Application of Acid Dyes on Nylon Fabric and Evaluation of Fastness Properties Part III

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Summary: A series of novel acid dyes, based on substituted aryl amines as diazo component and aminohydroxy-naphthalene sulfonic acid as coupling component were explored for their dyeing performance over nylon fabric. The dyes were applied on fabric by exhaust dyeing procedure and the resulting dyed fabrics were characterized for washing, light, perspiration and rubbing fastness properties. The results revealed excellent fixation, binding strength and fastness properties which indicate that the newly synthesized dyes are suitable for dyeing nylon fibers.

Keywords: Acid dyes, Synthesis, Fastness Properties, Nylon, Dyeing.

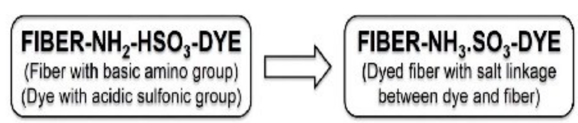
Introduction

Acid dyes are commercially important class of dyes frequently employed for dyeing various natural and synthetic fibers. They drive their name from the fact that they contain acidic moieties (such as $–SO_3H$). Besides, the dyeing process is often carried out in a low pH conditions (pH: 2-6) [1]. Similar to direct dyes, acid dyes are also water-soluble anionic dyes with a general formula RSO_3Na. However, in contrast to direct dyes, they are either ineffective or give poor results on cellulosic fibers [2]. Chemically, acid dyes contain a chromophore as an acidic group, usually $–SO_3H$ in the form of sodium salt that are soluble in water [2, 3]. Most important acid dyestuffs are sulphonic acid derivatives of azo dyes [3]. The practical uses of these dyes are characterized by their capacity to dye protein and polyamide based fibers such as Wool, Silk, Angora, Alpaca, Mohair and Nylon.

Chemically, acid dyes react with fibers that contain ionizable moieties, such as amino and carboxyl groups which can be ionized to NH^{3+} and COO^-, respectively [3]. Under certain conditions, they may be used for dyeing polyacrylonitrile fibers [3, 4]. The interactions between the dye and fiber are thought to be hydrogen bonding, van der Waals forces and ionic bonding [3]. Wool, silk, nylon and protein based natural fibers also have amino groups that can form bond with acid dyes using salt linkages (Scheme-1).

Belonging to the polyamide family, nylon possesses several amide groups in the main chain along with free terminal amine groups. These groups provide excellent hydrogen bonding sites and are believed to be responsible to impart substantivity towards various classes of anionic dyes [3]. Under acidic conditions, the terminal amino groups in the fiber become protonated. Fixation of acid dyes on polyamide fibers proceeds through electrostatic interaction between anionic moieties in the dye molecule (such as sulfonate) and the protonated amino groups in the fiber [3].

This work investigates the dyeing performance on nylon fibers, of a series of novel acid dyes. These dyes were previously synthesized in our laboratory using substituted aryl amines as diazo component and aminohydroxy-naphthalene sulfonic acid as coupling component [5]. After synthesis and purification by conventional procedures, the synthesized dyes were thoroughly characterized by routine analytical procedures prior to their application on nylon. The dyes were applied on nylon fabric by exhaust dyeing process and the resulting dyed fabrics were characterized using standard ISO procedures for washing fastness, rubbing fastness, light fastness and color fastness to perspiration. The results revealed good dyeing performance and fastness properties and it was therefore concluded that the newly synthesized dyes are suitable for dyeing nylon fibers.



Scheme-1: Interaction of acid dyes with fiber

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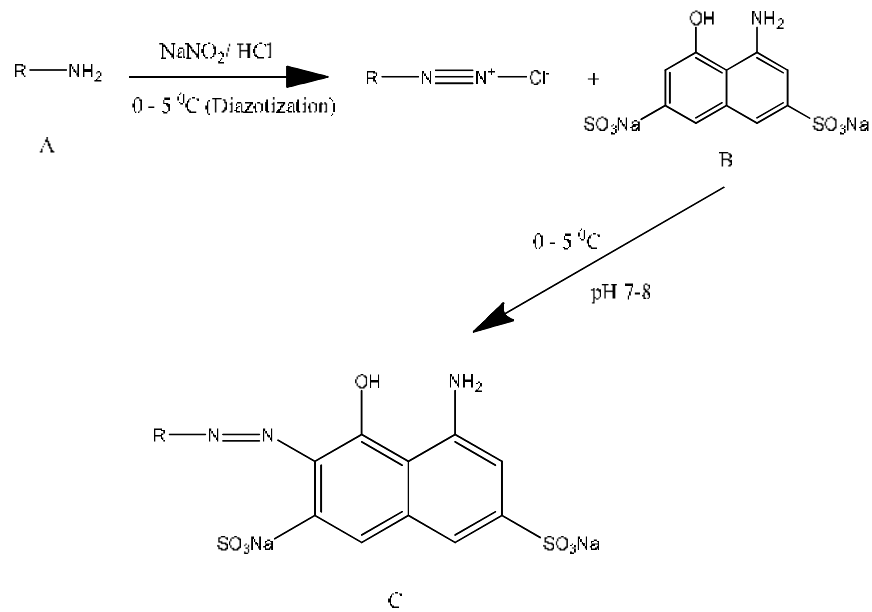

Scheme-2: Dye Formation Reaction [5].

Table-1: Diazo and coupling components [5].

Dyes Code	A	A Diazo Component	B	B Coupling Component
C1	A1	2- Methoxyaniline -5- sulfonic acid	B1	1-Amino-8-naphthol-3,6-disulfonic acid (H-acid)
C2	A2	4- Amino-acetophenone	B2	1- Amino-8-naphthol-3,6- disulfonic (H-acid)
C3	A3	3- Amino acetophenone	B3	1- Amino-8-naphthol-3-, 6- disulfonic acid (H-acid)
C4	A4	3- Amino sulfonic acid	B4	1- Amino -8- naphthol-3, 6- disulfonic acid – (H-acid)
C5	A5	4- Amino sulfonic acid	B5	1- Amino-8-naphthol-3,6- disulfonic acid (H-acid)
C6	A6	4- Amino sulfonic acid	B6	1- Aminoacetye-8-naphthol-3,6- sulfonic acid (N-Acetyl H-acid)
C7	A7	3-Amino sulfonic acid	B7	1-Aminoacetye-8-naphthol-3,6- disulfonic acid (N-Acetyl H-acid)
C8	A8	4-Aminoacetophenone	B8	1-Aminoacetye-8-naphthol-3,6- disulfonic acid (N-Acetyl H-acid)
C9	A9	3-Aminoacetophenone	B9	1-Aminoacetye-8-naphthol-3,6- disulfonic acid (N-Acetyl H-acid)

Experimental

Material and Characterizations:

All the employed reagents and solvents were of technical grade. UV-visible spectroscopy was performed on a Spectromiczo Baush and Lomb spectrophotometer using de-ionized water as solvent. Dyeing was carried out on an I. R dyeing machine (Roaches Int.) equipped with a touch-screen control system.

Synthesis of compounds

Nine different acid dyes were synthesized using substituted aryl amines as diazo component and aminohydroxy-naphthalene sulfonic acid as coupling component. A detailed synthesis procedure and the structure elucidation of the resulting dyes using routine analytical techniques such as FTIR, UV-Visible, ^{1}HNMR and Maldi-TOF (negative ion mode) mass spectroscopy are already reported in our earlier publication [5]. A general synthesis procedure is depicted in Scheme-2 and the corresponding diazo (A) and coupling components (B) are all listed in Table-1.

Application of acid dyes on Nylon fabric

The newly synthesized dyes (C1-C9) were applied on nylon fabric by exhaust dyeing process following a previously described procedure [5]. Briefly, scoured and bleached nylon fabric was dyed using 1% of dye based on the weight of fabric (o.w.f.). With liquor-to-fabric ratio of 1:20 and the pH of the dyeing bath was maintained between 2.5 and 3.5, respectively. The temperature of the dye bath was gradually raised to 60 $^{\circ}$C at a gradient of 2 $^{\circ}$C/min. The Glauber's salt was added and the temperature was further raised to around 90 $^{\circ}$C. After attaining desired temperature and the dyeing process was continued for another 30 minutes. The dye bath was then removed and the dyed fabric was washed with cold water, followed by a hot wash at 50 $^{\circ}$C using a nonionic detergent. The washed, dyed fabric was then air-dried at room temperature before any further characterization.

Fastness properties

Various fastness properties such as wash fastness (ISO 105 C06 C2S:1994 (E)), light fastness

(ISO 105 B02:1988 (E)), color fastness against rubbing (ISO105-X12:1993 (E)), color fastness to perspiration (ISO 105 - E04:1994 (E)) were evaluated using the mentioned standard ISO procedures and SDC laboratory consumables. The CIE color coordinates were recorded on a Datacolor Spectroflash SF-600 spectrophotometer.

Determination of dyebath exhaustion and color strength

The percentage dyebath exhaustion (%E) was determined spectrophotometrically by measuring the absorbance at λ_{max} of the dyebath, before and after the dyeing process using a UV/visible spectrophotometer. If A_1 and A_2 represent the absorbance of the dyebath before and after dyeing, respectively, the % exhaustion (% E) can be calculated using [6]:

$$\%E = \frac{A_1 - A_2}{A_1} \times 100$$

The color strength (K/S) values of the dyed fabric (before and after wash) were calculated by measuring the light reflectance using Datacolor spectrophotometer and then applying the Kubelka-Munk equation:

$$K/S = \frac{(1-R)^2}{2R}$$

where K and S represent the absorption and scattering coefficients, respectively, and R is the decimal fraction of the reflectance.

Results and Discussion

Nine novel derivatives of sulfonic acid dyes, based on substituted aryl amines as diazo component and substituted amino hydroxy sulfonic acid as coupling component, were explored for their dyeing performance on nylon fibers. The dyes (C1-C9) were applied on nylon fabric by a standard exhaust dyeing process, as reported in the experimental section, and the resulting shades were found to be in correlation with UV-visible spectra λ max (nm) from red to blue red.

To elucidate the dyeing performance further, the color parameters and the fastness properties (wash, light, alkaline perspiration and rubbing) of pre and post-washed (using a nonionic detergent at 50 ºC) dyed fabric, were explored using Datacolor spectrophotometer SF600.

The Color Parameters obtained for fabrics dyed using the synthesized dyes (C1 to C9) are listed in Table-2 which indicates that the dyeing resulted in the shades of moderate depth. The positive a* values were obtained for all the dyes samples and for the dyes C1 to C5, negative b* values were obtained. Remarkably, for the dyes C6 to C9, positive b* values were recorded. This change is also reflected in the hue values which exhibit a drastic change from 310.80 for C5 to 9.36 for C6. This is an expected result owing to the fact that the dyes from C6 to C9 were synthesized using a different coupling component (Table-1). For the dyes C1 to C5, 1-Amino -8- naphthol-3, 6- disulfonic acid – (H-acid) was used as coupling components which was replaced with 1- Aminoacetye-8-naphthol-3,6-sulfonic acid for synthesizing the dyes C6 to C9. Similar trends were obtained in the color parameters recorded for light exposure, and alkaline perspiration (Table-3 and 4). These results indicated the satisfactory performance of all the synthesized dyes on nylon fabric [6-8].

Table-2: Color Parameters* of dyed nylon fabric before and after washing with a nonionic detergent at 50 °C.

Sample		L*	a*	b*	C*	h*	X	Y	Z	X	y
C-1	Before Wash	22.45	23.31	-6.23	24.13	345.03	5.12	3.64	5.12	0.3691	0.2623
	After Wash	20.64	24.33	-5.27	24.89	347.78	4.59	3.15	4.30	0.3813	0.2617
C-2	Before Wash	18.31	9.98	-7.89	12.72	321.67	2.98	2.59	4.04	0.3104	0.2692
	After Wash	17.50	9.95	-7.13	12.24	324.38	2.79	2.41	3.66	0.3147	0.2718
C-3	Before Wash	17.12	10.00	-5.57	11.45	330.89	2.70	2.33	3.30	0.3245	0.2793
	After Wash	17.28	10.15	-5.35	11.47	332.22	2.75	2.36	3.31	0.3264	0.2805
C-4	Before Wash	17.67	6.34	-8.70	10.77	306.06	2.63	2.44	3.99	0.2906	0.2696
	After Wash	16.93	5.09	-7.63	9.17	303.74	2.41	2.29	3.58	0.2911	0.2762
C-5	Before Wash	17.08	7.13	-8.01	10.73	311.69	2.55	2.32	3.69	0.2975	0.2711
	After Wash	17.78	6.96	-8.06	10.64	310.80	2.69	2.47	3.91	0.2969	0.2722
C-6	Before Wash	32.67	52.66	8.68	53.37	9.36	13.71	7.39	5.71	0.5114	0.2755
	After Wash	37.63	45.92	4.42	46.13	5.49	16.13	9.88	9.15	0.4588	0.2809
C-7	Before Wash	35.01	50.33	5.91	50.68	6.69	14.96	8.50	7.41	0.4847	0.2754
	After Wash	36.01	52.82	7.82	53.39	8.42	16.12	9.01	7.35	0.4962	0.2774
C-8	Before Wash	30.69	47.28	14.03	49.32	16.53	11.64	6.52	3.94	0.5268	0.2950
	After Wash	29.46	45.73	12.99	47.54	15.86	10.71	6.02	3.75	0.5229	0.2940
C-9	Before Wash	40.65	51.74	16.40	54.28	17.59	19.65	11.65	7.20	0.5105	0.3025
	After Wash	41.15	53.41	19.19	56.75	19.77	20.42	11.96	6.70	0.5226	0.3060

*(values obtained using Datacolor spectrophotometer SF600 with D65 light and 10 Deg. observer.

Table-3: Color parameters* of dyed nylon fabric before and after light exposure.

Sample	L*	a*	b*	C*	h*	X	Y	Z	x	y
C-1 Untreated	22.45	23.31	-6.23	24.13	345.03	5.12	3.64	5.12	0.3691	0.2623
C-1 Treated	21.90	23.61	-6.78	24.56	343.99	4.96	3.49	5.03	0.3679	0.2588
C-2 Untreated	18.31	9.98	-7.89	12.72	321.67	2.98	2.59	4.04	0.3104	0.2692
C-2 Treated	18.12	10.38	-8.08	13.15	322.11	2.96	2.54	4.02	0.3109	0.2672
C-3 Untreated	17.12	10.00	-5.57	11.45	330.89	2.70	2.33	3.30	0.3245	0.2793
C-3 Treated	16.96	10.14	-5.25	11.42	332.63	2.68	2.29	3.21	0.3271	0.2805
C-4 Untreated	17.67	6.34	-8.70	10.77	306.06	2.63	2.44	3.99	0.2906	0.2696
C-4 Treated	17.40	6.56	-7.81	10.20	310.04	2.59	2.39	3.75	0.2965	0.2736
C-5 Untreated	17.08	7.13	-8.01	10.73	311.69	2.55	2.32	3.69	0.2975	0.2711
C-5 Treated	23.21	27.49	10.41	29.39	20.75	5.75	3.86	2.51	0.4746	0.3185
C-6 Untreated	32.67	52.66	8.68	53.37	9.36	13.71	7.39	5.71	0.5114	0.2755
C-6 Treated	31.74	52.01	8.85	52.76	9.66	13.00	6.97	5.32	0.5139	0.2757
C-7 Untreated	35.01	50.33	5.91	50.68	6.69	14.96	8.50	7.41	0.4847	0.2754
C-7 Treated	33.48	50.61	8.66	51.35	9.71	13.94	7.76	6.04	0.5025	0.2798
C-8 Untreated	30.69	47.28	14.03	49.32	16.53	11.64	6.52	3.94	0.5268	0.2950
C-8 Treated	29.77	46.59	12.56	48.26	15.09	11.00	6.14	3.92	0.5223	0.2916
C-9 Untreated	40.65	51.74	16.40	54.28	17.59	19.65	11.65	7.20	0.5105	0.3025
C-9 Treated	41.42	54.80	18.67	57.90	18.82	20.96	12.13	6.95	0.5234	0.3030

*(values obtained using Datacolor spectrophotometer SF600 with D65 light and 10 Deg. observer.

Table-4: Color parameters* of dyed nylon fabric subjected to alkaline perspiration.

Sample	L*	a*	b*	C*	h*	X	Y	Z	x	y
C-1 Untreated	22.45	23.31	-6.23	24.13	345.03	5.12	3.64	5.12	0.369	0.262
C-1 Treated Alkaline	18.36	6.05	-8.62	10.53	305.09	2.78	2.60	4.19	0.290	0.272
C-2 Untreated	18.31	9.98	-7.89	12.72	321.67	2.98	2.59	4.04	0.310	0.269
C-2 Treated Alkaline	17.42	9.55	-7.93	12.42	320.29	2.75	2.39	3.78	0.308	0.268
C-3 Untreated	17.12	10.00	-5.57	11.45	330.89	2.70	2.33	3.30	0.324	0.279
C-3 Treated Alkaline	17.11	11.21	-4.52	12.09	338.05	2.77	2.33	3.14	0.336	0.283
C-4 Untreated	17.67	6.34	-8.70	10.77	306.06	2.63	2.44	3.99	0.291	0.270
C-4 Treated Alkaline	16.76	5.78	-8.30	10.11	304.86	2.41	2.25	3.65	0.290	0.271
C-5 Untreated	17.08	7.13	-8.01	10.73	311.69	2.55	2.32	3.69	0.298	0.271
C-5 Treated Alkaline	17.02	6.04	-7.48	9.62	308.89	2.48	2.31	3.59	0.296	0.276
C-6 Untreated	32.67	52.66	8.68	53.37	9.36	13.71	7.39	5.71	0.511	0.275
C-6 Treated Alkaline	30.96	50.30	9.64	51.21	10.85	12.24	6.63	4.87	0.516	0.312
C-7 Untreated	35.01	50.33	5.91	50.68	6.69	14.96	8.50	7.41	0.485	0.275
C-7 Treated Alkaline	32.38	47.82	9.78	48.81	11.55	12.78	7.26	5.36	0.503	0.286
C-8 Untreated	30.69	47.28	14.03	49.32	16.53	11.64	6.52	3.94	0.527	0.295
C-8 Treated Alkaline	30.33	47.21	14.86	49.50	17.48	11.42	6.37	3.69	0.532	0.297
C-9 Untreated	40.65	51.74	16.40	54.28	17.59	19.65	11.65	7.20	0.511	0.303
C-9 Treated Alkaline	42.58	53.85	18.02	56.78	18.51	21.80	12.88	7.66	0.515	0.304

*(values obtained using Datacolor spectrophotometer SF600 with D65 light and 10 Deg. Observer.

To explore the fastness properties of the dyes C1 to C9, washing, light, perspiration and rubbing fastness test were performed on dyed nylon fabric. For this entire test, standard ISO procedures [9-14] were adopted and the obtained are listed in Table-5. The ratings representing the change in shade were assigned by comparison with a standard color grey scale where the ratings for change in color were in the range from 1 to 5. The rating 1 represents the highest loss of color (poor performance) and rating 5 representing no color change (excellent performance). Similarly, the degrees of staining were also assigned using a grey scale for staining. For the fastness test, multi-fiber fabric consist of six (06) different fibers namely wool, acrylic, polyester, nylon, cotton and acetate was employed as adjacent fabric. From the values listed in Table-5 and 6, it is evident that 5 and 4-5 ratings values were obtained for all the dyes used (C1 to C9). However, the dyes C1, C6 and C9 give 3-4 ratings on cotton fabric. Besides, the dyes C1, C2, C4, C5, C7 and C9 exhibit reasonably good results whereas the dyes C3, C6 and C8 performed poorly in alkaline perspiration test. On the basis of the change in color, these values indicate that the synthesized dyes exhibit satisfactory wash fastness properties on nylon substrate.

The values obtained for the percentage of dye bath exhaustion are listed in Table-6. These values were determined using absorbance measurements (at λ max) of the dyebath, before and after the dyeing process. These values reveals that the dye exhaustion was the higher for the dyes C1, C2, C3, C5 and C6. For the dyes C4, C7, C8 and C9 moderate to low values were obtained which may likely be the result of their comparatively lower solubility. These values however, can be improved with various parameters, such as by the addition of electrolytes.

Table-5: Washing, crocking, and light fastness of dyed nylon fabric.

Sample	Change in Shade	CA	CO	PA	PES	PAC	WO	Crocking		Light Fastness
								Dry	Wet	
C-1	4-5	5	3-4	5	5	5	5	5	5	4-5
C-2	4-5	5	4	5	5	5	5	5	4-5	4-5
C-3	4-5	5	4	5.0	5	5	5	5	4-5	4-5
C-4	4-5	5	4	4-5	5	5	5	5	5	4
C-5	4-5	5	4	4-5	5	5	5	5	5	4-5
C-6	4	5	3-4	5	5	5	5	5	5	4-5
C-7	4-5	5	4	4-5	5	5	5	4-5	4-5	4
C-8	4-5	5	4	5	5	5	5	5	4-5	4
C-9	4-5	5	3-4	4-5	5	5	5	5	4-5	4

Description of Multi-fiber Fabric: *CA = Cellulose Acetate, CO = Cotton, PA = Polyamide, PES= Polyester, PAC= Polyacrylic, WO = Wool*

Table-6: Results of various fastness properties of dyes on silk fabric on multi-fiber.

Dye Code	Fastness To							% Dye Fixation by *K/S* Values	% Exhaustion
	Light hours	Wash		Perspiration alkaline		Rubbing			
	100	y	s	y	s	dry	wet		
C-1	4-5	4-5	3-4	4-5	3-4	5	5	91.74	80.23
C-2	4-5	4-5	4	4	3	5	4-5	92.91	79.37
C-3	4-5	4-5	4	4	1-2	5	4-5	96.41	80.36
C-4	4	4-5	4	4-5	5	5	5	92.0	59.09
C-5	4-5	4-5	4	4-5	4-5	5	5	92.14	79.28
C-6	4-5	4	3-4	3-4	2-3	5	5	97.77	74.42
C-7	4	4-5	4	4	3	4-5	4-5	90.0	65.33
C-8	4	4-5	4	4	2	5	4-5	96.0	65.57
C-9	4	4-5	3-4	4	3-4	5	4-5	95.55	59.39

y = Wash fastness test was performed before washing the dyed fabric using nonionic detergent at 50 ºC. **s** = Wash fastness test was performed after washing the dyed fabric using nonionic detergent at 50 ºC.

Conclusion

This work explored performance of nine derivatives of sulfonic acid dyes which were synthesized using substituted aryl amines as diazo component and substituted amino hydroxy sulfonic acid as coupling component. Nylon was selected as substrate and the dyeing performance was evaluated using various standard characterization tests.

All the dyes tested (C1 to C9) were found to be suitable to dye using exhaust dyeing procedure. Besides, these dyes exhibit intense colors and the resulting shades were found to be in correlation with UV-visible spectra λ max (nm) from red to blue red. To explore the performance further, washing, light, rubbing and perspiration fastness studies were also performed using standard ISO procedures and data color spectrophotometer SF600. From the results obtained for these tests, it can be concluded that the all the dyes exhibit reasonably good dyeing properties on nylon fabric. Future, work includes bulk application these dyes on large scale to explore their potential for commercialization.

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