

## Light Fastness of Bi-Functional Reactive Dyes with Pad-Batch and Pad-Dry Cure Methods on Cellulosic Substrate

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**Summary:** Two bifunctional reactive dyes containing two different reactive groups (sulphatoethylsulphone and monochlorotriazine) have been applied on cellulosic substrate with pad-batch and pad-dry cure methods and their light fastness was examined on Mercury Blended Tungsten Filament lamp at different time intervals. It was observed that the light fastness results obtained with pad-batch process were better than with pad-dry cure method. The colorimetric data clearly shows the extent to which the dyeing methods affect the light fastness in terms of fading of color from the original dyeings. Further, it was concluded that the addition of urea at a concentration of 100-120 g/l exhibited pronounced effect on light fastness of the dyed fabric with pad-dry cure method.

### Introduction

Reactive dyes are important in cotton dyeing, because of their excellent wet fastness and very wide color palette. Pad-batch and pad-dry cure are the two most widely used methods in the textile processing industry. The semi-continuous pad-batch process offers a means of producing moderate length typical of each color at low capital cost. In fact, this process is an exhaustive method carried out at extremely low liquor ratio and ambient temperature in which all the dye is entrained in the substrate. The impregnated batch is stored separately from the padding equipment and this allows wide variation of dwell time according to the reactivity of the dyes selected and the pH of the impregnated fabric [1-2]. Continuous dyeing represents the highest level of productivity, in which the dwell time after impregnation is reduced to a few seconds or minutes by heating the fabric to a high temperature. This approach however, entails much higher capital cost [3]. Current trends in the development of cotton dyeing with reactive dyes are in favor of semi-continuous and small scale continuous installation. In the present work, two bifunctional reactive dyes were used. These dyes mainly react with the hydroxy group in the cellulose chain either by nucleophilic substitution of a reactive chlorine atom (monochlorotriazine reactive site) or by nucleophilic addition (sulphatoethylsulphone reactive site) to an activated double bond [4]. Investigations have been made previously of the fading of reactive dyes bound to cellulosic fabrics. It was found that reactive dyes

applied to cotton by pad-batch method gave better light fastness compared with pad-dry cure method [5-6].

The aim of creating the CIE system is to tell us how a color might be reproduced (by a mixture of three primary light sources) rather than described. The amounts of the three primaries required to match a particular color provide a numerical specification of the color. A different color would require different amounts of primaries and hence the specification would be different. Some idea of the color seen can be deduced from CIE color specifications. Furthermore, we would never attempt to reproduce a color by actually mixing the CIE primaries. A color has a three dimensional property that is apparent in various ways. Color atlas arranges colors based on three-scale system combining hue, value and chroma, in the Munsell system [7].

Present paper reports on the fading of some bi-functional reactive dyes dyed by two different dyeing methods when exposed to Mercury Blended Tungsten Filament lamp at different time intervals and the changes, which occurred in their color coordinates.

### Results and Discussion

Dyeings with different depth of shades were prepared by both pad-batch and pad-dry cure

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methods. The effect of light (MBTF) on the fading and color change of reactive dyes on fabric has been investigated. The spectral characteristics and color coordinates were measured for original and faded samples.

#### Relation Between Dyeing Methods and Light Fastness

Light fastness is largely correlated with the dyeing methods. A relation between typical dyeing methods and light fastness is better shown in Figs. 1-4.

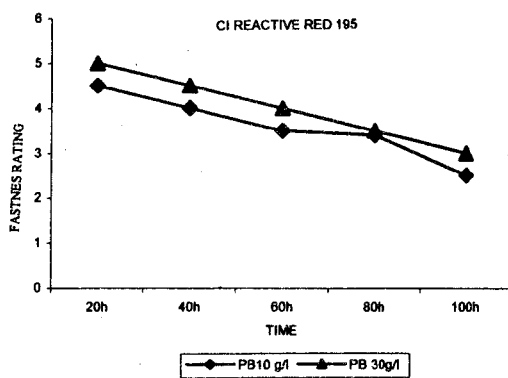


Fig. 1

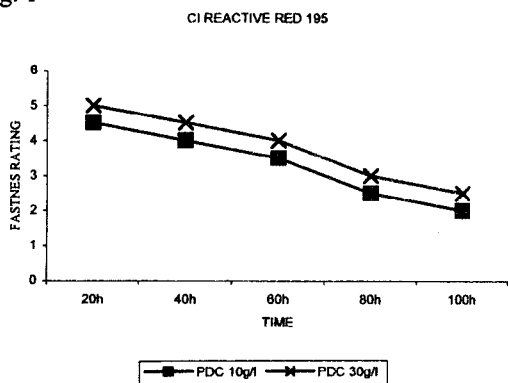


Fig. 2

Figs. 1-2: Color fading of C.I Reactive Red 195 at different concentrations

From the results given in Tables-1 and 2, it has been observed that dyeing by pad-batch method at concentrations of 10 g/l and 30 g/l offers better fastness to light as compared with dyeing by pad-dry cure method. This result is mainly due to low dyeing temperature and the process dwell time, which results in the complete diffusion of dye into the fiber and also an excellent

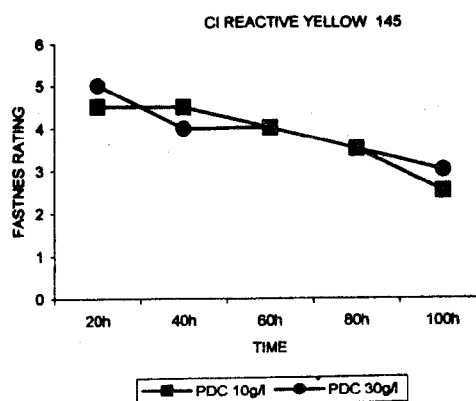


Fig. 3

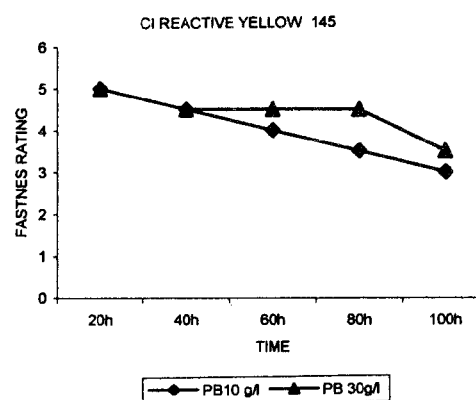


Fig. 4

Figs. 3-4: Color fading of C.I Reactive Yellow 145 at different concentrations

dye cellulose and dye-water reaction rate. Similarly, by increasing the exposure time the light fastness decreases. Pad-dry cure method caused more fading of a dye than pad-batch method. This poor light fastness may be attributed to short dyeing time and dry thermo fixation at temperature 150 °C~200 °C which results in the degradation of dye molecules [8- 9].

The color coordinates recorded for original and faded samples showed changes in values. Higher values of  $L^*$  are obtained for faded samples as compared to the original samples, which means a decrease in the depth of color. The fading gradually increases as the exposure time increase, which shows the depth of shade gradually decreases. When we compare both the dyeing processes, it is clearly observed that there is a

Table-1: Light fastness data and color coordinates of CI Reactive Yellow 145.

Dye Process/ Conc.	Hrs	CIE Lab			Munsell Renotation			Tristimulus Values			Chromaticity Coordinates	
		Light fastness	L*	a*	b*	c*	h	X	Y	Z	x	y
C.I Yellow 145 10g/l P.B	original	5	86.59	7.12	35.63	36.33	78.70	69.39	69.77	38.21	0.3912	0.3934
	20	5	86.89	6.38	32.21	35.56	80.56	67.73	69.17	40.61	0.3816	0.3897
	40	4~5	87.26	5.34	32.69	33.12	80.73	69.31	70.54	41.18	0.3829	0.3896
	60	4	87.51	5.33	31.76	32.17	80.84	69.71	71.05	42.35	0.3805	0.3880
	80	3~4	87.76	5.12	31.56	32.01	80.86	70.30	71.56	42.89	0.3805	0.3873
C.I Yellow 145 10g/l P.D.C	100	3	87.77	4.69	30.09	30.45	81.14	70.03	71.59	44.21	0.3769	0.3852
	original	5	83.25	8.44	40.54	41.39	78.31	64.83	64.55	31.07	0.4041	0.4023
	20	4~5	84.50	8.41	40.85	41.71	78.36	65.31	65.03	31.14	0.4045	0.4027
	40	4~5	84.60	8.38	40.62	41.49	78.27	63.89	63.57	30.39	0.4049	0.4027
	60	4	84.71	8.36	39.98	40.84	78.19	64.70	64.42	31.38	0.4031	0.4014
C.I Yellow 145 30g/l P.B	80	3~4	84.84	7.18	38.39	38.98	80.03	61.99	62.38	31.20	0.3985	0.4010
	100	2~3	84.97	6.78	37.01	37.70	80.43	65.45	65.72	34.39	0.3953	0.3970
	original	5	73.33	28.90	72.72	78.25	68.33	53.80	45.67	7.21	0.5043	0.4201
	20	5	73.50	28.22	71.67	77.02	68.51	53.81	45.92	7.57	0.5015	0.4280
	40	4~5	73.61	27.42	72.40	77.42	69.66	53.19	45.63	7.28	0.5013	0.4301
C.I Yellow 145 30g/l P.D.C	60	4~5	73.40	28.32	71.52	76.96	68.69	53.69	45.78	7.55	0.5017	0.4277
	80	4~5	73.72	27.69	71.52	76.69	68.84	53.35	45.69	7.54	0.5006	0.4287
	100	3~4	73.89	27.74	69.78	75.10	68.93	53.00	45.35	7.91	0.4988	0.4268
	original	5	66.60	35.74	75.45	83.19	65.45	45.64	36.34	4.07	0.5303	0.4223
	20	5	66.63	35.70	73.77	81.14	65.40	44.97	36.14	4.35	0.5262	0.4229
C.I Yellow 145 30g/l P.D.C	40	4	66.69	33.67	73.12	81.05	65.34	44.85	36.10	4.46	0.5251	0.4227
	60	4	66.73	33.53	73.65	80.93	65.22	45.04	36.28	4.40	0.5254	0.4232
	80	3~4	66.84	33.34	74.37	80.66	64.70	44.72	35.51	4.08	0.5304	0.4212
	100	3	67.90	33.15	73.94	80.45	64.36	45.61	36.66	4.45	0.5260	0.4228

Table-2: Light fastness data and color coordinates of CI Reactive Red 195

Dye Process/ Conc.	Hrs	CIE Lab			Munsell Renotation			Tristimulus Values			Chromaticity Coordinates	
		Light fastness	L*	a*	b*	c*	h	X	Y	Z	x	y
C.I Red 195 10g/l P.B	original	5	77.52	26.13	-7.82	27.28	343.34	59.98	52.40	64.81	0.3385	0.2957
	20	4~5	78.31	25.37	-6.92	26.29	344.05	60.55	53.23	64.74	0.3392	0.2982
	40	4	78.29	25.62	-7.31	26.65	344.59	60.25	52.86	64.76	0.3388	0.2972
	60	3~4	78.01	24.75	-6.74	25.65	344.76	60.27	53.22	64.54	0.3386	0.2989
	80	3~4	78.46	23.94	-6.40	24.49	344.85	58.83	52.29	63.07	0.3377	0.3002
C.I Red 195 10g/l P.D.C	100	2~3	78.47	23.61	-6.48	24.78	344.83	60.78	54.02	65.16	0.3377	0.3002
	original	5	68.40	34.99	-8.21	35.94	346.79	48.09	38.51	48.73	0.3554	0.2846
	20	4~5	69.14	36.53	-9.03	37.63	346.11	49.83	39.53	50.74	0.3556	0.2822
	40	4	69.76	34.84	-8.82	35.94	345.79	50.19	40.40	1.59	0.3530	0.2842
	60	3~4	70.06	34.02	-7.95	34.94	346.05	50.37	40.83	51.24	0.3536	0.2867
C.I Red 195 30g/l P.B	80	2~3	70.78	33.56	-8.14	34.53	346.37	51.36	41.86	52.65	0.3521	0.2870
	100	2	71.14	33.10	-8.24	34.11	346.01	51.78	42.39	53.39	0.3509	0.2873
	original	5	65.21	24.31	-5.21	25.81	326.41	43.89	43.21	57.82	0.3182	0.1851
	20	5	66.02	23.21	-5.18	24.91	326.79	44.76	40.39	57.95	0.2938	0.1868
	40	4~5	66.06	23.01	-5.02	24.06	326.82	44.89	40.24	58.36	0.3022	0.1888
C.I Red 195 30g/l P.D.C	60	4	68.12	21.56	-4.83	23.56	327.25	45.02	41.57	57.97	0.3082	0.1898
	80	3~4	68.41	21.78	-4.76	22.27	327.98	45.35	40.12	58.65	0.3017	0.1901
	100	3	68.62	20.98	-4.24	21.40	328.07	45.78	39.81	58.87	0.3014	0.1932
	original	5	39.88	55.79	-3.06	55.87	356.86	19.80	11.18	13.18	0.4484	0.2532
	20	5	40.45	56.18	-1.89	56.21	358.07	20.37	11.52	13.10	0.4528	0.2561
C.I Red 195 30g/l P.D.C	40	4~5	41.46	56.35	-2.71	56.42	357.60	21.32	12.16	14.14	0.4477	0.2562
	60	4	41.53	56.28	-2.36	56.33	357.60	21.37	12.20	14.05	0.4487	0.2562
	80	3	41.65	57.23	-3.04	57.31	356.96	21.67	12.27	14.41	0.4481	0.2538
	100	2~3	42.24	54.41	-3.37	54.52	356.45	21.61	12.66	14.99	0.4387	0.2569

marked difference in the value of  $L^*$  at same concentrations. In P.B the shade is lighter less saturated more greener but in the P.D.C method the shade is darker more saturated more greener. The difference between the shade *i.e.* lighter or darker, affects on chroma and hue of the resulting shade. The lower value of chroma indicates that the faded samples are paler than the original ones. Lower values of  $a^*$  and  $b^*$  have been recorded for faded as compared to original ones.

We also calculated the percentage difference of  $L^*$  between the original and faded samples. After 100hrs exposure the fading by P. B dyeing at a concentration of 10g/l is 1.362 % while at 30 g/l, is 0.763 %. Similarly, fading by P. D. C dyeing at a concentration of 10 g/l is 2.066 %, while at 30 g/l is 1.951 %. These results clearly indicate that light shades fade faster and darker shade fade slowly. It is also inferred that fading by P.B dyeing is less than the fading of P.D.C dyeing. In P.D.C, the curing energy gives the shade a redder tinge. These results are in good agreement with CIE Lab coordinates as given in Munsell book of color [10]. This finding further substantiates the effect of dyeing methods on light fastness of reactive dyes.

#### *Relation Between Dye Mass on the Dyed Fabric and Light Fastness*

Energy in the form of light is absorbed by the dye and causes some of its molecules to become unstable. They are in a so-called excited state and under these conditions, the dye may react with surrounding materials, such as oxygen in the air, or sometimes with the fiber itself, thus decomposing and losing its color [11].

Pad-dry cure process involves two steps: in the first step when the fabric is cured at 150 °C~200 °C some dye mass on the fabric is degraded. When this fabric is exposed to MBTF light, the dye observed on the fabric reacts with the surrounding oxygen which causes further degradation of the dye, which results in poor light fastness.

In the pad-batch process all the dye applied is subsequently fixed to the substrate and retains its original mass. Fading occurs only when the dye is exposed to MBTF light, which results in good light fastness.

#### *Relation Between Amount of Urea Addition and Light Fastness*

Urea mediates both the dyeing processes and is included up to a concentration of 100 g/l~150 g/l. Urea increases the solubility of the dye in the liquor, acts as a solvent for the dye during fixation (m.p 133 °C) and prevents browning of the cellulose fiber. The effect of urea concentration on light fastness is shown in Table-3. It is observed that in pad-dry cure method best light fastness results are obtained at a concentration of 100 g/l~120 g/l of urea. A further increase in urea concentration results in poor light fastness, which is suggested as the cause of the thermal degradation of urea at high drying temperatures (150~200 °C) which leads to loss of color strength. On the other hand in the pad-batch process, there is no chance of thermal degradation of urea. Hence, light fastness results are better for pad-batch than pad-dry cure method.

Table-3: Effect of urea on light fastness by PDC method using Reactive Red 195 and Yellow 145 at a concentration of 10 g/l.

UREA	CI Reactive Red 195		CI Reactive Yellow 145	
	60 Hrs	80 Hrs	60 Hrs	80 Hrs
80 g/l	3.5	3.5	4	3.5
100 g/l	4	3.5	4.5	4
120 g/l	3.5	3	4	3.5
140 g/l	3	2.5	3.5	3
150 g/L	2.5	2	3	2.5

#### **Experimental**

##### *Materials*

Scoured and bleached, fluorescent brightener-free woven cotton (118g/ m<sup>2</sup>, 1/1 plain weave) was used for dyeing. Two commercial dyes CI Reactive Yellow 145 and CI Reactive Red 195 were used. All the auxiliary products were of commercial samples.

##### *Equipment*

Pad dyeing was carried out by using a laboratory scale vertical Padder (Rapid). The samples were cured on a curing machine (Rapid). MBTF lamp [luminous efficiency = 20, correlated color temp/k = 3800° and color rendering index R =45] was used as a light source for the determination of light fastness. The color coordinates were recorded by using data color SF650X.

### Dyeing Procedures

For pad-batch dyeing the dyeing solutions were prepared by dissolving 10g / l and 30g / l dye in boiled distilled water. The dissolution of dye may be assisted by the addition of urea up to 100 – 150 g/ l. 10 g/ l sodium hydroxide of 50 Be for dark shade, 6 g/ l for light shade, and 70 g/ l of 45 Be sodium silicate were also added. The fabric was padded by the above mentioned dye solutions through a padder with 60~80 % pick up. The fabric roll was wrapped in a plastic sheet to avoid evaporation of water and was stored at room temperature for 12 ~18 hrs.

In the pad-dry cure process, the fabric was padded with a dye solution containing 2~4 g/ l wetting agent, 100~150 g/ l urea, 10~30 g/ l sodium carbonate and a small quantity of sodium alginate thickener at 20~30 °C. After padding the fabric was dried and fixation took place in hot air (1-2min at 150 °C~200 °C).

### Color Fastness to Light

The color fastness to artificial light of the dyed samples was done by exposing the fabric to MBTF light [12] at different time intervals. The color fastness was then assessed by comparing the change in color with that of the reference gray scale. Results are given in Fig. 1-4.

### Color Coordinates

The tristimulus values and chromaticity coordinates were recorded for all the dyed sample by using a colorimeter and the data is recorded in Tables-1 and 2. Changes in color brought about by light exposure were also measured on the basis of CIE lab color space in terms of L\* a\* b\* (Cartesian coordinates) and Munsell renotation.

Where

L\* = Lightness of sample.

a\* = redness/ greenness of sample.

b\* = yellowness/ blueness of sample.

### Conclusions

This study demonstrated that pad-batch process of dyeing gives much better light fastness

results than pad-dry cure process for a given amount of dye fixed on the same fabric. It is also observed that low temperature, long contact time, large amount of water also facilitate to improve the light fastness in the pad-batch process. Colorimeter properties also support the results obtained for the two dyeing methods. Furthermore the thermal degradation of urea under dry conditions (Dry heat effect) is the main contributing factor in lowering the light fastness to some extent. In order to minimize the effect of urea on light fastness by pad-dry cure method, it is found that an optimum quantity of urea, 100-120 g/ l, is required. This study provides a basis for future assessment of the fact that pad-batch process supersedes pad-dry cure process in terms of energy consumption and chemicals used which ultimately reduce the production cost.

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