Dyes and Pigments, Vol. 37, No. 1, pp. 1–14, 1998

PII: S0143-7208(97)00041-7
0143-7208/98 $19.00 + 0.00

The Light Stability of Azo Dyes and Azo Dyeings
I. Light Stability of Dyeings with Reactive and Non-reactive Derivatives, Respectively, of Two Selected Azochromophores

Zs. Csepregi,[a] P. Aranyosi,[a] I. Rusznák,[a] L. Töke,[a] J. Frankl[a]
& A. Víg[b]

[a]Department of Organic Chemical Technology T.U. Budapest, H-1521 Budapest,
PO Box 91, Hungary
[b]Organic Chemical Technology Research Group of Hungarian Academy of Sciences,
Hungary

(Received 7 January 1997; accepted 11 April 1997)

ABSTRACT

The light stability of RC-dyed (conventional reactive dyeing) and N-dyed (substantive dyed without subsequent rinsing) cotton fabric dyeings produced with the members of two groups of dyes, viz., 'A'-dye and 'B'-dye groups, respectively, have been studied. The best light stability was achieved in the 'A'-dye group on the sample RC-dyed with A(MCT-VS). N-ethyl substitution on the NH-bridge between the two reactive groups ($A(MCT\text{-}VS)_{Et,RC}$) *did not improve the fastness, whereas methoxy substitution on the diazo component* ($A(MCT\text{-}VS)_{Met,RC}$) *deteriorated the light stability. No detectable difference could be observed in the light stability of RC-dyeings with A(MHT-VS) and A(MCT-VH), but the values achieved were not as good as that obtained with the original bifunctional variety* ($A(MCT\text{-}VS)_{RC}$)*. The light stability of all the RC- or N-dyeings produced with reactive group containing members of the 'A'-group were better than those of N-dyeings produced with A(Chr) and A(MHT-VH), respectively. All the RC- and N-dyeings (except* $B(Chr)_N$) *of the 'B'-group had identical light stability. No explanation could be found for the good light stability of the* $B(MHT\text{-}VH)_N$ *dyeing. RC-dyeings within the 'A'-group are more stable to light than those within the 'B'-group, equatable to the difference in the light stability of the respective chromophores.* © *1998 Elsevier Science Ltd*

Keywords: azodyeing, light fastness, chromophore effect, dye–fibre bonds.

INTRODUCTION

The light-induced photofading of dyed systems is a complex process and among many factors, the chemical structure of the dyes plays an important role.

Egerton and Morgan [1] stated that the structure of the chromophore of the dye is the major influencing factor, but that nevertheless the nature and position of substituents also significantly influences the results. Very different light stabilities can be achieved with dyes of the same chromophore carrying different substituents.

It has been known since 1902 [2] that phenols and their sulphonated or carboxy derivatives as well as certain aminonaphthol-sulphonates, improve the light stability of the dyed system. However, anilines, naphthols, naphthylamines, and certain amino-naphthols have a deteriorating influence.

Meuly [3] in studying disazo dyed systems, observed that sulfonic acid substituents on the coupling component decreased the light stability, but that similar substitution, in the diazo component, however, increased the light stability.

The light stability decreasing effect of –OH, $-NH_2$, and –NHR groups in the azo dye molecule was observed by Blumberger [4]. Acetylation or benzoylation of these groups improved the light stability, whereas methylation of –OH groups acted in the opposite way.

Electron accepting groups in phenylazonaphthol dyes significantly deaccelerate the photodecomposition of the dyes [5]. From a more generalised viewpoint, the light stability of azo dyes is improved by electron accepting substituents and deteriorated by electron donating ones. However, the presence of too many electron accepting groups in an azo dye may cause a drastic drop in the light stability [5].

Substituents in the dye molecule which enhance the reduction of the dye chromophore accelerate photofading in the case of a reductive mechanism, and substituents acting in the opposite way cause a lowering of photofading. This observation has been noted for substituents helping or preventing oxidative reactions in the case of an oxidative photofading mechanism [6].

Correlation between the nature of the substituent and the absorption maxima of the dyes has been demonstrated by Biteba [7], and the influence of different dye tautomers and interaction of the dyes with the substrate also noted. The electron donor or acceptor nature of the substituents influences the light fastness, but these parameters can be changed in the photo excited state of the dyes.

Hladic and Svec [8] showed that the role of the chromophore is predominant in estabilishing light stability. Azo groups connected to a naphthyl residue in the dye chromophore usually result in the dye having poor light stability.

Improved light stability of azo dyes can be brought about by the presence of a reactively derived bond between the dye chrompophore and the substrate [8]. It can be assumed that the reactive group is linked to the conjugated system of the chromophore, thus raising the light stability. Azo reactive dyes with chlorotriazinyl reactive groups show a significant improvement in light stability after covalent bonding to cellulose, the effect being more significant with dichlorotriazinyl groups than with monochlorotriazinyl groups.

Dyeings with azo reactive dyes without the formation of a dye–fibre covalent bond have poorer light stability than dyeings with a reactive bond. If, however, the reactive groups have been hydrolysed prior to dyeing, no unambiguous tendency can be noted in the light stability of the non-reactive dyeings.

Baumgarte [9] has reported similar results concerning the influence of chlorotriazine groups in dye molecule in light stability.

Krichevskii assumed [10] that the light stability improving effect of the dye–fibre covalent bond might be due to transfer of the light induced energy surplus from the dye molecule to the fibre substrate.

Absorption and diffusion phenomena, as well as the parameters influencing the formation of dye–fibre bonds in the course of reactive dyeing of cellulose with A(MCT-VS) and B(MCT-VS) dyes, have been studied by Morita *et al.* [11]; they did not report on the light stability of the dyeings.

The aim of this present work was to reevaluate the effect of different substituents, as well as the effect of different dye–fibre interactions, on the light stability of the dyeings. Two azo reactive dye groups and their derivatives were used in the studies.

EXPERIMENTAL

Materials

Dyes

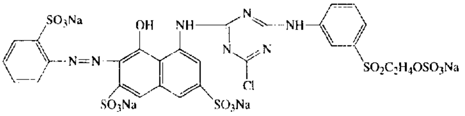
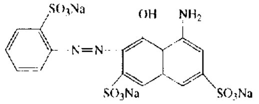
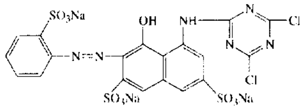
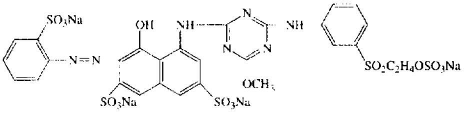
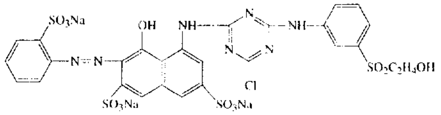
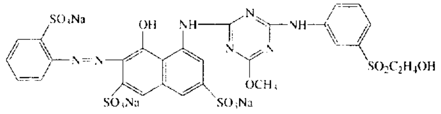
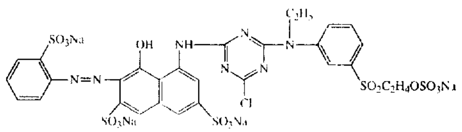
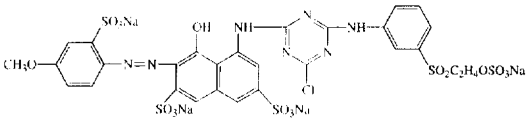
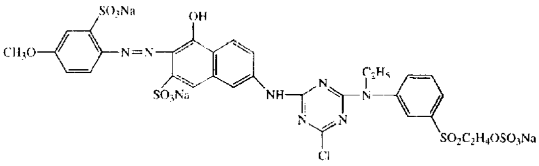
The studied dyes, produced by Sumitomo Chemical Co. Ltd., Japan, are shown in Table 1.

Cotton fabric

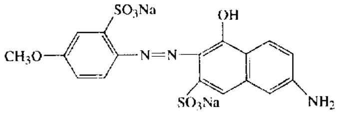
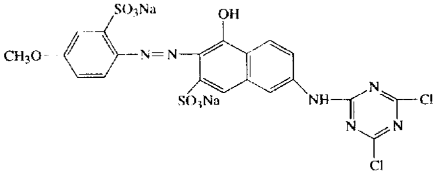
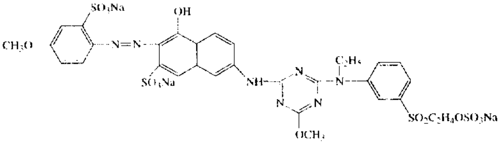
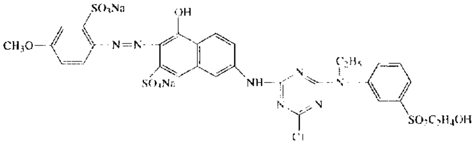
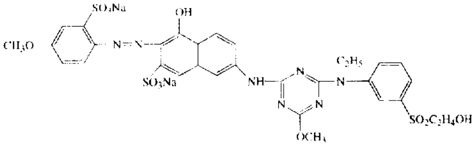
Plain woven scoured, bleached and mercerised cotton fabric:

—yarn density:	warp: 288/10 cm; weft: 256\10 cm
—surface density:	108 g m^2
—tensile strength:	warp: 265 [N/5 cm]; weft: 235 [N/5 cm]
—elongation at break:	warp: 8.25%; weft: 13.91 [%]
—yarn fineness:	warp 20 [tex]; weft 20 [tex]

TABLE 1
Characteristics of Dyes and Respective RC-Dyeings

Code	*Structure*	*Molar mass*	*Dye concentration in RC-dyeing (10^{-5}mol g^{-1} substrate)*	λ_{max} *(nm)*
A(MCT-VS)		984	1.95	510
A(Chr)		569	–	526
A(DCT)		717	2.31	512
A(MHT-VS)		981	1.89	534
A(MCT-VH)		882	1.92	534
A(MHT-VH)		878	–	534
A(MCT-VS)$_{\mathrm{Et}}$		1012	2.08	512
A(MCT-VS)$_{\mathrm{Met}}$		1014	1.90	534
B(MCT-VS)		940	2.05	502

continued

Code	*Structure*	*Molar mass*	*Dye concentration in RC-dyeing (10^{-5} mol g^{-1} substrate)*	λ_{max} *(nm)*
B(CHR)		497	–	494
B(DCT)		645	2.28	502
B(MHT-VS)		936	1.96	502
B(MCT-VH)		838	1.89	502
B(MHT-VH)		834	–	502

—equilibrium moisture regain at 65% rh: 7.33 [%]
—water retention: 44.74%
—degree of polymerization: 1495 ± 50

Methods

Dyeing procedures

The dye-to-fibre ratio was 3:100, using a fibre-to-liquor ratio 1:50. The dyeing system was continously stirred during the whole procedure in a Multi-Dye equipment.

RC-procedure. At the beginning of the procedure the dyeing system contained distilled water, dyestuff, the substrate and 50 g l^{-1} Na_2SO_4 at ambient temperature. The temperature of the bath was raised to 60°C and was kept at that level for a further 10 min. After the addition of 20 g l^{-1} K_2CO_3 the system was kept at 60°C for a further 60 min. The dyed sample was washed subsequently for 5 min at ambient temperature followed by rinsing in aqueous acetic acid solution for 3 cm^3 l^{-1} at 50°C for 5 min, followed with hot rinsing at 90°C as many times necessary to obtain a colourless washing liquor. The sample was then air-dried at room temperature.

The RC-dyeing procedure was considered as completed if an extraction of the dyed sample in dimethylformamide applying a liquor ratio of 1 : 50 for 5 min at boiling point, did not cause dissolution of traces of dye in the liquor 0.1 g of air-dry RC-dyeing was stirred in 5 cm^3 of concentrated sulphuric acid (96%) at 0–5°C until complete dissolution of the dyeing (approximately for 1–2 h). The solution was poured into distilled water, diluted to 25 cm^3, and the dye concentration of the solution was determined colorimetrically (data in Table 1).

N-procedure. This procedure was distinguished from the RC one by the following: no K_2CO_3 was added to the system after 20 min of dyeing and the second stage of the procedure (dyeing for further 60 min) was not followed by any washing of the dyed sample. It was padded to a liquor pick-up of 100% and dried at room temperature in open air. The dye pick-up of the N-dyed samples exceeded that of the RC-dyeings by approximately 50%.

Exposure to light

Dyeings were exposed to light for 264 h in a Xenotest 450 apparatus. During this period samples were periodically removed to study the kinetics of the photofading.

Colour measurement

Colour coordinates of dyeings before and after exposure for different periods were measured by ICS Texicon colour measuring instrument. The data enabled the calculation of the colour difference (ΔE^*_{ab}) between the samples before and after the exposure to be made.

Alkali and acid sensitivity, respectively, of the dye–fibre bond

Samples dyed with the hetero-bifunctional reactive dyes were extracted with 10^{-3} molar NaOH (pH = 11) and 10^{-3} molar HCl (pH = 3) aqueous solutions, respectively, at boiling temperature for 255 min. The fibre to liquor ratio was 1:50. To follow the kinetics of dissolution of the cleaved dye the absorbance of the extraction liquor was measured at each 30 min interval. The released amount of dye was then calculated by means of a calibration curve (dye concentration versus absorbance). The two extractions (alkaline and acidic) were also combined with an intermediate washing for evaluating the alkali solubility of the dye from the previously acid treated samples, as well as measuring the acid solubility of the dye from the formerly alkali treated sample.

RESULTS AND DISCUSSION

Comparison of the members of the 'A'-group of dyes

Among the three hetero-bifunctional members of the 'A'-group no significant difference was observed in the light stability of A(MCT-VS)$_{RC}$ and A(MCT-VS)$_{Et,RC}$, whereas the light stability of A(MCT-VS)$_{Met,RC}$ dyeing was lower than that of the other two dyeings (Fig. 1).

The light stability of the A(DCT)$_{RC}$ dyeing was better than that of the other monofunctional dyeings A(MCT-VH)$_{RC}$ and A(MHT-VS)$_{RC}$ (Fig. 2). The light stability of the A(DCT)$_{RC}$ dyeing slightly exceeded the roughly identical values of the A(MCT-VS)$_{Met,RC}$, A(MHT-VS)$_{RC}$ and A(MCT-VH)$_{RC}$ dyeings, but did not reach that of the A(MCT-VS)$_{RC}$ and A(MCT-VS)$_{Et,RC}$ dyeings, respectively.

The light stability of the A(Chr)$_N$ chromophore dyeing was much lower than that of the A(MHT-VH)$_N$ dyeing in the initial period (24–96 h) of

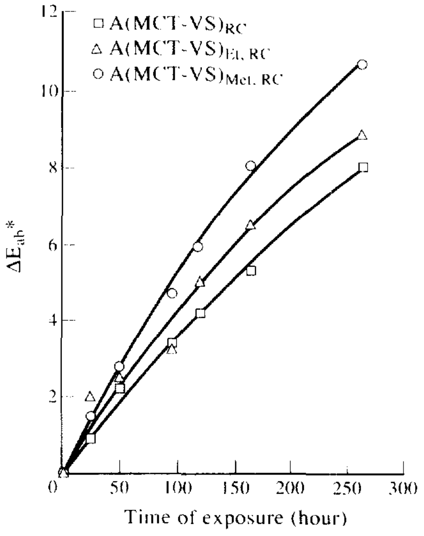


Fig. 1. Kinetics of photofading of the hetero-bifunctional reactive dyeings in the 'A'-dye group.

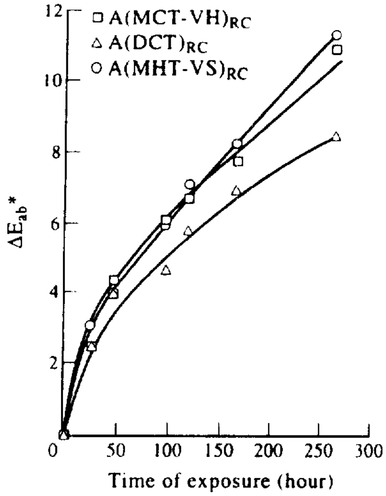


Fig. 2. Kinetics of photofading of the monofunctional reactive dyeings in the 'A'-dye group.

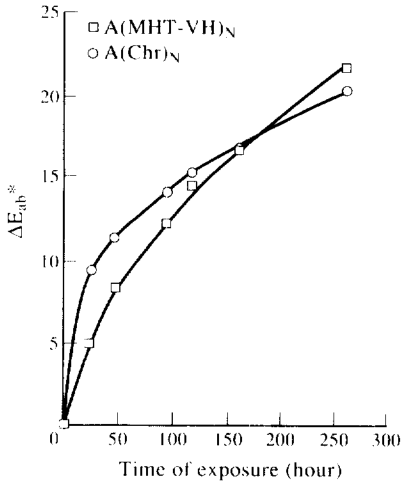


Fig. 3. Kinetics of photofading of the N-dyeings with 'A'-dye group members non-containing reactive groups.

exposure (Fig. 3). Identical light stability occurred after exposure for 165 h and the light stability of $A(Chr)_N$ dyeing was better than that of $A(MHT\text{-}VH)_N$ dyeing in the final period of exposure (165–264 h).

On comparing RC- and N-procedure dyeings in the case of the A(MCT-VS) dye, no significant difference was observed. Comparison of the light stability of the $A(DCT)_{RC}$ and $A(DCT)_N$ dyeings showed the latter to be

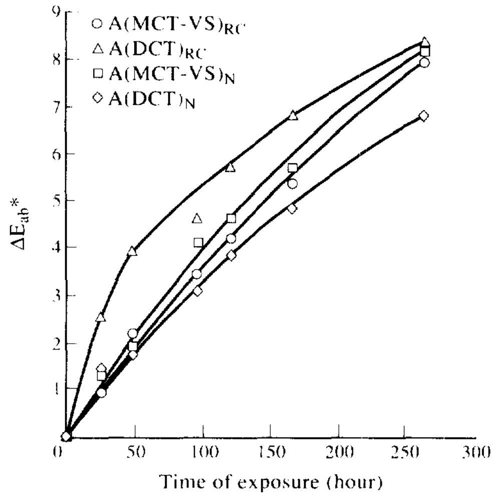


Fig. 4. Comparatory kinetics of photofading between RC- and N-dyeings with A(MCT-VS) and A(DCT) dyes, respectively.

markedly better than the former (Fig. 4). In the exposure period from 165 h to 264 h, the light stability of the $A(DCT)_N$ dyeing was distinctly better than that of the $A(MCT\text{-}VS)_{RC}$ dyeing.

After exposure for 264 h, the $A(DCT)_N$ dyeing was the most stable to light, and the $A(MHT\text{-}VH)_N$ dyeing was the least stable.

Comparison among the members of 'B'-group

$B(MHT\text{-}VS)_{RC}$ and $B(MCT\text{-}VH)_{RC}$ dyeings were slightly more stable to light than $B(MCT\text{-}VS)_{RC}$ and $B(DCT)_{RC}$ dyeings (Fig. 5). The light stability of the $B(MHT\text{-}VH)_N$ dyeing is very significantly better than that of the $B(Chr)_N$ dyeing (Fig. 6). The light stability of the former dyeing is also slightly better than that of the best RC-dyeings in the 'B'-group.

No difference was observed in the light stability of the $B(MCT\text{-}VS)_{RC}$ and $B(MCT\text{-}VS)_N$ dyeings, whereas the light stability of the $B(DCT)_N$ dyeing was slightly better than those of $B(DCT)_{RC}$ and $B(MCT\text{-}VS)_{RC}$ dyeings (Fig. 7).

$B(MHT\text{-}VH)_N$ dyeing proved to be the most stable to light and the $B(Chr)_N$ dyeing the least stable within the 'B'-group.

Comparison among the members of the two dye groups

Comparison of the light stability values of the four hetero-bifunctional dyeings showed that the $B(MCT\text{-}VS)_{RC}$ dyeing proved to be the least stable.

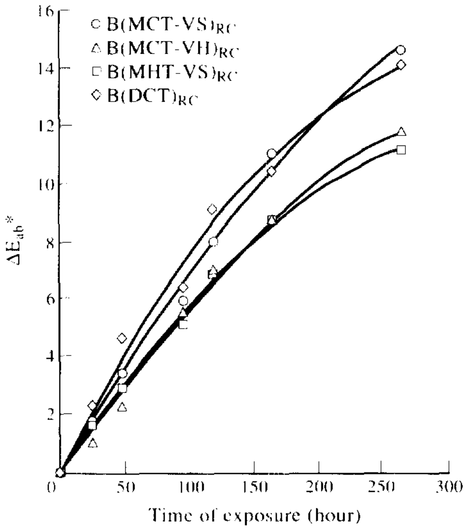


Fig. 5. Kinetics of photofading of one hetro-bifunctional and three monofunctional reactive dyeings in the 'B'-dye group.

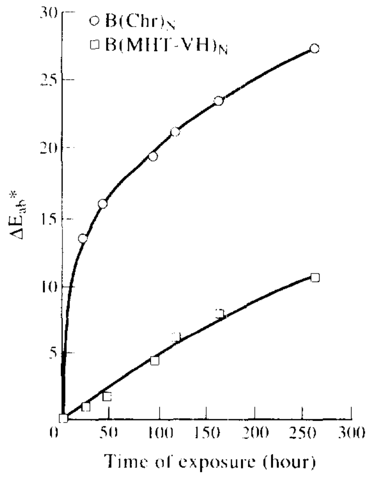


Fig. 6. Kinetics of photofading of N-dyeings with 'B'-group members non-containing reactive groups.

The light stability among the six monofunctional dyeings was generally better within the 'A'-group than within the 'B'-group. However, there was no difference between the worst light stable A_{RC} dyeings and the best light stable B_{RC} dyeings after exposures shorter than 165 h. The chromophore of the 'A'-group is more stable to light than that of the 'B'-group.

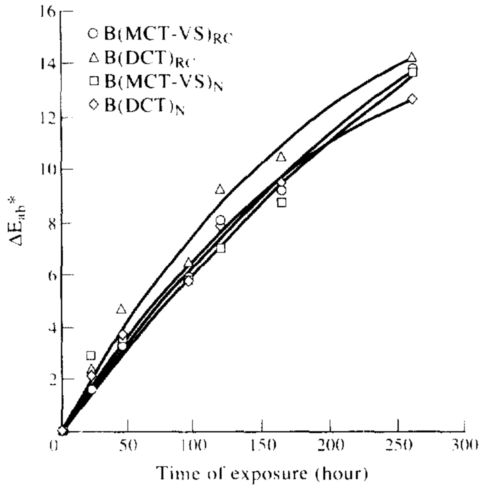


Fig. 7. Comparatory kinetics of photofading between RC- and N-dyeings with B(MCT-VS) and B(DCT) dyes, respectively.

The non-reactive B(MHT-VH)$_N$ dyeing was very significantly more stable to light than the A(MHT-VH)$_N$ dyeing.

When the RC- and N-dyeings are compared within the same group of dyes in the case of MCT-VS dyeings, no differences were apparent. However, on comparing the two pairs to each other, the 'A'-dyeings were more stable to light than the 'B'-dyeings, which can be attributed to the difference in the light stability of the two chromophores.

A similar tendency was observed in the comparison of RC- and N-dyeings in the case of the DCT members, vis., N-dyeings are more stable to light than RC-dyeings. The difference in light stability between A(DCT)$_N$ and B(DCT)$_N$ dyeings is again relatable to the difference in light stability of the two chromophores.

The hetero-bifunctional RC-dyeings can be divided into two groups as far as the preferential bonding with one of the two functional group is concerned. In the case of A(MCT-VS)$_{RC}$ and A(MCT-VS)$_{Met,RC}$ dyeings the formation of chlorotriazinyl-cellulose covalent bond is markedly preferred, whereas a slightly preferred state of the VS-cellulose bond formation could be observed in A(MCT-VS)$_{Et,RC}$ and B(MCT-VS)$_{RC}$ dyeings.

Acid and alkali sensitivity of the dye–fibre bonds, respectively, in the hetero-bifunctional reactive dyeings of the 'A'- and 'B'-groups

The sensitivity of the MCT-fibre covalent bond to acid, and that of the VS-fibre covalent bond to alkali has been previously noted [12]. The separately

TABLE 2

Amount and Percentage of Released Dyes Liberated by Acidic, Alkaline and Combined Extractions, Respectively, from Hetero-bifunctional Reactive Dyeings

Medium of extraction	*Extracted dye (mg dye g^{-1} fabric) after a treatment of 255 min*			
	A(MCT-VS)$_{RC}$	*A(MCT-VS)*$_{Met,RC}$	*A(MCT-VS)*$_{Et,RC}$	*B(MCT-VS)*$_{RC}$
Acidic followed by alkaline	5.8 (39%)	-	—	3.6 (24%)
Alkaline	0.8 (5%)	1.1 (7%)	2.0 (13%)	2.3 (15%)
Acidic	5.2 (35%)	3.9 (26%)	1.4 (9%)	1.3 (9%)

applied acidic, alkaline and combined extractions, respectively, result in bonds fission and removal, released dyes from the substrate to varying extents. The proportion of non-cleaved dye was 60% of the total for the A(MCT-VS)$_{\mathrm{RC}}$ dyeing, 67% for the A(MCT-VS)$_{\mathrm{Met,RC}}$, dyeing, 78% for the A(MCT-VS)$_{\mathrm{Et,RC}}$ dyeing and 76% for the B(MCT-VS)$_{\mathrm{RC}}$ dyeing.

The released amount of dye due to acidic cleavage was six times higher in the case of the A(MCT-VS)$_{\mathrm{RC}}$ dyeing than that cleaved by alkali, and four times higher in the case of the A(MCT-VS)$_{\mathrm{Met,RC}}$ during, whereas the proportion of the alkaline and acidic extraction liberated dyestuff content was between 1.4 and 1.6 in the case of A(MCT-VS)$_{\mathrm{Et,RC}}$ and B(MCT-VS)$_{\mathrm{RC}}$ (Table 2).

It can be concluded from the data of Table 2 that only 22–40% of the covalently fixed dye could be removed from the four studied dyeings by means of combined extraction. It can also be concluded that in case of A(MCT-VS)$_{\mathrm{RC}}$ dyeing, the amount of cleared MCT-fibre covalent bonds was six times higher than that of VS-fibre covalent bonds, and the proportion was 4: 1 in the case of the A(MCT-VS)$_{\mathrm{Met,RC}}$ dyeing.

The relative extent of alkali sensitive covalent bonds in both A(MCT-VS)$_{\mathrm{Et,RC}}$ and B(MCT-VS)$_{\mathrm{RC}}$ dyeings was 1.5 times higher than that for the acid sensitive bonds.

CONCLUSIONS

No significant difference occurred between the light stabilites of RC- and N-dyeings in both studied dye groups. This implies that in the range of hetero-bifunctional and monofunctional members of the groups, the formed dye–fibre covalent bonds—both MCT- and VS-type—do not increase the light stability of the dyeing.

The presence of a dichlorotriazinyl reactive group in the dye molecule leads to a relatively higher light stability of N-dyeings. On elimination of the chlorine substituents from the reactive group in RC-dyeings (one is eliminated in the course of covalent bonding and the other is simultaneously hydrolysed), the resultant dyeings show light stability similar to those obtained with the further bifunctional and monofunctional RC-dyeings. Improved light stability is due consequently to the presence of the two chlorine substituents in the unchanged reactive group.

The light stability of the members of 'A'- and 'B'-groups is—with one exception—evidently dependent on the light stability difference between the two chromophores. The only exception is the $B(MHT\text{-}VH)_N$ dyeing, whereas with identical deactivation of the reactive groups in the corresponding 'A'-member, $(A(MHT\text{-}VH)_N)$ is the worst member in the 'A'-group. Further studies are needed for an explanation of this unexpected difference in the light stability.

The presence of two reactive groups in the dye molecule in the course of the RC-procedure leads to a slightly better light stability of dyeings in the 'A'-group than for any of those for the two reactive groups alone. No difference occurs in the 'B'-group, which might be due to the difference in the relative proportion of the two types of covalent bonding.

Neither the acidic nor the alkaline treatment could remove more than 60–67% of the covalently fixed dye from the $A(MCT\text{-}VS)_{RC}$ and $A(MCT\text{-}VS)_{Met,RC}$ dyeings, respectively, whereas the retained percentage of fixed dye on $A(MCT\text{-}VS)_{Et,RC}$ and $B(MCT\text{-}VS)_{RC}$ dyeings was 78–76%, respectively, after similar extractions.

It can be concluded that—probably due to the C_2H_5 substitution in the NH-bridge between the two different reactive groups—the detectable amount of VS-fibre bond was slightly higher than that of MCT-fibre bond. In the other two hetero-bifunctional dyeings, however, the marked preference of MCT-fibre bond over the VS-fibre bond could be detected.

The other significant difference between the chemical structure of A(MCT-VS) and B(MCT-VS) dyes, namely of methoxy substitution of the latter on its diazo component, does not influence the proportion of the two types of covalent bond after fixation.

To explain the remarkable high proportion of unbroken covalent bonds in the dyeings, the following can be assumed.

—Narrow channels (voids) penetrated by the bifunctional reactive dyes enable the simultaneous formation of both covalent bonds with the substrate. After such fixation of the dye, the penetration of the hydrolysing system becomes difficult or impossible. The formed cross-linking prevents swelling, necessary for the above-mentioned penetration.

—The formed cross-linking enables the close approach of hydrophobic-sites between dye and fibre, generating the formation of van der Waals bonds which counteract the approach of the covalent linkages by the hydrolysing system.

—The hydrolysing system can penetrate the narrow channels breaking the covalent bonds but leaving the van der Waals interaction unchanged, and thus preventing the release of the dye from the narrow channel.

ACKNOWLEDGEMENTS

The authors express their gratitude for the synthesis of the studied dyes and for the financial support of the present work to Sumitomo Chemical Co. Ltd., Japan. The support of the Hungarian National Scientific Research Foundation (OTKA, T-016307) is also highly appreciated by the authors.

REFERENCES

1. Egerton, G. S. and Morgan, A. G., *Journal of the Society of Dyers and Colourists*, 1970, **86**, 242.
2. Brownlie, D., *Journal of the Society of Dyers and Colourists*, 1902, **18**, 288.
3. Meuly, W., *Helvetica Chimica Acta*, 1923, **6**, 931.
4. Blumberger, J. S. P., *Chemical Weekblad*, 1931, **28**, 310.
5. Allen, N. S., *Review of Progress in Coloration*, 1987, **17**, 61.
6. Shakra, S. and Ali, N. F., *American Dyestuff Reporter*, 1992, **81**, 28.
7. Biteba, I. M., Gurbzsijan, L. M., Kalija, O. L., Karpov, V. V., Korolev, B. A., Osmolovskaja, L. A., Savina, I. B. and Stepanenko, B. O., *Zhurnal Obshchei Khimii*, 1991, **61**, 2657.
8. Hladik, V. and Svec, Z., *Journal of the Society of Dyers and Colourists*, 1979, **95**, 147.
9. Baumgarte, U. and Wegerle, D., 1986, *Melliand Textilberichte*, 1986, **67**, 567.
10. Kricsevszkij, G. E. and Gombköto, J., Svetostojkostj Okrazsenii Textilnij Izdelij, Moszkva. *Legkaja Industrija*, 1975, **85**.
11. Morita, Z., Kai, T. and Motomura, H., *Dyes and Pigments*, 1991, **17**, 241.
12. Matsui, M., Meyer, U. and Zollinger, H., *Journal of the Society of Dyers and Colourists*, 1988, **104**, 425.