

## Study of Color Parameters of Light Exposed and Light Unexposed Wool Fabrics Dyed With 1:1 Chromium (III) Based Complex Dyes

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**Summary:** Derivatives of *o*-amino benzoic acid (anthranilic acid) were synthesized using 1-naphthol-3,6-disulfonic acid, 1-Naphthol-8 amino-3, 6-di-sulfonic acid; 1-naphthol-3-sulfonic acid, 6-methylamino-1-naphthol-3-sulfonic acid or 1-naphthol-3-sulfonic acid, 6-phenylamino-1-naphthol-3-sulfonic acid as a coupling component. These derivatives were used to synthesize chromium (III) complexes. After isolation, these complexes were applied on pure wool fabric by exhaust process to evaluate hue, wash fastness and light fastness properties. The complexes delivered a change in color equivalent to gray scale step 3/5 to 4/5 for wash fastness test. During the study of light fastness, it was monitored that the hue of dyed fabrics enhanced after exposing them to light.

### Introduction

It is well known that metal complexes of chromium and cobalt are widely used to dye wool, polyamide fibers and blends of both these fiber with excellent light and wash fastness properties [1, 2]. Nevertheless, high migration and leveling capacity, the brighter hues compared with mordant dyes, and the single-bath dyeing process, the 1:1 chromium complexes are of commercial interest. In addition, metal-complexes are also preferred in high technology areas such as lasers, electro-optical devices and ink-jet printers [3-7]. The present study is focused on to develop a series of 1:1 chromium (III) mono azo complexes by following the well-known literature procedures [8, 9] and applied them on wool fabric for evaluating the effect of changed coupling component of the chelating ligand on the dyeing properties and color parameters of the dyed fabric. The color parameters were measured on a color measuring system (Datacolor Spectraflash SF650X) using reflectance method, that is mainly used for quantifying color sensationally and comparison of color difference in the field of textiles [10].

### Results and Discussion

Metal-complex dyes are very versatile in term of applications. Virtually all substrates apart from a few synthetic fibers can be dyed and printed with this class of dyes. Countless shades can be

generated depending upon the metal, the dye ligand and the combination of dye ligands in mixed complex dyes. In commercial terms, most important chelated metals are chromium, cobalt, copper, iron, and nickel but for textile fibers, only the chromium, cobalt, and copper complex dyes achieve desired technical effects [11]. By far the most important and widely used metal-complex dyes are derived from azo compounds. The most useful starting materials are amines, which serve as diazo components for reaction with suitable coupling components to give tridentate azo ligands. So azo dyes were developed using *o*-amino benzoic acid (anthranilic acid) as a diazo component and 1-naphthol-3, 6-disulfonic acid, 8 amino-1-naphthol-3-sulfonic acid, 6-methylamino or 1-naphthol-3-sulfonic acid, 6-phenylamino as a coupling component [8]. These azo dyes were refluxed separately with a chromium (III) chloride salt to obtain the 1:1chromium (III) complexed mono azo dye I-III, Fig. 1. The variable part of the complexes is the component used to couple diazotized anthranilic acid. The use of 1-naphthol-3, 6-disulfonic acid, 8 amino; 1-naphthol-3-sulfonic acid, 6-methylamino or 1-naphthol-3-sulfonic acid, 6-phenylamino as a coupling components leads to shift the absorption maximum of the aqueous solution of the azo-metal chelates, Table-1. This class of dyes is applied on the substrate under strong acidic conditions in the presence of Glauber's salt and dyeing is carried out to near boiling for 60 to 90

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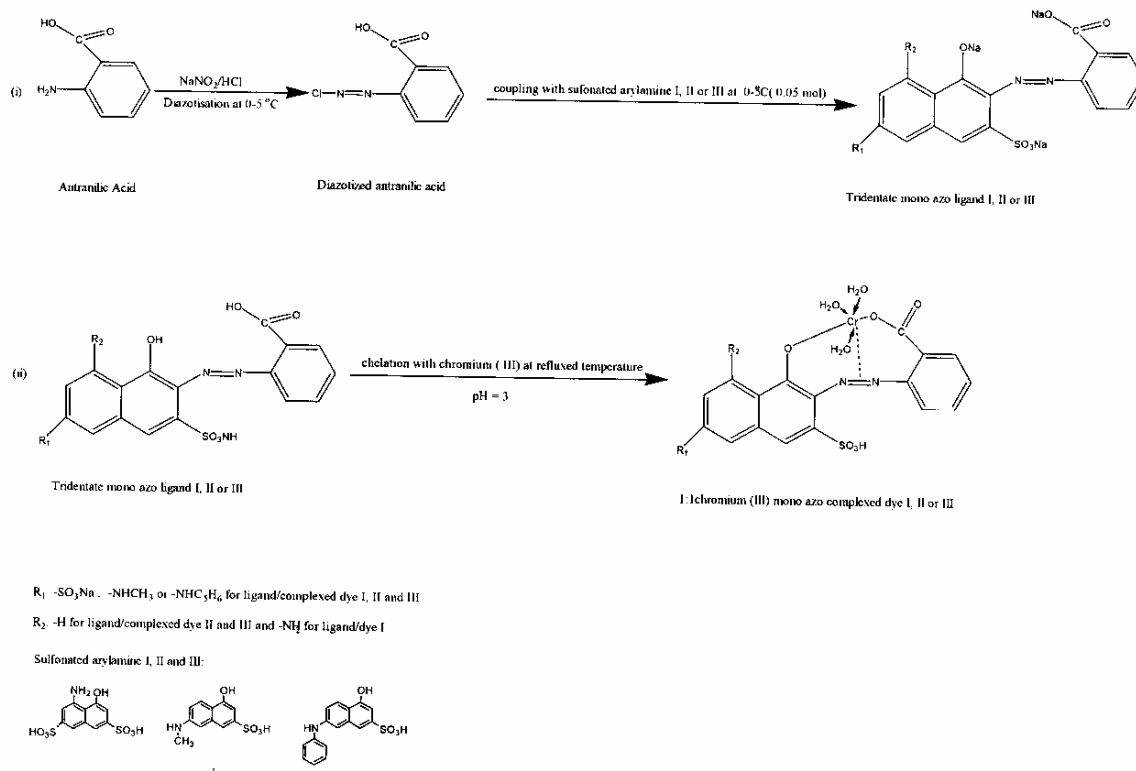


Fig. 1: Reaction scheme to synthesize 1:1 chromium (III) complexed mono azo dyes I-III.

Table-1: Yield,  $R_f$  and  $\lambda_{max}$  of derivatives of *o*-amino benzoic acid.

Specification	Coupling components	Metal	<sup>a</sup> Color of the aqueous solution	Yield %	<sup>b</sup> $R_f$	<sup>b</sup> $\lambda_{max}$ in water (nm)
Tridentate ligand I	1-naphthol-3,6-disulfonic acid,8 amino	-	Dark Orange	95	0.30	503
Tridentate ligand I	1-naphthol-3-sulfonic acid, 6-methylamino-	-	Orange red	81	0.58	510
Tridentate ligand I	1-naphthol-3-sulfonic acid, 6-phenylamino	-	Deep red	59	0.57	525
1:1 chromium (III) complexed mono azo dye I	1-naphthol-3,6-disulfonic acid,8 amino	Cr (III)	Purple	92	0.47	557
1:1 chromium (III) complexed mono azo dye II	1-naphthol-3-sulfonic acid, 6-methylamino	Cr (III)	Red	87	0.55	503
1:1 chromium (III) complexed mono azo dye III	1-naphthol-3-sulfonic acid, 6-phenylamino	Cr (III)	Reddish brown	64	0.74	556

<sup>a</sup>0.0150g/50 ml, 0.03 % <sup>b</sup>BuOH:EtOH:NH<sub>4</sub>OH:pyridine/4:1:3:2

minutes [14]. In acidic dye liquor, the anion of the dye (I, II or III) binds to the ammonium cation, formed from the amino end groups of the wool fabric. In dye II and III only one anionic group is attached to form ionic bond between the anion of the dye molecule and the positively charged quaternary amino group of the fabric that lead the lower exhaustion and fixation rates as compared to dye I that containing two anionic groups (Table-2). The percentage of dye fixation was found lowest for dye

III, because of the phenyl group attached with the amino group of the dye molecule. It rapidly promotes the formation of Switterion -SO<sub>3</sub><sup>-</sup> - NRH<sub>2</sub><sup>+</sup> (R = -C<sub>6</sub>H<sub>5</sub>) that caused to split the ionic bond of the dye molecule with the cationic group of the fabric. Surprisingly when we exposed dyed samples to light to assess the fastness property to light according to a standard test method (AATCC 16 E: 1998) the depth of all dyed wool fabrics enhanced. Definitely, the exposure of dyed fabrics to light promotes the

Table-2: Application of dyes I-III on wool fabric at 1% depth of shade to study dye ability and fastness properties.

Dye	Visual color shade	A <sub>1</sub>	A <sub>2</sub>	(K/S) <sub>AS</sub>	(K/S) <sub>BS</sub>	% E	% F	% T
I	Brown	3.466	0.066	21.30	22.90	98	93	91
II	Reddish Brown	4.053	0.152	18.50	20.79	96	89	85
III	Golden Brown	2.321	0.201	28.00	37.33	91	75	68

formation of the coordinate bond between the lone pair of amino group of the wool and the chromium mono positive ion of the complex. The recorded color parameters tabulated in the Table-3 are supporting the visual observations.

### Experimental

#### Materials and Methods

Chemicals used in this study were obtained from the Aldrich, Sinochem and Clariant Textile Chemical Companies. Wool fabric (Wool Jersey Knit Fabric, lot # 3670, style # 532, Testfabric, Inc. USA) was purchased from S. R. Traders, Anarkali, Lahore. Thin layer chromatography (TLC) was conducted using silica gel, GF<sub>254</sub> (coated on 20 x 20 cm glass plates). The pH of dyeing bath was set using a calibrated pH meter, HANNA Instruments HI 8314. The fabrics were dyed in IR dyeing machine, SDL. Necolet Evaluation 100 Spectrophotometer was used to record ultra violet and visible (UV-visible) absorption spectra. The reflectance of fabrics were measured on a calibrated color measuring system interfaced with color tools QC software, Datacolor Spectraflash SF650X (USA) in order to determine the color parameters, color difference and color strength values (K/S). The light fastness test was performed in the Weather-Ometer Ci3000, SDL ATLAS using xenone arc light for 20 hr (test method, AATCC 16 E :1998). The change in color was assessed in a color assessment cabinet, Verivide G210, under the illuminant D<sub>65</sub>. Tested fabrics were rated by using Gray Scale for assessing change in color and Gray Scale for assessing stain (BSI, 3 York Street Manchester M2 2AT).

#### Synthesis of 1:1 Chromium (III) Complexed Mono Azo Dye I, II and III

*o*-amino benzoic acid, commonly known as anthranilic acid (0.05 mol) was diazotized and coupled with 1-naphthol-3, 6-disulfonic acid, 8 amino; 1-naphthol-3-sulfonic acid, 6-methylamino or 1-naphthol-3-sulfonic acid, 6-phenylamino (0.05 mol) to obtain anthranilic acid based, tridentate ligands I - III, respectively [8, 9]. It was isolated by adding NaCl to effect precipitation. The precipitated ligand (I, II or III) was collected by filtration and dried. It was further purified by dissolution in dimethylformamide (DMF), followed by filtration to eliminate the salt contents. Dropping the filtrate in acetone precipitated the pure ligand. It was filtered, washed three times with acetone and finally dried at 60 °C. The Purified tridentate mono azo ligand I, II or III (0.002 mol) was dissolved in water and refluxed with chromium (III) chloride hexahydrated (0.002 mol) at pH 3 to obtain 1:1 chromium (III) mono azo complexed dye I, II or III, respectively. The progress of the reaction was followed by thin layer chromatography (BuOH:EtOH:NH<sub>4</sub>OH:pyridine/4:1:3:2), data is tabulated in Table-1. The reaction mixture was precipitated at pH 6, filtered hot and washed in ethyl alcohol twice. The IR spectra of 1:1 chromium (III) complexed mono azo dye I, II and III showed a broad band peak in the range of 3407-3430 cm<sup>-1</sup> due to the -OH stretching vibration of water of hydration. The distinct band appearing in the 755-760 cm<sup>-1</sup> region in all complexes is typical of Cr-O stretching. The proposed molecular structures of the synthesized dyes I-III, on the basis of theoretical evidences is shown in Fig. 1 [8, 9, 12, 13].

Table-3: Study of color parameters of light exposed and light unexposed dyed fabrics.

Dye	Fabric's face to light	L	a	b	c	h	X	Y	Z	ΔE
I	Unexposed	34.75	8.95	7.89	11.93	41.41	08.96	08.38	6.77	2.16
	Exposed	34.07	9.21	06.60	11.33	35.60	08.64	08.04	6.80	
II	Unexposed	27.12	21.08	08.62	22.77	22.25	06.72	05.14	3.81	1.90
	Exposed	25.98	22.36	07.95	23.73	19.58	06.37	04.74	3.59	
III	Unexposed	44.93	13.88	37.35	39.84	69.61	16.04	14.49	4.16	11.73
	Exposed	51.38	07.19	45.59	46.16	81.03	20.00	19.60	4.72	

*Application of Dyes on Wool Fabric*

The fabric was prepared for dyeing by scouring in a solution of nonionic detergent, Lissapol N (0.5g/liter) and common salt, sodium chloride (1 g/l) at 50 °C for 45 minutes using liquor ratio 1: 50 and rinsed several times to wash out contaminants of detergent and sodium chloride. The wetted out fabric (2 grams) was introduced to the dyeing pot containing 54 ml aqueous solution containing Glauber's salt [10 % on the weight of fabric, (owf)] and sulphuric acid (enough to maintain pH of dyeing bath at 3) at 40 °C and agitated for 10 minutes, then dye solution (0.04 gram/ 6 ml of distilled water) was added and agitated again for 10 minutes [14]. Dyeing pot was mounted in the dyeing machine and the temperature was increased to 80 °C at a rate of 3 °C/min. The fabric was allowed to rotate in the dyeing pots (20 rounds per minutes) for 60 minutes then cooled to room temperature at a rate of 3 °C/min by keeping the rotation on. The dyed fabric was rinsed several times with hot distilled water (50 °C) to wash out un-exhaust dye and finally squeezing the fabric. The solution of each dye bath and the rinsing bath were recovered for colorimetric measurements in order to determine the quantity of un-exhaust dye. For the study of percentage fixation of dye, half part of the dyed fabric was soaped with nonionic detergent, Lissapol N (5 g/l) using fabric to liquor ratio 1:50 at 50 °C for half an hour then rinsed under running tap water for 10 minutes. The dyeing cycle is shown in Fig. 2.

*Exhaustion*

The percentage degree of exhaustion (%E, percentage of the dye absorbed or chemically bounded to the fabric) was measured by sampling the dye bath before and after the dyeing process. The absorbance value of a dye-liquor sample was measured at its wavelength of maximum absorbance using UV/Visible spectrophotometer and the exhaustion value was calculated using equation 1 [15].

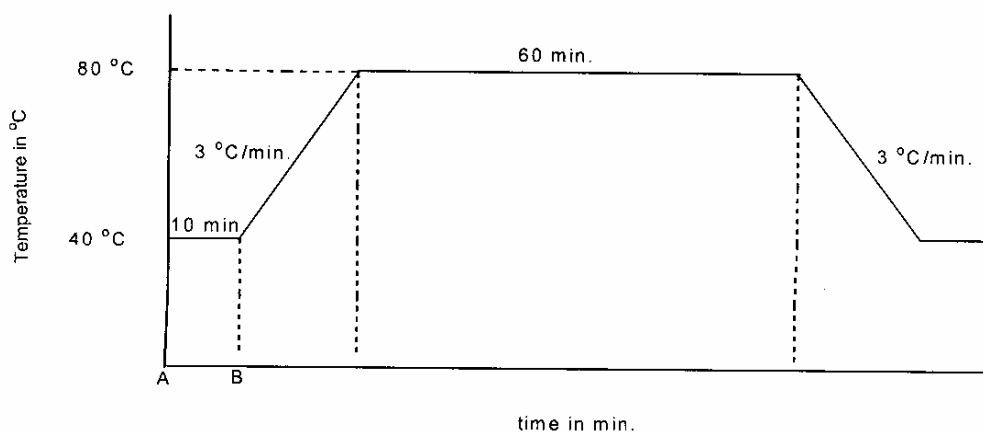
$$\% E = [1 - (A_2/A_1)] \times 100 \quad (1)$$

where  $A_1$  and  $A_2$  are the absorbance values of the diluted dye solution, before and after the dyeing processes, respectively.

*Fixation*

In order to determine the percentage fixation of each dye (the percentage of dye chemically bounded to the fabric), the half part of the dyed sample was retained and not processed for soaping and rinsing. The color strength values (K/S) of the dyed samples before and after soaping were determined on a calibrated color measuring system interfaced with color tool v3.1.2 software, (Datacolor Spectraflash SF650X, USA) using CIE supplement 10° observers and illuminant D<sub>65</sub>. The formula is used to calculate the color strength values (K/S) value is,

$$K/S = (1-R)^2/2R \quad (2)$$



A = Na<sub>2</sub>SO<sub>4</sub> (10% owf), H<sub>2</sub>SO<sub>4</sub> (enough to maintain a pH at 3) /54 ml aqueous solution and wool fabric  
B = Dye solution/6 ml H<sub>2</sub>O

Fig. 2: Dyeing cycle to apply dye I, II or III (1% owf) on wool.

Table- 4: Study of washing fastness and light fastness.

Dye	Change in shade due to light fastness test	Change in shade	Washing fastness test					
			Acetate	Cotton	Staining			Wool
					Nylon	PES	Acrylic	
I	7	4/5	5	5	4/5	5	5	4/5
II	4	4	5	5	4/5	5	5	4/5
III	3	3/4	5	5	4/5	5	5	3/4

where R is the reflectance of dyed fabric before or after soaping at the wavelength of maximum absorption ( $\lambda_{max}$ ) of dye.

Finally, the fixation of each dye on fabric in percentage was calculated using the Kubelka-Munk equation 2 [16].

$$\% F = [(K/S)_{\text{after soaping}} / (K/S)_{\text{before soaping}}] \times 100 \quad (3)$$

#### Fixation Efficiency

The overall fixation efficiency (% T, the amount of dye originally applied which is covalently fixed) was calculated using equation 3 [15].

$$\% T = (\% F \times \% E) / 100 \quad (4)$$

#### Color Measurements

The color parameters of dyed fabrics were determined from its daylight reflectance Y and chromaticity coordinate x and y, in CIE system, Datacolor Spectraflash SF650X (USA). Before recording the data for samples, the color measuring system was calibrated as per instructions stated in the operational manual of the color measuring system. The recorded values of Y X Z and L a b for each fabric are the mean value of four readings that were taken by rotating the dyed fabric by 90, 180, 270 and 360 degree angle from a fixed point. Color difference was calculated using the formula given as under by comparing the un-exposed dyed fabric with the mean L a b value of target fabric that was exposed dyed wool fabric [17].

$$\Delta E (H) = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

#### Fastness Tests

Washing and light fastness were determine using standard method of ISO CO1, BS 1006:1990 and AATCC 16 E-1998. The data were tabulated in Table-4. Light fastness rating was accomplished by evaluation versus a simultaneously exposed series of

AATCC blue wool light fastness standards 1-8. These standards are exposed simultaneously to ensure the equipment and the test procedure variation. The test result of the exposed blue wool standard 4 was determined as 4 on Gray Scale for assessing change in color, that is not different from the standard procedure requirement.

#### Conclusion

The developed 1:1 chromium III based azo dyes showed excellent results for wash and light fastness properties and these are suitable to dye wool substrate. In additional, exposure of dyed fabric to light enhanced the depth of the shade it is confirmed because the unexposed dark part of the blue wool standard 7, 4 or 3 was always matched to the exposed part of the dyed wool fabric dyed with dye I, II or III, respectively. This property makes them suitable to dye those fabrics that remain for longer time under the sunlight such as cover of the vehicles or other stuff.

#### References

1. K. Venkataraman, *The Chemistry of Synthetic Dyes*, Academic Press, New York and London, **3**, 303 (1970).
2. I. J. Wang, Y. H. Husu and J. H. Tian, *Dyes and Pigments*, **16**, 83 (1991).
3. P. Gregory, *High-Technology Applications of Organic Colorants*, Plenum Press, New York and London, p. 1 (1991).
4. B. R. Hsieh, *Dyes and Pigments*, **14**, 165 (1990).
5. H. Kocaokutgen and S. Özkinalı, *Textile Research Journal*, **74**, 78 (2004).
6. A. T. Peters and H. S. Freeman, *Colour Chemistry. The Design and Synthesis of Organic Dyes and Pigments*, Elsevier App. Sci. Publ., Barking Essex, p. 193 (1991).
7. S. C. Catino and R. E. Farris, *Azo Dyes*, M. Grayson, Editor, Concise Encyclopedia of Chemical Technology, John Wiley & Sons, New York, p. 142 (1985).
8. K. M. Shah, *Application, Usage of Dyes and*

- Pigments on Textiles, Handbook of Synthetic Dyes and Pigments, Synthetic Dyes Vol. I, Multi-Tech Publishing Co. Ghatkopar (East), Mumbai, India, p. 99 (1998).
9. E. N. Abrahart, *Dyes and their Intermediates*, Edward Arnold Ltd., London, p. 109 (1977).
  10. A. R. Priemon, J. L. Cornillot and Assistant Editors, Annual Book of ASTM Standards, Vol. 06.01, Easton, MD, USA, p. 240 (1983).
  11. K. Hungr (editor), in *Industrial Dyes*, Wiley-VCH Verlag GmbH & Co. KgaH, Weinheim, Germany, p. 302 (2003).
  12. K. Hungr (editor), in *Industrial Dyes* Wiley-VCH Verlag GmbH & Co. KgaH, Weinheim, Germany, p. 16 (2003).
  13. E. N. Abrahart, in *Dyes and their Intermediates*, Edward Arnold Ltd., London, p. 108 (1977).
  14. K. M. Shah, in *Application, Usage of Dyes and Pigments on Textiles, Handbook of Synthetic Dyes and Pigments, Synthetic Dyes Vol. I, Multi-Tech Publishing Co. Ghatkopar (East), Mumbai, India, p. 257 (1998).*
  15. D. M. Lewis and J. Yao, *Journal of the Society of Dyers Colourists*, **116**, 285 (2000).
  16. R. M. El-Shishtawy, Y. A. Youssef, S. E. A. Nahed and A. A. Mousa, *Coloration Technology*, **120**, 195 (2004).
  17. A. K. R. Choudhury, in *Modern Concepts of Color and Appearance*, Oxford & IBH Publishing Co. Pvt. Ltd., New Delhi, India, p. 197 (2000).