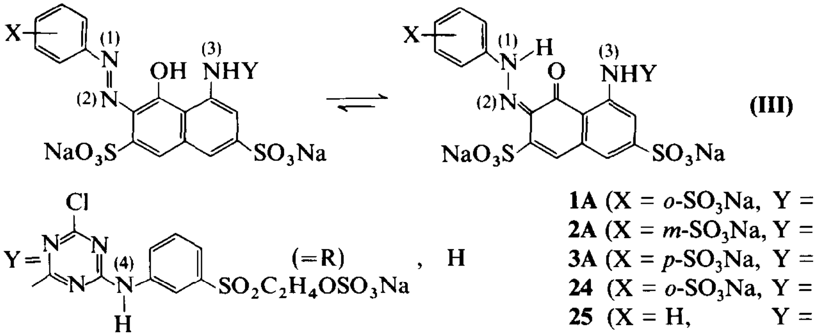
Dye No.	*Structure*	λ_{max} *(nm)* $(\varepsilon_{max} \times 10^{-4})$	*Chlorine fastness*
20		487 (1·69)	1–2
21		486 (1·65)	1–2
22		496 (1·98)	1
23		485 (1·68)	3–4

R = hetero-bifunctional reactive system (I).

groups adjacent to the —NH—N= group, although the azo-hydrazone tautomerism of these dyes varies with differences in the medium.[16]

In designing chlorine-fast reactive dyes of the arylazonaphthol system, therefore, we have concluded that steric protection of the —NH—N= group with both the 2'-SO_3Na and 3-SO_3Na groups in the 2-arylazo-1-naphthol system as shown by formula (IV) in Fig. 2, and with both the 2'-SO_3Na and 8-SO_3Na groups in the 1-arylazo-2-naphthol system as shown by formula (V), is essential in improving the chlorine fastness.

TABLE 7
^{15}N NMR Data of Dyes **1A–3A**, **24**[14] and **25**[15]

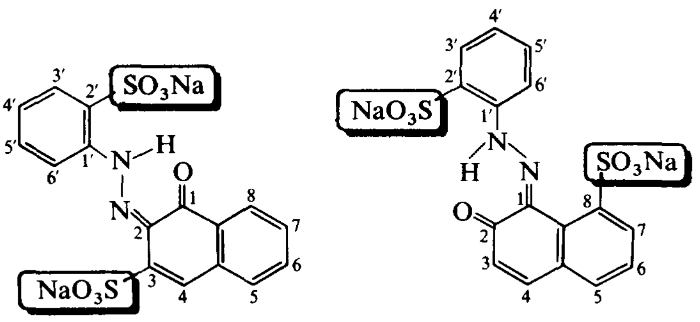


(III)

1A (X = *o*-SO_3Na, Y = R)
2A (X = *m*-SO_3Na, Y = R)
3A (X = *p*-SO_3Na, Y = R)
24 (X = *o*-SO_3Na, Y = H)
25 (X = H, Y = H)

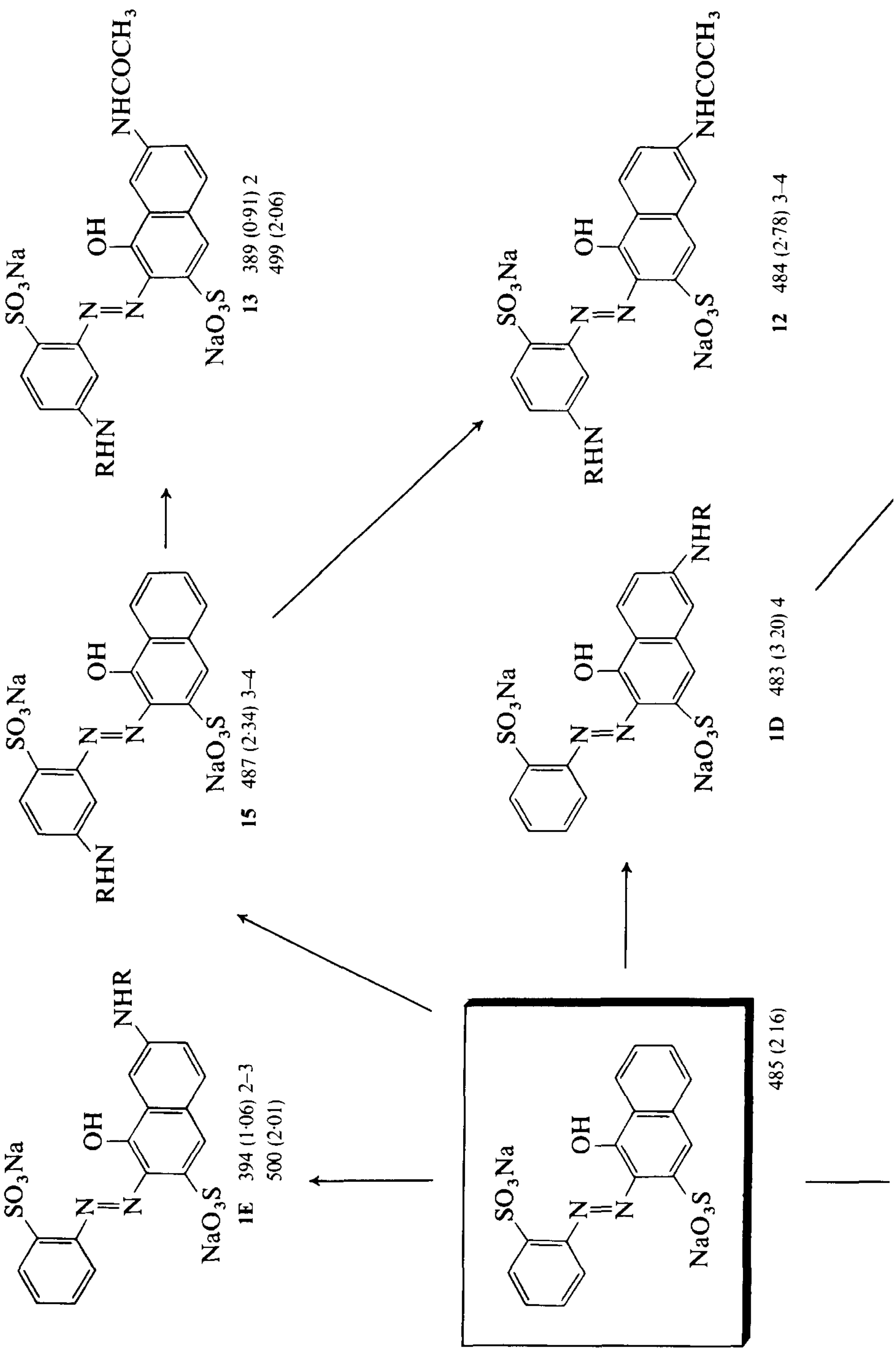
Dye No.	*Chemical shifts (ppm)*[a]			
	δ(N¹)	*δ(N²)*	*δ(N³)*[b]	*δ(N⁴)*[b]
1A	−191·1	0·2	−262·5	−266·1
2A	−188·9	3·5	−262·6	−265·8
3A	−189·2	3·8	−262·6	−265·6
24	−203·8	14·1	−302·0	—[d]
25	−200·6	−7·6	—[c]	—[d]

[a] In DMSO/DMSO-d_6 (9/1) solution at 27°C.
[b] Assignment of δ(N³) and δ(N⁴) for dyes **1A–3A** is not strict.
[c] Not reported.
[d] No N⁴ nitrogen atom.



(IV) **(V)**

Fig. 2. Chromogens of chlorine-fast dyes based on 2-arylazo-1-naphthol and 1-arylazo-2-naphthol. The formulae are shown as a hydrazone form which predominates in azo-hydrazone tautomerism. The two SO_3Na groups in each structure effectively protect the —NH—N= group from electrophilic attack of active chlorine.


485 (2·16)
1E 394 (1·06) 2–3
500 (2·01)
15 487 (2·34) 3–4
13 389 (0·91) 2
499 (2·06)
1D 483 (3·20) 4
12 484 (2·78) 3–4
SO3Na
NaO3S
OH
N=N
NHR
RHN
NHCOCH3

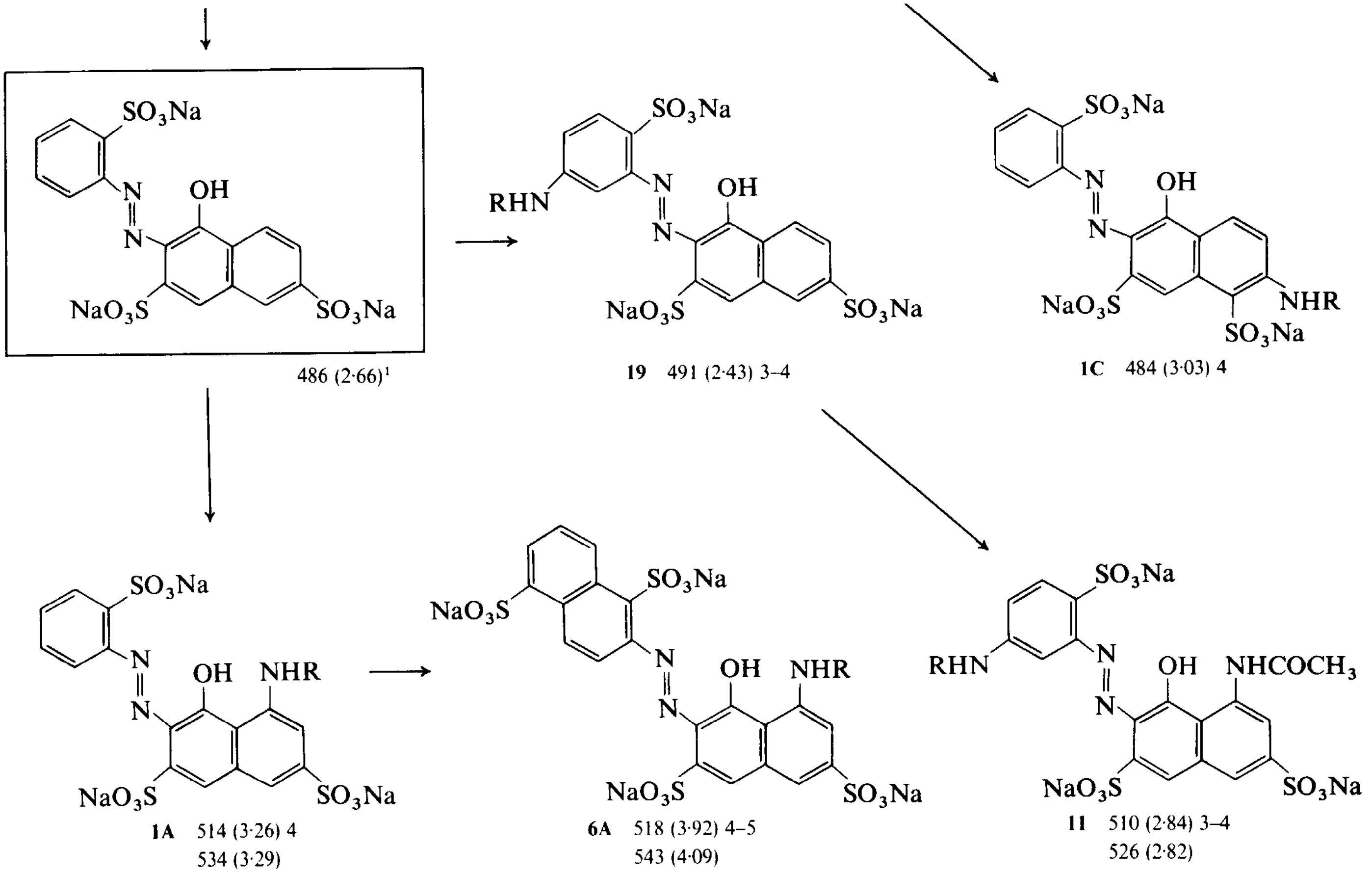
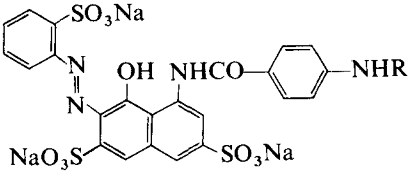
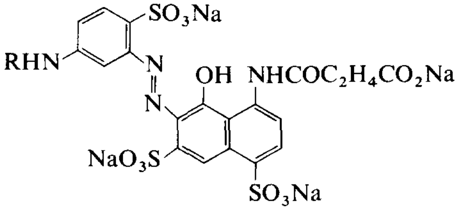
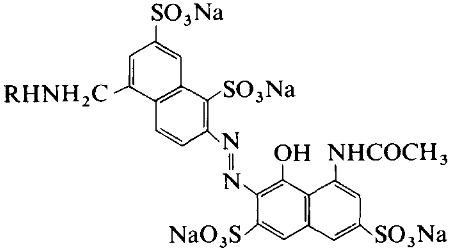
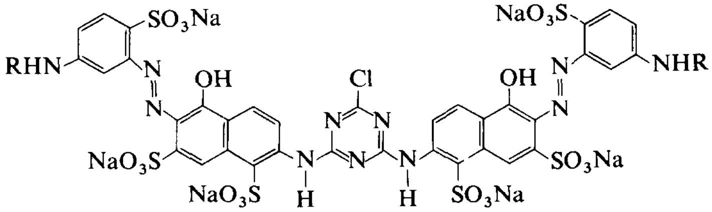


Fig. 3. Design process for chlorine-fast reactive dyes. The notation under each structure shows dye No., λ_{max} in nm, (ε_{max} in dm^3/(mol . cm) × 10^4) and chlorine fastness, whereas that under the structures framed shows only λ_{max} and ε_{max} because of a non-reactive dye. R is a hetero-bifunctional reactive system (I).

TABLE 8
Chlorine-fast Reactive Dyes Developed

Dye No.	*Structure*	*Chlorine fastness*
26		4
27		4
28		4–5
29		3–4

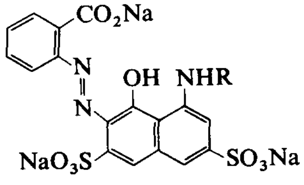
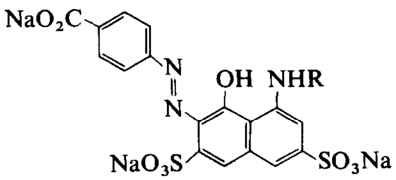
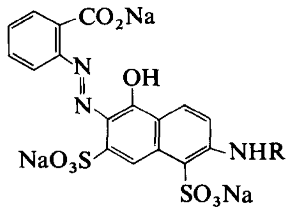
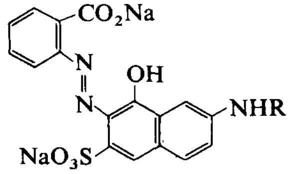
R = hetero-bifunctional reactive system (I).

This chlorine-fastness-improving effect is also relevant to chromogens where the benzene rings in formulae (IV) and (V) are replaced with naphthalene rings. The NHR group and/or its analogues can be introduced into the chromogens to lead to chlorine-fast reactive dyes. As the other positions do not substantially influence the chlorine fastness within the range of dyes examined, an additional SO_3Na group can be introduced into a suitable position to increase water-solubilising properties and to adjust the colour or substantivity to cellulose. Figure 3 illustrates a flow diagram to design chlorine-fast reactive dyes.

Table 8 is a representative example of chlorine-fast reactive dyes

TABLE 9

Chlorine Fastness of Reactive Dyes Containing a CO_2Na Group

Dye No.	*Structure*	*Chlorine fastness*
30		4–5
31		1
32		4
33		2

R = hetero-bifunctional reactive system (I).

ranging in shade from orange through scarlet to red, which have been developed on the basis of the design process.[17–19]

Table 9 indicates that the chlorine-fastness-improving effect of a CO_2Na group in a diazo component residue is the same as that of an SO_3Na group.

3 EXPERIMENTAL

3.1 Materials

First-grade reagents or technical-grade ones were used for synthesis. Special-grade reagents or their equivalents and water purified by ion exchange were used for analysis, dyeing and chlorine fastness test. 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 solvent. [^{15}N] NMR spectra were recorded on a JOEL GX-270 spectrometer at 27°C, using DMSO solution containing 10% of DMSO-d_6 as solvent and nitromethane as external standard.

3.3 Synthesis

Dyes **1A–10E**, **11–23** and **26–33** were synthesized as sodium salts following the method published previously[17-20] and purified by repeated recrystallization. They were chromatographically pure. λ_{max} (nm) in water of all the dyes except dyes **1A–10E** and **11–13** noted in Tables 1 and 4–6 are as follows:

26; 520, 539, **27**; 506, **28**; 514, 536, **29**; 488, **30**; 517, 544,
31; 526, 547, **32**; 490, **33**; 505

3.4 Dyeing

Each of dyes **1A–10E**, **11–23** and **26–33** (0·10 g) was dissolved in water (200 ml), and 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 was carried out at the same temperature for 60 min. The dyed cotton was rinsed with cold water, and then thoroughly with boiling water to remove unfixed dyes, and finally, dried in an oven at 80°C. Of the respective controls for comparison, those giving dyeings of relatively high or low colour depth were redyed so as to give dyeings having a similar colour depth to each other.

The above method was repeated using dyes **1E**, **4B**, **5C**, **6A**, **7D** and **9A** but 0·05 g and 0·15 g were used instead of 0·10 g.

3.5 Chlorine fastness testing

The test was carried out on the dyeings prepared in 3.4 according to the ISO method (ISO 105-E03: effective chlorine 20 mg/dm^3, 25°C, 4 h). The results were assessed in ratings; 1: poor, 2: fair, 3: good, 4: very good, 5: excellent.

4 CONCLUSION

It has been shown that the two SO_3Na groups adjacent to the azo group in arylazonaphthol dyes play a vital role in specifically protecting the chromogens against oxidative decomposition by active chlorine; it then becomes possible to design chlorine-fast reactive dyes. Fortunately, there are many dye intermediates which are readily available for the synthesis of such reactive dyes. The results of the present investigation have been successfully applied to the development and commercialization of chlorine-fast monoazo reactive dyes in orange to red shade areas.[20-22] The results are also applicable to the development of disazo and trisazo dyes which are fast to active chlorine.

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