

Stability of Reactive Dyes in Sunlight Changes in their Colour Coordinates

S. WAHEED AND C.M.ASHRAF
*Applied Chemistry Research Centre
PCSIR Laboratories Complex
Lahore-54600, Pakistan*

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Summary: Fading on exposure in light is undoubtedly the most complex of the reactions which dyes undergo on a fibre. Energy in the form of light is absorbed by the dye and causes some of its molecules to become unstable and under these conditions, the dye may react with surrounding materials. The decomposition of the dye subsequent to its photochemical activation occurs usually by reduction and in azo dyes the azo linkage seems to be attacked. Dyes containing strongly electron donating substituents tend to fade oxidatively, whereas those with strongly electron withdrawing groups prefer a reductive degradation pathways. In dry state a reductive fading mechanism becomes oxidative. Fastness to washing, wet rubbing and perspiration also showed changes in colour coordinates of the dyes studied.

Introduction

Reactive dyes are the most recently developed amongst the major dye classes. Their ease of application, wide shade range, high brilliancy and excellent wet fastness properties make them the preferred choice for many cellulosic fibre dyeing applications. Improvements in the structure of reactive dye chromogens and in the structure, selection and number of reactive groups have led to an increased use of reactive dyes. Reactive dyes are gradually becoming the main class of dyes for cellulosic fibres and are used extensively to dye or print casual wear and sportswear goods [1-4].

Different reactive groups were patented [5] and these can be classified according to their reaction mechanism [6].

- Groups that react by a nucleophilic bimolecular substitution.
- Groups that react by a nucleophilic addition mechanism.
- Groups that react via several additions and elimination steps with a nucleophilic group of the fibre.
- Groups that react by ester formation of a phosphonic acid group.

Until now reactive dyes with a high degree of light fastness have been selected to solve fading problems. Yet the mechanism involved in fading due

to combination of perspiration and light is not always the same as fading by light alone [7]. The development and use of new reactive dyes depend on the fastness to light and the substrate to which it is attached. The main factors which cause fading of dye, are the wave length distribution of the incident light, the aggregation state of the dye, humidity and the permeability of the dyed substrate to gases like oxygen [8-10].

The substrate absorbs the radiations from the region between 300 and 400 nm (near ultraviolet) and photochemical reactions initiated result in dye fading. In their investigations Chang, Miller and Giles reported that substituent effects can be used to determine the dominant pathway of oxidation and reductive fading [11,12]. Earlier work has shown that free radicals may be formed during irradiation of dyed cellulose in the 250-500 nm wavelength range. They may be generated from the fibre forming polymers and /or from small molecule colouring, incrusting or soiling the fibre [13]. The role of radical reactions in the fading of reactive dyes and of reactive-dyed cellulosic had been studied by Sirbilaze *et al* [14]. Experimental evidence for radical formation and for its role in the fading of reactive dyes had been presented. Similar studies were made by Anisimov *et al.* who reported the effectiveness of the reactive dyes, four azo and one anthraquinone dye in generating radicals on irradiation [15].

The mechanism of photodestruction of reactive dyes in solution had been studied by

Gurdzhiyan *et al.* The products of photodestruction were analysed and a radical mechanism involving reduction of the dye was proposed. The inhibiting effect of oxygen was also explained [16]. Byteva *et al.* indicated the oxidative and reductive mechanism of fading of reactive azo dyes in cellulose hydrate films. Thin film chromatography was used to show that amines which were formed as the products of reductive cleavage during the fading of 3 red monochlorotriazine reactive oxyazo dyes in cellulose hydrate films [17].

Ha and Lee investigated the specific features of the light fading of reactive dyes on cellulose as a function of the nature of different kinds of bonds between the dye and substrate. It was found that the fading rate constant was clearly correlated to the strength of the dye-substrate bond, the stronger the bond the greater the light stability resulting in higher light fastness of the covalent-bonded dye [18]. Some monochlorotriazine dyes were applied to cellophane and cotton substrate. The fading rates and colour changes of the dyes where dye/substrate covalent bonds were formed were less marked than those of the analogues dyed without covalent bonds. Therefore, covalent bonding was important in the lightfastness of reactive dyes [19].

The photosensitivity of ten monochlorotriazinyl reactive dyes had been estimated by exposing the binary mixtures of each dye together with an aminopyrazolinyl azo dye on cellulose in aerated water. The reactive dyes underwent reductive or oxidative fading depending upon the conditions of exposure [20]. Okada reported potential photochemical properties for ten monochlorotriazinyl reactive dyes and their manifestations in the fading of dyed cellulose [21]. The fading of seven monochlorotriazinyl reactive azo dyes on cellulose had been investigated under wet conditions. Spectral analysis showed that these dyes faded via photoreduction on exposure in deaerated water; oxygen suppressed the reductive fading for some of the dyes or inhibited it. The fading process was determined by the chemical structure and the concentration of oxygen [22].

The fading on cellulose of six vinylsulphone reactive dyes and copper complex azo dye was investigated on exposure to light under dry and wet conditions. The rate of fading on cellulose decreased with increase in concentration [23]. The fading of dyeing of vinylsulphone reactive dyes on cellulose by

simultaneous action of light and perspiration was examined by Okada *et al.* Based on tests with vinylsulphone reactive dyes carried out on cellophane it was found that in general the oxidative fading on cotton fabrics occurred mainly in the initial stages of exposure whilst reductive fading occurred mainly in one of the subsequent exposure stage [24,25]. In similar studies Okada and Moria described that the properties of the dye itself and the conditions of exposure, especially the concentration of oxygen and the substrate on which the dye was absorbed, determine whether reductive and/or oxidative fading occurred [26].

This paper reports the fading of some vinylsulphone and monochlorotriazinyl reactive dyes when exposed to sunlight for many hours and the changes which occurred in colour coordinates. Studies are made for their fastness properties against washing, wet rubbing and perspiration.

Results and Discussion

The effect of sunlight on the fading and colour change of vinylsulphonyl and monochlorotriazinyl reactive dyes on fabric has been investigated. The present studies were made for eight vinylsulphone and monochlorotriazinyl reactive dyes containing H-acid and J-acid as coupling components. Cotton fabric was dyed with each of the dyes and the percentage exhaustion investigated at liquor ratio 40:1 have higher exhaustion values than the monoazo dyes. The exhaustion values depend on the substantivity of dyes, which in turn are influenced by the chromogen structure. The diazo dye due to two monoazo chromogens have bigger molecular size than the monochlorotriazinyl monoazo dyes and therefore are more substantive.

The fastness to sunlight, washing, wet rubbing and perspiration of all the dyed samples fabrics were measured by conventional method. The spectral characteristic and colour coordinates were measured for original and faded dyed cotton samples. In Table-2 fastness properties of eight vinylsulphonyl and monochlorotriazinyl reactive dyes containing H-acid and J-acid coupling agents are shown.

The stability of the chromophore to sunlight is greater for azo dyes containing J-acid (dye # 5-8) than the azo dyes containing H-acid. It appears from the data that the position of the amino group in

Table-1: Characteristics of Reactive Dyes

Dye Ref #	λ_{max} nm	Exhaustion %	Tristimulus Value			CIE LAB Original			CIE LAB Faded			Chromaticity Coordinates	
			Y	X	Z	L*	a*	b*	L*	a*	b*	x	y
1.	600	72.9	12.10	11.76	19.13	41.88	-10.18	-10.95	42.05	-05.99	-11.15	0.2504	0.2899
2.	602	74.8	18.14	16.77	26.43	50.15	-13.99	-09.54	50.80	-08.36	-06.46	0.2601	0.3001
3.	605	75.5	25.76	24.15	36.93	58.28	-06.01	-09.42	58.61	-04.15	-06.78	0.2842	0.3019
4.	540	76.4	33.98	38.81	45.82	65.19	18.35	-05.11	65.32	21.02	-06.13	0.3294	0.2892
5.	510	73.3	34.01	46.41	23.08	65.75	40.10	23.89	65.99	23.98	16.22	0.4501	0.3314
6.	500	70.9	15.12	22.08	11.62	46.93	37.73	14.09	47.02	30.09	14.38	0.4530	0.3121
7.	505	74.9	16.98	24.71	12.49	48.11	40.83	15.36	48.42	36.15	18.25	0.4601	0.3197
8.	490	76.1	30.11	38.34	13.97	62.09	30.99	36.01	62.38	22.18	30.53	0.4753	0.3657

Table-2: Light Fastness and Colour Coordinates Before and After Light Exposure

Dye Ref #	Light Fastness	ΔE %	Munsell rennotations						
			Original			Faded			
			Hue	lightness	chroma	hue	lightness	chroma	
1.	5-6	2.61	3.40B	4.08	3.20	7.97B	4.15	3.12	
2.	5-6	3.11	0.50B	4.85	3.51	3.07B	4.97	3.40	
3.	5-6	2.12	6.81B	5.78	2.49	7.41B	5.88	2.03	
4.	5-6	2.59	2.11RP	6.41	4.79	2.21RP	6.53	4.41	
5.	6	2.48	6.99R	6.39	9.99	5.73R	6.47	9.63	
6.	6	2.45	3.53R	4.44	8.24	4.24R	4.78	7.87	
7.	6	2.21	3.64R	4.68	9.01	4.65R	4.97	8.38	
8.	6	2.09	1.11YR	6.05	8.85	2.52YR	6.25	8.12	

Table-3 Wash Fastness and Colour Coordinates Before and after Washing.

Dye Ref #	Wash Fastness		ΔE %	Munsell rennotations					
	Change In Shade	Staining of cotton		Original			Treated		
			hue	lightness	chroma	hue	lightness	chroma	
1.	4	4	2.72	3.40B	4.08	3.20	8.01B	4.20	3.10
2.	4	4	3.21	0.50B	4.85	3.51	3.68B	5.01	3.33
3.	4	4	2.20	6.81B	5.78	2.49	7.52B	5.92	2.99
4.	4-5	4	2.61	2.11RP	6.41	4.79	2.25RP	6.63	4.35
5.	4	4	2.52	6.99R	6.39	9.99	6.12R	6.54	9.01
6.	4	4	2.60	3.53R	4.44	8.24	4.50R	4.85	7.77
7.	4	4	2.25	3.64R	4.68	9.01	4.69R	5.05	8.01
8.	4-5	4	2.18	1.11YR	6.05	8.85	2.59YR	6.40	7.99

relation to the hydroxy group located ortho to the azo group is important, as such dye chromophore can undergo azo-hydrazone tautomerism. The ratio between azo and hydrazone forms can be affected by the position of amino group in the coupling component. As shown in Scheme-2 the proportion of the hydrazone form is lower in H-acid azo dyes than in J-acid azo dyes and therefore have lower stability to photoreduction.

Good fastness to light of the dyes (1-8) had been ascribed to the deactivation of excited electronic states. The strong covalent bond between the dye and fibre seems to facilitate the transfer of energy from the excited dye molecule to the fibre resulting in increased stability of the reacted dyes [27].

The wash fastness of eight dyes had been presented in table-3. It has been found that the group of dyes depending on a nucleophilic displacement

reaction showed good stability toward washing as compared to dyes which act by nucleophilic addition. Dye # 4,8 had high fastness to washing as the dye molecule contain aminomonochlorotriazine as the reactive group which is more stable to washing since amino group is strongly electron releasing than the celluloseyl grouping.

The results of wet rubbing fastness of eight dyes had been shown in Table-4 and predicted that the dyeings from dyes # 1-8 did not have dye-hydrolysat with high degree of substantivity for non-covalently bonded reactive dyes and therefore there was no significant deterioration in fastness to wet rubbing. Minor changes in colour coordinates had been observed.

Table-5 and 6 shows the relationship between colour change and perspiration. The fastness to perspiration assessed by the Grey scale method

predicted that the severity of the effect depends on the structure of the dye in the vicinity of the reactive group. The bifunctional dyes that react by the nucleophilic addition mechanism form dye-fibre bonds that are less stable under alkaline conditions as compared to the reactive dyeings that contain dyes of the halohetrocyclic type which are sensitive to acid bleaching of the dyed material. The fastness of dyes # 4 and 8 had been found to be 4 after acid treatment whereas the other dyes had better fastness (4-5) to acid perspiration. The results for alkali treatment showed high fastness rating (4) for the dyes # 4 and 8 as compared to the other dyes which are sensitive to alkali and had low rating of fastness to perspiration (3-4).

The colour coordinates recorded for original and faded (treated) samples showed changes in

values. As shown in Table-1 higher values of L* are obtained for faded sample as compared to the original samples, which means a decrease in the depth of colour. In Tables 2-6 difference in values measured in terms of CIE LAB colour space is indicated as ΔE . Lower values of a* have been recorded for faded as compared to the original samples; whereas, the value of b* are higher for faded samples as compared to the original ones.

Marked changes in Munsell renotation are recorded for original and faded (treated) samples (tables 2-6). Higher values of lightness and lower values of chroma indicate that there is a clear trend in change of colours, the faded samples being paler than the original ones. The change in hue in all cases is in good agreement with the coordinates a* and b* as given in the Munsell book of colours [28].

Table-4: Fastness to Wet Rubbing and Colour Coordinates Before and After Treatment

Dye Ref #	Fastness to Wet Rubbing		ΔE %	Munsell rennotations					
	Change in Shade	Staining of cotton		Original			Treated		
				hue	lightness	chroma	hue	lightness	chroma
1.	4-5	4-5	1.90	3.40B	4.08	3.20	3.41B	4.09	3.18
2.	4-5	4-5	1.87	0.50B	4.85	3.51	0.52B	4.49	3.33
3.	4-5	4-5	1.84	6.81B	5.78	2.49	6.84B	5.81	2.19
4.	4-5	4-5	1.78	2.11RP	6.41	4.79	2.40RP	6.45	4.35
5.	4-5	4-5	1.72	6.99R	6.39	9.99	7.01R	6.41	9.61
6.	4-5	4-5	1.60	3.53R	4.44	8.24	3.58R	4.49	8.17
7.	4-5	4-5	1.56	3.64R	4.68	9.01	3.69R	4.70	8.88
8.	4-5	4-5	1.10	1.11YR	6.05	8.85	1.15YR	6.10	8.75

Table-5: Fastness to Perspiration and Colour Coordinates Before and After Treatment

Dye Ref #	Fastness to Perspiration ACID	ΔE %	Munsell rennotations					
			Original			Treated		
			hue	lightness	chroma	hue	lightness	chroma
1.	4-5	1.90	3.40B	4.08	3.20	3.41B	4.09	3.10
2.	4-5	1.87	0.50B	4.85	3.51	2.52B	4.49	3.33
3.	4-5	1.84	6.81B	5.78	2.49	6.84B	5.81	2.99
4.	4	1.78	2.11RP	6.41	4.79	2.40RP	6.45	4.35
5.	4-5	1.72	6.99R	6.39	9.99	7.61R	6.52	9.01
6.	4-5	1.60	3.53R	4.44	8.24	4.21R	5.21	7.77
7.	4-5	1.56	3.64R	4.68	9.01	4.10R	4.78	8.01
8.	4	1.10	1.11YR	6.05	8.85	1.31YR	6.10	7.99

Table-6 Fastness to Perspiration and Colour Coordinates Before and After Treatment

Dye Ref #	Fastness to Perspiration Alkali	ΔE %	Munsell rennotations					
			Original			Treated		
			Hue	lightness	chroma	hue	lightness	chroma
1.	3-4	3.5	3.40B	4.08	3.20	8.02B	4.20	3.11
2.	3-4	3.02	0.50B	4.85	3.51	3.79B	4.95	3.46
3.	3-4	3.12	6.81B	5.78	2.49	7.96B	6.02	2.15
4.	4	2.96	2.11RP	6.41	4.79	2.69RP	6.64	4.44
5.	3-4	2.88	6.99R	6.39	9.99	6.01R	6.93	9.83
6.	3-4	2.99	3.53R	4.44	8.24	4.85R	4.89	7.97
7.	3-4	3.11	3.64R	4.68	9.01	4.99R	5.11	8.38
8.	4	3.09	1.11YR	6.05	8.85	2.75YR	6.87	8.22

Similar results were reported by other authors who investigated and compared the fading of azo reactive dyes by light. It was found that the reactive dyes containing H-acid azo chromophore J-acid azo chromophore. The results suggest that a photo-oxidation mechanism operates when dyed fabric fade under light only [29]. Okada *et al.* also reported the potential photochemical properties for monochlorotriazinyl reactive dyes and their manifestation in the fading of dyed cellulose. They suggested that behaviour of dyes towards light fastness depended on the chemistry of the dyes and their interaction with the surroundings [21].

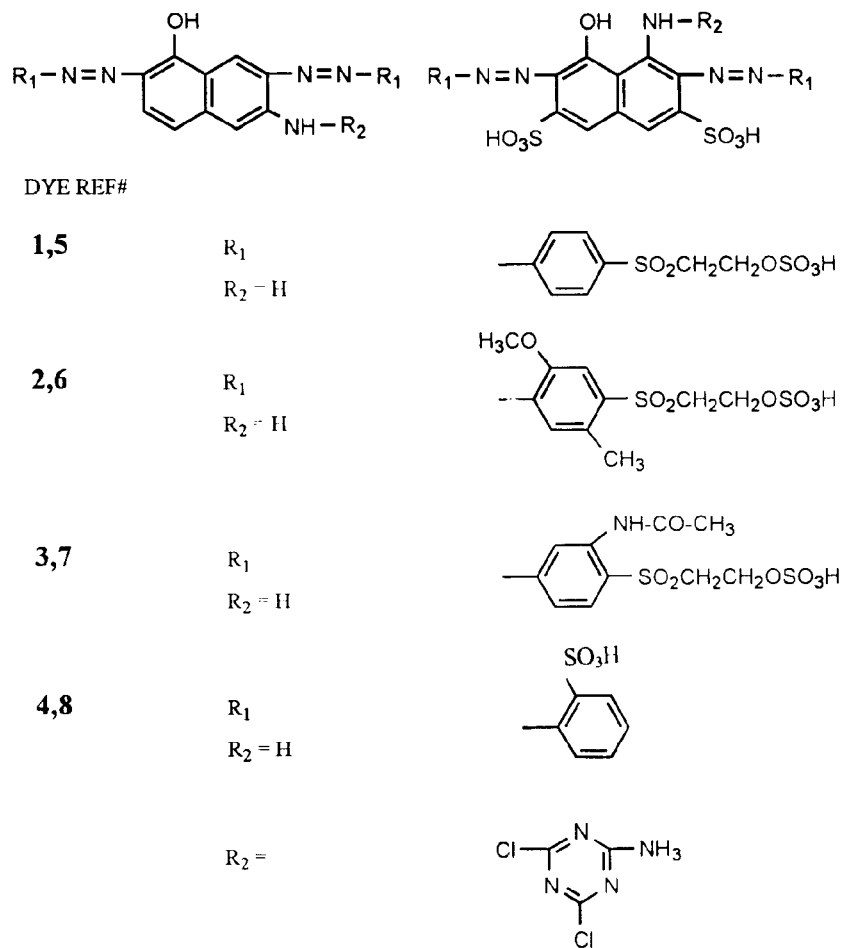
Experimental

Vinylsulphone and monochlorotriazinyl reactive dyes were synthesised by conventional

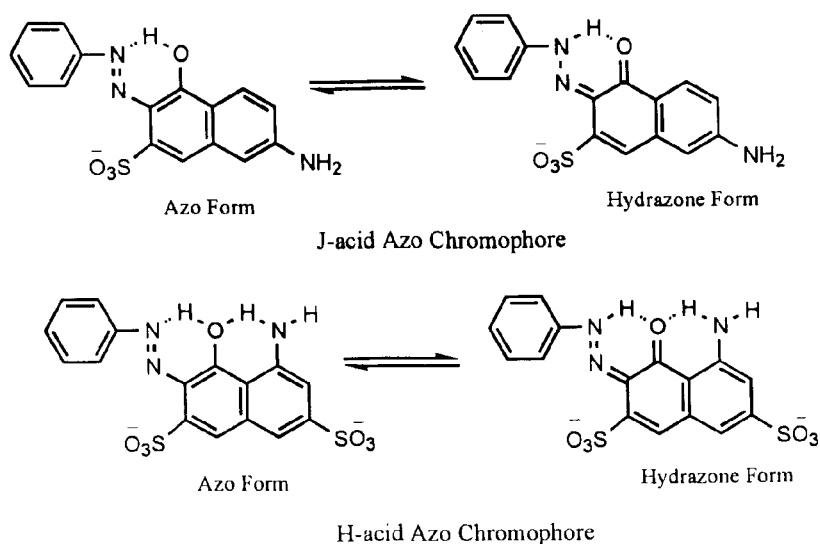
method of diazotization of amine and coupling with H-acid and J-acid. The amines used were: 1-amino-4-phenyl- β -sulfatoethylsulphone, 1-amino-[2-methoxy-5-methyl-4-phenyl]- β -sulfatoethyl sulphone, 1-amino-3-acetanilide- β -sulfatoethyl sulphone and orthoanilic acid. Cyanuric chloride was used to prepare monochlorotriazinyl dyes. The structures of the dyes are given in scheme-1.

Dyes

Azo reactive dyes were prepared on laboratory scale by coupling the diazo salts of the aromatic amines using H-acid and J-acid as coupling component, according to the conventional method of azo coupling. The dyes were purified by dissolving crude dyes in hot water and then extracting with butanol. The recrystallization from solvent yielded



Scheme-1: General structure of reactive dyes with different substituents



Scheme 2: Tautomerism in reactive dyes

pure dyes. The visible spectra of pure dyes were measured on the Hitachi Spectrophotometer and the results are indicated in table-1.

Dyeing of Fabric

Bleached 100% knitted cotton fabric was used for dyeing. The sample, weighing 2g was dyed in 200ml stainless steel beaker with reactive dye. Glauber's salt (6g) and sodium silicate (2g) were added to the dye liquor. For each dyeing the liquor volume was 80 ml. The amount of dye used was 2% based on the weight of fabric at a liquor ratio of 40:1. The samples were dyed with each dye for further studies.

Aftertreatment

After the completion of dyeing, the samples were treated to remove unfixed and hydrolysed reactive dyes. The washing was carried out at a liquor ratio of 30:1 according to the following sequence: (a) Cold rinsing for 5-10 minutes at 20-30°C (b) Acetic acid neutralisation (2-4 ml/L) for 5-10 minutes at 40-50°C (c) Hot rinsing for 5-10 minutes at 20-30 C (d) Detergent (1-3g/L) for 10 minutes (e) Warm rinsing for 5-10 minutes at 40-50 C and (f) Cold rinsing for 5-10 minutes at 20-30 C. The rinsing liquor was returned to the original dyebath and made up to standard volume for measuring the absorbance.

The exhaustion percentage (E) of the dyes on cotton was calculated according to equation -1

$$E = \frac{A_0 - A_t}{A_0} \times 100 \text{ ----- (1)}$$

Where A_0 and A_t are the absorbances of original and residual dye in the dyebath respectively. The results are presented in Table-1.

Fastness Testing

The dyed samples were tested according to ISO standard methods. The specific tests used were: ISO 105-BO2 (1988), colour fastness to daylight; ISO 105-CO2 (1989), colour fastness to washing; ISO 105-X 12 (1987), colour fastness to rubbing and ISO 105-EO4 (1989), colour fastness to perspiration.

Light Fastness

Samples dyed with reactive dyes and then aftertreated were air dried. Effect of light on samples was inspected by following the change in SDC internal standard (1-8) of blue wool for 24hr. The change in colour was assessed by comparing the SDC standards. The results of light fastness are given in Table-2.

Washing Fastness

In this test soap solution was prepared containing 5g/l and 2g/l sodium carbonate in distilled water. Each of the specimen (4cm x 5cm) was cut and placed between two adjacent white cotton fabric of the same dimensions and then stitched together. The composite was then placed in the container and necessary amount of soap solution previously heated to 60°C was added to give a liquor ratio of 50:1. Washing was carried out in an assembly which supports, radially, stainless steel container (75 ± 5mm x 125 ± 10mm high) of capacity 500 ± 50ml, the bottom of the container being 45 ± 10mm from the centre of the shaft. The shaft/container assembly is rotated at a frequency of 40 ± 2 min⁻¹. The temperature of the water bath is thermostatically controlled to maintain the test solution at the prescribed temperature ± 2°C. The washing was continued at this temperature for 30 minutes. The composite were then removed, rinsed, opened, dried and finally assessed with the aid of grey scales. The change in colour of the specimen and the staining of the adjacent fabrics was assessed with the grey scale. The results obtained are summarized in Table-3.

Wet Rubbing Fastness

This method is intended for determining the resistance of the colour of textiles of all kinds to rubbing off and staining other materials. For testing two pieces of fabric not less than 5cm x 14cm are required for wet rubbing. The test specimens are fastened by means of clamps to the base board of the testing device. With a rubbing cloth that has been wetted with water, rubbed it to and fro in a straight line along a track 10 cm long on the dry specimen, 10 times to and fro in 10 seconds, with a downward force on the finger. After rubbing, dried the cloth at room temperature and assessed the change in shade of the dyed specimen and the staining of the rubbing cloth with grey scale.

Fastness to Perspiration

Portions of dyed specimens (1.5 cm x 6 cm) were dipped into the artificial perspiration solutions at room temperature for 30 minutes and then nipped between glass rods to give 120 % wet pick-up. The wet samples were attached to a glass plate and placed in day light for 20hr. The degree of perspiration was judged using a grey scale for assessing colour changes.

Colour coordinates

The Tristimulus values and Chromaticity coordinates were recorded for all the dyed samples by using a colorimeter and the data is recorded in Table-1. Changes in colour brought about by sunlight exposure were also measured on the basis of CIELAB colour space in terms of L* a* b* (Cartesian coordinates) and Munsell notation, where

L* = lightness of sample

a* = redness/greenness of sample

b* = yellowness /blucness of sample

The difference in values obtained for original and faded samples were measured as ΔE and the results are given in Table-2.

Conclusions

All the samples studied showed negligible change in colour even after

80 hr of exposure. The rate and extent of change in colour (ΔE) and change in other colour coordinates was different for different dyes. Low values of ΔE (2.0 % -3.11%) indicated that the dyes have high resistance to light. Studies on reactive dyes have shown that in a dyed material the structure and chemical nature influence the light fastness.

In general, the rate of fading of reactive dyeings is directly related to the strength of the dye-substrate bond. The stability of the bonds formed by reaction of aminohalotriazine dyes with cellulose is exceptionally good. Vinylsulphone dyes, on the other hand, exhibited low fastness to washing and alkaline perspiration because the dye-fibre bond in this case is liable to alkaline hydrolysis. Good rub fastness of the dyes indicated that the contents of unhydrolysed dyes are very low. Thus, the results are substantially supported by the available literature.

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