

The dyeing performance on cotton of reactive dyes containing the α -bromoacrylamido group

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Abstract

Three reactive dyes containing the α -bromoacrylamido group have been synthesised and their performance assessed for the exhaust dyeing of cotton. The results indicate that, when situated in the appropriate electronic environment in the dyestuff molecule, this reactive grouping is compatible with the sulphatoethylsulphonyl (vinylsulphonyl) group in delivering warm dyeing (60°C) characteristics. © 1999 Elsevier Science Ltd. All rights reserved.

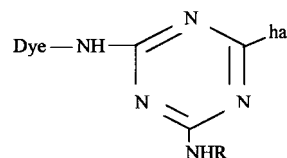
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1. Introduction

Cotton is currently responsible for approximately 50% of the world's fibre consumption and is expected to retain its dominant position into the next century [1]. Cotton is dyed with five major classes of dyes; the non-ionic vat, sulphur and azoic classes and the anionic direct and reactive classes. Reactive dyes, which form a covalent bond between the dye and the cellulosic substrate as a result of an alkaline "fixation" step during dyeing, are the fastest growing class of cellulosic dyestuff [1,2].

Since the introduction of reactive dyes for cellulose in the mid-1950s, a large number of different reactive groups have been commercially exploited [3]. However 40 years on, only a small number may be regarded to have withstood the technological test of time, viz:

a. Halotriazine



where NHR is a 'second leg' substituent and hal = Cl(MCT) or F(MFT).

Reactive dyes for direct printing are traditionally monochlorotriazinyl (MCT) dyes where the 'second leg' is usually a substituted arylamino residue. Such products appear under the Procion P and Cibacron P trade names.

The corresponding monofluorotriazinyl (MFT) dyes are marketed by Ciba as Cibacron F dyes and DyStar as Levafix E-N dyes. They are used for warm exhaust dyeing (60°C) and, to a lesser degree in (semi-)continuous dyeing.

If two chromophores are twinned together using a linking diamine as 'second leg' (e.g. *p*-phenylenediamine, ethylenediamine), then the resulting

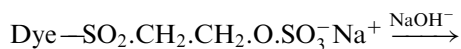
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homo bi-functional dyestuff is particularly suited to exhaust dyeing: e.g.

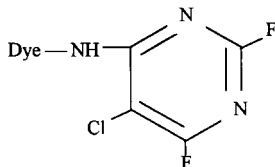
Procion H-E/H-EXL (BASF)	; <i>bis</i> MCT (substituted) <u>arylene</u> as 'second leg'
Drimaren XN (Clariant)	; <i>bis</i> MCT (substituted) <u>alkylene</u> as 'second leg'
Cibacron LS (Ciba)	; <i>bis</i> MFT (substituted) <u>alkylene</u> as 'second leg'

b. Sulphatoethylsulphone (SES)/Vinylsulphone (VS)



This reactive system has been exploited by DyStar in their Remazol range and is well suited to both (warm) exhaust dyeing and (semi-)continuous dyeing.

c. Difluorochloropyrimidine



Nowadays this reactive system, marketed by both DyStar (as Levafix E-A dyes) and Clariant (Drimaren K dyes) is probably the most important of the remaining pyrimidinyl reactive systems.

The introduction in the early 1980s of Sumifix Supra dyes (Sumitomo) [4] heralded the start of commercial reactive dye ranges containing *two different* reactive residues within the same molecule (mixed bi-functional reactive dyes). The incorporation of the sulphatoethylsulphone (SES) grouping as a second leg of a monochlorotriazine (MCT) dye structure (see Fig. 1), allowed a warm (60°C) exhaust dyeing range to be produced, which incorporated the technical benefits of both the MCT and the SES reactive groups. Indeed the success of this mixed bi-functional approach helped to establish warm dyeing at 60°C (a temperature at which Remazol dyes, Cibacron F and Levafix E-A/Drimaren K dyes can also be applied)

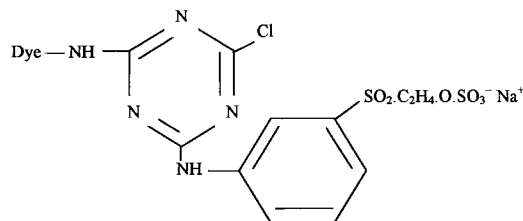


Fig. 1.

as the major exhaust application procedure. [The market share enjoyed by warm dyeing ranges of reactive dyes is currently considered to be at least twice that of the hot dyeing (MCT, 80°C) ranges.]

Ciba, in the late 1980s, introduced a new range of hetero bi-functional dyes for the (semi-)continuous dyeing of cellulose, viz the Cibacron C range [5,6]. The chemistry employed for this range brought together the monofluorotriazine group with an alkylvinylsulphone residue to give products with high fixation levels and easy wash-off properties.

Indeed reactive dyes nowadays regularly appear with a number of different reactive groups within the molecule. The 'molecular engineering' approach of the 1980's [7,8], in which correct selection of reactive groups was considered vital as a means of ensuring that the dyes exhibited high degrees of compatibility, is less widely used by dyestuff manufacturers today. Machinery developments offering much improved dye liquor-fabric interchange, together with automated dosing systems [9–11] and microprocessor control of the dyeing parameters means that the need to build in level dyeing and shade reproducibility factors into the chemistry of the dye molecule is not as necessary as it was 10 years ago! Hence the reactive dye chemist these days is able to concentrate on producing increasingly more cost effective products, via the use of tinctorially strong products with high fixation efficiency, which can be applied in short, highly productive processes so as to minimise adverse environmental impact. Nowadays a dyestuff may contain an MFT group, and MCT group and a SES/VS group within the same molecule!

It was therefore of interest to see the introduction in the early 1990s of a warm dyeing reactive dyestuff for cellulose, Cibacron Navy F-R, containing the α -bromoacrylamido reactive group twinned

with a sulphatoethylsulphone grouping. The α -bromoacrylamido reactive group, widely exploited by Ciba in their Lanazol range of reactive dyes for wool, was not, in the authors' experience, previously used as a reactive grouping for cellulose. The purpose of this study was to evaluate the technical performance of the α -bromoacrylamido reactive grouping with cellulose and to speculate on its potential for use in warm exhaust dyeing. Three dyestuffs were synthesised (yellow, red, navy) to allow this technical evaluation to be conducted. The performance of the navy dye was compared with that of both Cibacron Navy F-R and Everzol Black B (C.I. Reactive Black 5).

2. Experimental

2.1. Dye synthesis

Samples of the different diazo and coupling components (of manufacturing quality) were kindly supplied by Everlight Chemical Industrial Corporation (Taiwan). A sample of α,β -dibromopropionyl chloride was kindly provided by Ciba.

2.1.1. Synthesis of yellow dye (Fig. 2)

A solution of sodium nitrite (12.5 g, 28%,) was added dropwise, with stirring, to a suspension of 2-aminonaphthalene-3,6,8-trisulphonic acid (0.05 mol) in water (150 ml) containing hydrochloric acid (13 ml, 32%) at 15–20°C. After 90 min excess nitrous acid was destroyed by the addition of small amount of sulphamic acid. 3-Ureidoaniline (7.7 g, 0.051 mol) dispersed in water (100 ml), was added over 10 min to the suspension of diazonium salt. The pH was raised to 6–7 with 10% aqueous sodium carbonate and kept at this pH until coupling was complete. α,β -Dibromopropionyl chloride (13.7 g, 0.055 mol) was added dropwise to the solution of dyebase, the mixture stirred for 90 min and then caustic soda solution (0.05 mol) was

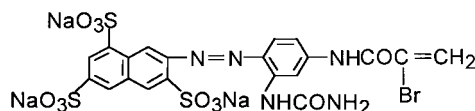


Fig. 2.

added (pH 10.5) to cause elimination of hydrogen bromide. Common salt was added to the dye solution to precipitate the dyestuff, which was filtered and dried at 60°C (yield: 27.19 g).

2.1.1.1. NMR data of yellow dye. δ_H (DMSO): 11.62 ppm (s, $NHCO$), 10.69 ppm (s, $NHCO$), 9.03 ppm (s, $Ar-H$), 8.98 ppm (s, $Ar-H$), 8.43 ppm (s, $Ar-H$), 8.30 ppm (s, $Ar-H$), 8.15 ppm (s, $Ar-H$), 7.98 ppm (d, $Ar-H$), 7.68 ppm (d, $Ar-H$), 7.5–7.4 ppm (broad, NH_2), 6.82 ppm (s, $C\equiv CH_2$), 6.34 ppm (s, $C\equiv CH_2$).

2.1.2. Synthesis of red dye (Fig. 3)

α,β -dibromopropionyl chloride (13.75 g, 0.055 mol) was added dropwise over 75 min at 5–8°C to a vigorously stirred neutral solution of the sodium salt of H-acid (19.95 g, 0.05 mol) in water (100 ml). The pH was allowed to fall to 2.0 and kept at 2.0–2.5 by the addition of sodium bicarbonate. 2-Aminobenzenesulphonic acid (8.65 g, 0.051 mol) was diazotized with sodium nitrite (3.65 g) and hydrochloric acid (13 ml, 32%). The 1- α,β -dibromopropionylamino-8-hydroxynaphthalene-3,6-disulphonic acid solution was poured into the diazonium solution using 10% sodium bicarbonate solution to control the pH and optimise the dyestuff yield; 0.05 mol of caustic soda solution was added to eliminate HBr and produce the reactive species. Common salt was added to the dye solution to precipitate the dye, which was filtered and dried at 60°C (yield: 26.68 g).

2.1.2.1. NMR data of red dye. δ_H (DMSO): 16.16 ppm (s, $NH-N=$), 14.02 ppm (s, $NHCO$), 8.97 ppm (s, $Ar-H$), 8.25 ppm (d, $Ar-H$), 7.73 ppm (d, $Ar-H$), 7.62 ppm (s, $Ar-H$), 7.46 ppm (s, $C\equiv CH_2$), 7.23 ppm (m, $Ar-H$), 7.10 ppm (s, $Ar-H$), 6.40 ppm (s, $Ar-H$).

2.1.3. Synthesis of navy dye (Fig. 4)

2,4-Diaminobenzenesulphonic acid (16.92 g, 0/09 mol) was dissolved in 100 ml water. The pH

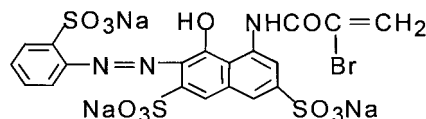


Fig. 3.

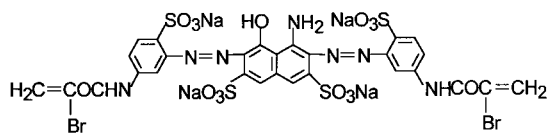


Fig. 4.

was adjusted to 6.5 using 20% sodium carbonate solution; then 1.0 g wetting agent (nonionic surfactant) and 50 g ice were added to this solution. α,β -Dibromopropionyl chloride (25, 0.10 mol) was added dropwise to this cold solution of the sodium salt of 2,4-diaminobenzenesulphonic acid over 75 min (temperature $5\sim 8^\circ\text{C}$), whilst stirring vigorously. The pH value was kept at 2.0–2.5 by adding 2.5 g sodium bicarbonate, portionwise. Hydrochloric acid (26 ml, 32%) was added to this solution of 4- α,β -dibromopropionylamino-2-aminobenzenesulphonic acid which was diazotised in the usual manner at $13\sim 15^\circ\text{C}$ with 25 g of 28% sodium nitrite solution. 100 ml of an aqueous solution (pH = 6.5) of 0.046 mol of H-acid (1-amino-8-hydroxynaphthalene-3,6-disulphonic acid) was dropped into the stirred diazonium salt solution over 2 h, controlling the pH < 3.5, until coupling *ortho* to the amino group of H-acid was complete. The pH of this mixture was adjusted to 6.5 to effect further coupling. 0.1 mol of caustic soda solution was added to eliminate HBr. Common salt was added to precipitate the dyestuff, which was filtered and dried at 60°C (yield: 28.95 g).

2.1.3.1. NMR data of navy dye. δ_{H} (DMSO): 11.25 ppm (broad, NH_2), 10.82 ppm (s, NHCO), 10.72 ppm (s, $\text{NH}-\text{N}$), 10.50 ppm (s, NHCO), 8.08 ppm (s, 1H), 7.89 ppm (d, 1H), 7.80 ppm (s, 2H), 7.71 ppm (s, 1H), 7.65 ppm (m, 1H), 7.40 ppm (dd, 2H), 6.80 ppm (m, $\text{C}=\text{CH}_2$), 6.30 ppm (s, $\text{C}=\text{CH}_2$).

2.2. Exhaust dyeing application studies

2.2.1. Temperature sensitivity of dyes

The three synthesised dyes, together with samples of Cibacron Navy F-R and Everzol Black B (C.I. Reactive Black 5), were applied at 3% depth of shade (on weight of fibre) at 40, 50, 60, 70 and 80°C using 60 g/l anhydrous Glaubers salt and 20 g/l soda ash (typical conditions for established

warm dyeing ranges). Each dyeing was conducted at 10:1 liquor ratio on bleached unmercerized knitted cotton, allowing 30 min exhaustion in salt and 60 min fixation in soda ash.

After a thorough rinsing and ‘soaping’ process, the dyed pattern was dried, conditioned and the visual yield expressed as a K/S value [12].

2.2.2. Build-up properties of dyes

Each dye was applied to bleached, unmercerized knitted cotton at six depths, viz 1, 2, 3, 4, 6 and 9% at 60°C , liquor ratio 10:1, using 60 g/l Glaubers salt (exhaustion for 30 min) and 20 g/l soda ash (fixation for 60 min). The visual yield of each pattern was expressed as a K/S value.

2.2.3. S.E.F. profile of dyes [8,13]

The substantivity, S , is defined as the percentage exhaustion of dye onto the fabric after 60 min in the presence of Glaubers salt.

The exhaustion, E , is defined as the percentage of dye on the fabric 60 min after addition of alkali.

The fixation, F , is defined as the percentage of dye fixed on the fibre at the end of the dyeing process.

The S.E.F. profile of each dye was measured at 3% applied depth at 60°C and a liquor ratio of 10:1 (60 g/l Glaubers salt and 20 g/l soda ash being employed).

2.2.4. Salt sensitivity of dyes

Each dye was applied at 3.0% depth using 30, 40, 50, 60, 70 and 80 g/l Glaubers salt at 60°C and at a liquor ratio of 10:1 on bleached unmercerized knitted cotton. Soda ash (20 g/l) was used to effect fixation. Washing off and colour measurement were carried out as described earlier.

2.2.5. Liquor ratio sensitivity of dyes

Each dye was applied at 3% depth of shade at five different ratios, viz 7.5:1, 10:1, 12.5:1, 15:1 and 20:1 using 60 g/l Glaubers salt and 20 g/l soda ash at 60°C on bleached, unmercerized knitted cotton. Washing off and colour measurement were carried out as described earlier.

2.2.6. Alkali sensitivity of dyes

Each dye was applied using five different alkali concentrations, viz 10 g/l soda ash, 15 g/l soda ash,

20 g/l soda ash. 2 g/l soda ash plus 1 ml/l 38° Be' NaOH and 2 g/l soda ash and 2 ml/l 38° Be' NaOH. A 3% depth of shade was dyed at 60°C and 10:1 liquor ratio using 60 g/l Glaubers salt. In the case of the mixed alkali systems, the soda ash and caustic soda were pre-mixed before adding to the dyebath to effect fixation. Washing off and colour measurement were carried out as described earlier.

2.2.7. Dye fibre bond stabilities

A 3% depth of shade of each dye was individually treated at six different pH values (buffer solutions at 2, 4, 6, 8, 10 and 12) at 80°C for 60 min and a liquor ratio of 20:1. After washing off, the change in colour yield compared with a control was measured (as before) using a Spectroflash 600 (Datacolor).

3. Results

3.1. Temperature sensitivity of the synthesised dyes

(see Table 1 and Illustration 1)

Table 1
Colour yield (K/S) data of reactive dyes at different temperatures

Temperature (°C)	Yellow	Red	Navy	Cibacron Navy F-R	Everzol Black B
45	8.75	4.42	16.60	17.07	16.79
50	7.54	3.32	17.31	17.78	17.61
60 (control)	6.62	2.70	17.70	17.19	17.69
70	4.94	1.30	17.46	17.41	14.29
80	2.02	1.08	14.45	15.39	12.97

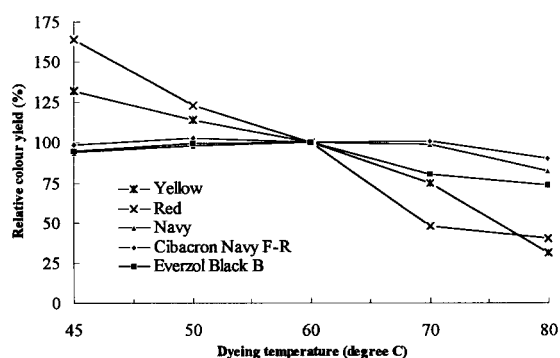


Illustration 1.

3.2. Build-up properties of the synthesised dyes

(see Table 2 and Illustration 2)

Table 2
Colour yield (K/S) data of reactive dyes at different depths

	Yellow	Red	Navy	Cibacron Navy F-R	Everzol Black B
1% o.w.f	2.88	1.72	6.52	6.04	5.67
2% o.w.f	5.36	2.62	12.09	12.04	12.04
3% o.w.f	7.40	4.02	17.15	17.76	17.99
4% o.w.f	9.62	5.37	21.29	21.85	20.67
5% o.w.f	12.42	5.30	27.20	27.77	28.86
6% o.w.f	15.56	7.17	31.26	31.56	33.17

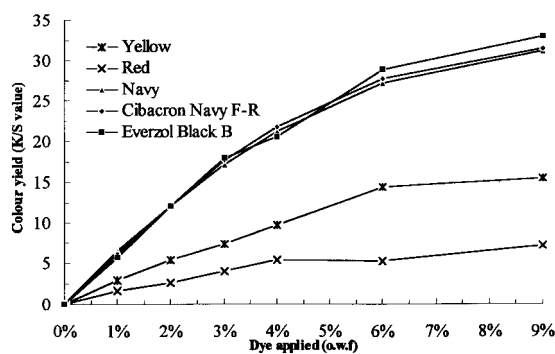


Illustration 2.

3.3. S.E.F. profiles of synthesised dyes

(see Table 3)

Table 3
S.E.F. profiles of reactive dyes applied at 60°C

	S	E	F	E-F
Yellow	40.02	59.86	25.88	33.98
Red	22.38	26.82	13.86	12.96
Navy	73.90	92.11	73.71	18.40
Cibacron Navy F-R	75.43	88.84	72.95	15.89
Everzol Black B	40.77	93.32	80.28	10.4

3.4. Salt sensitivity of synthesised dyes

(see Table 4 and Illustration 4)

Table 4

Colour yield (K/S) data of a 3% dyeing of each reactive dye with different quantities of anhydrous Glaubers salt

Salt conc. (g/l)	Yellow	Red	Navy	Cibacron Navy F-R	Everzol Black B
30	5.52	2.63	16.06	16.01	16.44
40	6.41	2.93	16.64	16.28	16.76
50	6.69	2.91	17.93	17.18	17.86
60 (control)	7.03	3.09	17.97	17.96	17.52
70	7.62	3.34	18.17	18.03	17.65
80	8.12	3.43	18.46	18.17	18.11

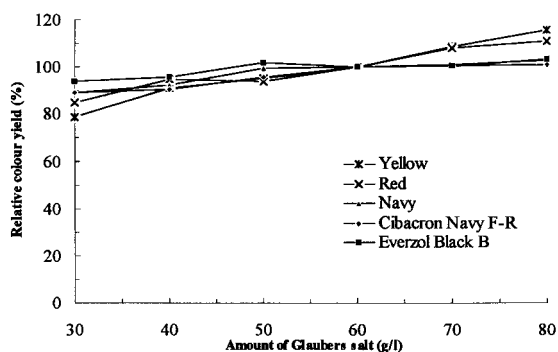


Illustration 4. Note: the colour yield obtained with 60 g/l Glaubers salt has been taken as control.

3.5. Liquor ratio sensitivity of synthesised dyes

(see Table 5 and Illustration 5)

Table 5

Colour yield (K/S) data of reactive dyes at different liquor ratios

	Yellow	Red	Navy	Cibacron Navy F-R	Everzol Black B
1:7.5	7.86	3.44	18.41	17.60	17.84
1:10 (control)	7.35	2.93	17.69	17.02	17.83
1:12.5	6.71	2.55	17.90	17.48	16.21
1:15	6.32	2.44	16.99	16.34	16.17
1:20	5.61	2.02	16.21	15.79	15.60

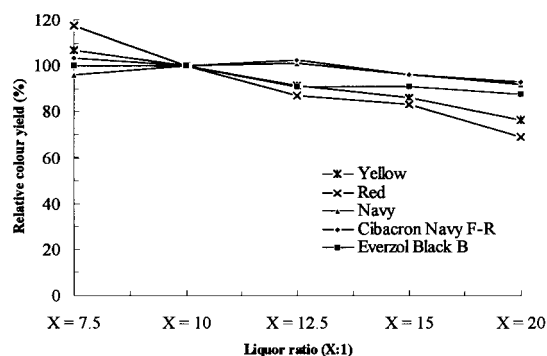


Illustration 5. Note: the colour yield obtained at liquor ratio (10:1) has been taken as control (100%).

3.6. Alkali sensitivity of synthesised dyes

(see Table 6 and Illustration 6)

Table 6

Colour yield (K/S) data of reactive dyes with different quantities of alkali

	Yellow	Red	Navy	Cibacron Navy F-R	Everzol Black B
10 g/l Soda ash	6.24	2.39	17.40	17.61	17.80
15 g/l Soda Ash	5.74	2.04	17.49	18.31	18.95
20 g/l Soda ash	5.54	2.00	17.50	18.32	18.06
(control)					
^a	5.02	1.95	16.82	17.48	17.15
^b	2.95	1.31	15.54	16.64	15.67

^a 2 g/l Soda ash + 1 ml/l NaOH (38° Be').

^b 2 g/l Soda ash + 2 ml/l NaOH (38° Be').

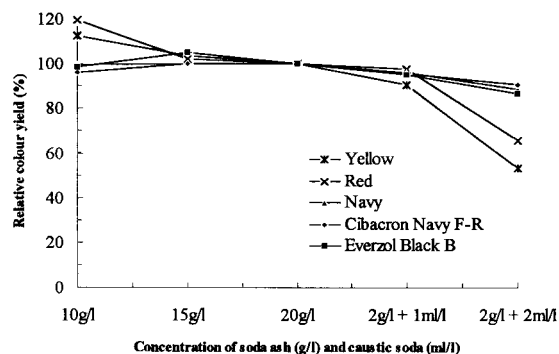


Illustration 6. Note: the colour yield obtained with 20 g/l of soda ash has been taken as control (100%).

3.7. Dye–fibre bond stability

(see Table 7 and Illustration 7)

Table 7
Colour yield (*K/S*) data of reactive dyes after treatment at different pH Values

	Yellow	Red	Navy	Cibacron Navy F-R	Everzol Black B
^a	5.82 (100%)	2.23 (100%)	18.04 (100%)	17.44 (100%)	17.61 (100%)
pH = 2	5.65 (97.08%)	2.94 (131.39%)	17.31 (95.95%)	16.89 (96.85%)	17.84 (101.85%)
pH = 4	5.74 (98.62%)	2.73 (122.42%)	17.76 (98.44%)	17.56 (100.68%)	17.76 (100.85%)
pH = 6	5.82 (100%)	2.42 (108.52%)	17.93 (99.39%)	17.34 (99.43%)	17.57 (99.77%)
pH = 8	5.94 (102.06%)	2.23 (100%)	17.92 (99.33%)	17.44 (100%)	17.62 (100%)
pH = 10	5.22 (89.69%)	1.94 (87%)	17.60 (97.56%)	16.97 (97.31%)	17.44 (99.03%)
pH = 12	4.41 (75.77%)	1.80 (80.72%)	17.61 (97.61%)	16.77 (96.16%)	16.69 (94.78%)

^a Represents the untreated sample.

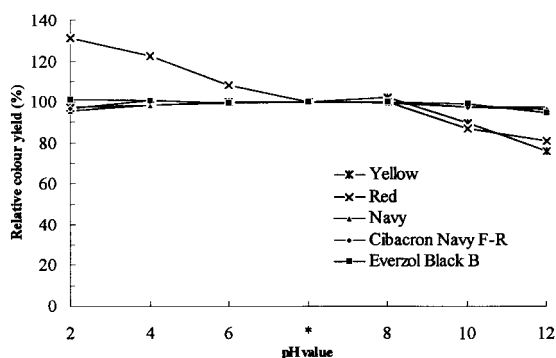


Illustration 7.

4. Discussion

4.1. Temperature sensitivity of the synthesised dyes

(see Table 1 and Illustration 1).

The synthesised yellow and red dyes, each containing one α -bromoacrylamido reactive group,

showed the highest visual yield at 45°C, the colour yield decreasing dramatically on raising the temperature. The navy dye, with two α -bromoacrylamido reactive groups, exhibited the best yield at 60°C, although the colour yields at temperatures between 50 and 70°C were very similar.

The reactive group in both the yellow and red chromophores is in an electronically activated position (in conjugation with the azo linkage) relative to the groupings in the navy dye. Hence the lower the application temperature the higher the dye yield! The synthesised navy dye exhibited a similar temperature profile to Cibacron Navy F-R and Everzol Black B (C.I. Reactive Black 5), with 60°C representing the optimum dyeing temperature.

It may therefore be concluded that a dye containing one or more (-bromoacrylamido reactive group in the correct electronic environment may have similar temperature sensitivity profile to that of both Cibacron Navy F-R and Everzol Black B.

4.2. Build-up properties of the synthesised dyes at 60°C (see Table 2 and Illustration 2)

The yellow and red dyes, when applied at the typical warm dyeing temperature of 60°C, not surprisingly, exhibited poor build-up properties.

However the build-up properties of the synthesised navy dye was similar to Cibacron Navy F-R and only a little inferior to C.I. Reactive Black 5, the market leading product as a means of achieving cost effective navy and black shades.

4.3. S.E.F. profiles of the synthesised dyes (see Table 3)

The substantivity (S), exhaust (E) and fixation (F) values of both the yellow and red dyes were low. This may be due, in the part, to their relatively small molecule size, their lack of any substantivity conferring moieties such as triazinyl groups and the above optimum temperature at which they were applied.

The synthesised navy dyestuff exhibited a profile similar to Cibacron Navy F-R. Its medium-high substantivity level might infer an inherently more level dyeing species than C.I. Reactive Black 5 where significant amounts of simultaneous

exhaustion and fixation will occur on alkali addition. The relatively high amounts of dye to be washed off at the end of the process ($E-F = 18.4$) suggests that the *bis* α -bromoacrylamido grouping is not as fixation efficient as its bis vinylsulphonyl counterpart.

4.4. Salt sensitivity of the synthesised dyes (see Table 4 and Illustration 4)

Not surprisingly, the low substantivity yellow and red dyes exhibited much higher salt sensitivity than the medium–high substantivity navy dye. The latter performed similarly to both Cibacron Navy F-R and Everzol Black B.

4.5. Liquor ratio sensitivity of the synthesised dyes (see Table 5 and Illustration 5)

The liquor ratio sensitivity of the three dyes mirrored the salt sensitivity.

4.6. Alkali sensitivity of the synthesised dyes (see Table 6 and Illustration 6)

The yield of the yellow and red dyes, not surprisingly dropped off significantly with increasing alkali at 60°C! The navy dye showed very little variation in yield with increasing concentrations of soda ash. Soda ash (alone) appeared to be the preferred alkali for fixing the α -bromoacrylamido group at 60°C.

4.7. Dye–fibre bond stability (see Table 7 and Illustration 7)

The stability of the bond formed between the α -bromoacrylamido group and cotton will depend, in part, on the electronic environment of the reactive grouping in the molecule. On the evidence of the yellow and navy dyes, the bond stability after treatment of the dyed substrate for 60 min at 80°C under acid conditions was very similar to that exhibited by Cibacron Navy F-R and Everzol Black B. Under alkaline conditions, the navy dye exhibited superior dye–fibre bond stability to the yellow dye, being very similar yet again to the two commercial navy dyes. The performance of the red dye was poor, exhibiting a shade change under

acid conditions and dye–fibre bond cleavage under alkaline conditions.

5. Conclusions

- a. The α -bromoacrylamido group, when situated in the appropriate electronic environment within a dyestuff molecule, is capable of giving optimum fixation yield at 60°C using soda ash as the alkali for fixation.
- b. The dye–fibre bond of a dyestuff fixed to cellulose via an α -bromoacrylamido reactive group is marginally more pH sensitive (particularly under alkaline conditions) than a dye fixed through a ‘vinylsulphone’ grouping.
- c. The α -bromoacrylamido group is broadly compatible (with respect to its reactivity, substantivity-conferring characteristics, dye–fibre bond stability) with the vinylsulphone group and therefore can be used in the synthesis of warm dyeing reactive dyes.
- d. The incorporation of a α -bromoacrylamido reactive group alongside vinylsulphone and monochlorotriazinyl reactive residues should allow the design of novel, highly fixation-efficient warm exhaust dyeing dyes with robust technical properties.

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