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Synthesis and Application of Bisazo Acid Dyes for Water Repellent Polyamides

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Simultaneous dyeing and finishing of textiles is known for its potential to reduce the cost, increase production and drastically reduce the effluent load. However, some of the finishes applied during dyeing or post dyeing operation are found to show lowering in performance properties due to their poor durability to washing. The present paper reports the results of the synthesis and application of bisazo acid dyes containing *m*-trifluoromethyl aniline and *m*-toluidine/*p*-nitro aniline reacted with the coupler H-acid, on the polyamide fabrics mainly silk, wool and nylon interms of wettability, water repellency, colour depth and fastness. The improved and durable water repellency with good performance properties was obtained in case of dyes containing trifluoromethyl group and *p*-nitro aniline.

Key Words: Colour depth, Bisazo acid dyes, Fastness properties, Water repellency, Wettability.

INTRODUCTION

Today, textile industry is one of the major consumers of auxiliaries, dyes and other chemicals. The textile finished products require to have antimicrobial, flame retardant, wrinkle free and water repellent properties depending upon their end uses. Many a times these functional finishes are not found to be durable to repeated washings. Hence, to get a functional finish on textile material with long durability is one of the challenges the researchers are facing today.

Keeping this in mind, a novel series of dyes were synthesized in our laboratory, which in turn have an inbuilt water repellent properties and also do not impair the conventional performance properties of the dyed fabric. Large quantities of fluorochemicals, perfluorinated ones were used to impart water repellency, which inturn favour resistance to water based stains. These finishes generally form a water repellent layer on the surface of the material without filling up the interstices, thereby keeping the fabric sufficiently porous to allow water vapour to circulate[1]. Fluorine is the most strongly electronegative element in nature and in fluorine atom the

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electrons are held close to the atomic nucleus. The interaction of fluorine atoms with carbon atoms to form strong carbon-fluorine bonds leads to the carbon atoms in fluorocarbons being closely surrounded by fluorine atoms[2]. This is the basis for the low reactivity of fluorochemical finishes and the high degree of protection provided by fluorine atoms to the shielded carbon atom. The fluorine group also exercises an electron withdrawing influence. This property has been used in synthesizing dyes containing fluorine atoms which have water repellency[1,3].

From our laboratory, the earlier paper reported the influence of substitution of trifluoromethyl group in place of methyl analogous giving improved water repellency. In order to complete the shade gamet, in the present investigation, an attempt is made to synthesize the novel disazo acid dyes containing trifluoromethyl group. The noval azo acid dyes based on trifluoromethyl group are subjected for examining their contribution to water repellency and performance properties when applied on polyamide fabric.

EXPERIMENTAL

m-Trifluoromethylaniline (1) was of commercial grade obtained from Merck, India. *m*-Toluidine (2), *para*-nitro aniline (3) were of commercial grade obtained from SD Fine Chemicals, India. H-acid (4) of commercial grade was obtained from Atul (India) Ltd.

Synthesis of dye I: The coupler solution was prepared by dissolving H-acid (3) (15.95 g, 0.05 mol) in 100 mL water at a pH 7-8 (using sodium carbonate) and cooled below 10 ºC. *m*-Toluidine (5.35 g, 0.05 mol) was added to 50 mL water containing 15.2 mL of 30 % concentrated HCl (0.125 mL) in a beaker surrounded by ice cubes and the reaction mixture was stirred with electric motor. When the temperature of the reaction mixture was below 10 ºC, 20 % $NaNO_2$ (3.50 g, 0.05 mol) was added. The reaction mixture was stirred for about 20 min after complete addition of $NaNO_2$. Then the reaction mixture was tested to give blue colouration with Congo red paper and weak blue coloration with starch iodide paper indicating a slight excess of nitrous acid.

The diazonium salt solution prepared as above was added to the coupler solution *i.e.*, H-acid in small amount continuously maintaining the pH between 7 and 8. The temperature of the reaction mixture was kept below 10 ºC. After complete addition of the diazotized solution to the coupler solution, the reaction mixture was tested for completion of reaction with R-acid. In the second step of the reaction, the *m*-trifluoromethylaniline (1) was diazotized as mentioned above and then added to the above reaction mixture maintaining the pH 3-4 to obtain disazo dye.

The mixture was heated to 75-80 ºC and 20 % w/v of sodium chloride was added with stirring for salting out. The separated dye was filtered at 50 ºC and dried at 60 ºC.

A small amount of the sodium salt of the dye was carefully neutralized using dilute HCl at 0-5 ºC. The free sulphonic acid thus obtained was filtered, dried at 60 ºC and elemental analysis was carried out.

Synthesis of dye II: The dye II was prepared in a similar manner as that of dye I by taking the appropriate amine and coupler. The scheme of synthesis, yield and elemental analysis data are presented in Table-1.

Characterization of dyes: The elemental analyses of all the dyes were in agreement with their molecular formula as shown in Table-1. The structures of both the dyes were confirmed by IR spectra recorded in KBr pellet, which showed the expected peaks and the data are presented in Table-1.

Dyeing of silk, wool and nylon fabric with synthesized disazo acid dyes: The synthesized disazo acid dyes were applied on polyamide fabrics namely silk, wool and nylon using standard dyeing methods[4-7].

Colour depth: Dyed samples were evaluated for the depth of the colour by determining K/S values using a Spectra flash ® SF 300, Computer Colour Matching System supplied by Datacolour International, USA. The average of 4 readings taken at 4 different sample areas was used to get the reflectance values and Kubelka Munk K/S function, which is given by:

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

where, R is the reflectance at complete opacity, K is absorption coefficient, S is the scattering coefficient.

Assessment of light and wash fastness: Light fastness and wash fastness tests were carried out using standard methods and assessed according to international blue scale (1-8) and grey scale (1-5), respectively[8,9].

Assessment of water repellency

Wettability test for silk fabric: Wettability of the fabric was determined by using the method AATCC Test 39-1980, where, a single drop of water was placed on the surface and time of its absorption by the cloth was measured[10].

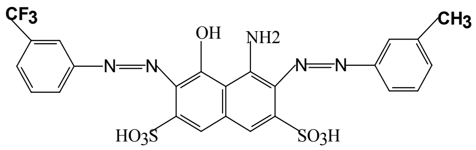
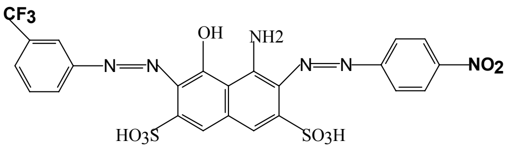
Wicking height test for silk fabric: 8" × 1" fabric strip was pinned over a stand supported at convenient height over a petridish containing water so that the end was just above the surface. A ruler was clamped parallel with the vertical edge of the strip. The strip was lowered, so that one end just touched the water and the stopwatch was just started. The height to which the water rises in 1, 3 and 5 min was noted[11].

Spray test (AATCC 32-1996) for wool and nylon fabric: The spray test measures a treated fabric's resistance to wetting by water. The spray test is carried out for wool and nylon dyed fabric[12].

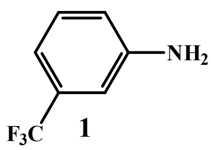
RESULTS AND DISCUSSION

At the outset 2 bisazo acid dyes were synthesized using *m*-trifluoromethyl-aniline and *m*-toluidine with H-acid as coupler (dye I) and *m*-trifluoromethylaniline and *p*-nitro aniline as the amines with H-acid as the coupling agent (dye II). Hence dye I and II are the bisazo acid dyes and their synthesis and characterization data are given in Table-1.

TABLE-1
DYE SYNTHESIZED, YIELD, INFRARED AND PROTON MAGNETIC RESONANCE SPECTRA AND ELEMENTAL ANALYSIS DATA

Dye No.	Scheme and structure of synthesis	Yield (%) [colour]	m.f.	IR spectra (KBr pellets)	Elemental analysis (%): Observed (Calculated)
I	Alkaline, Acidic: 2 ⟶ 4 ⟵ 1 	62 (Greenish blue)	$C_{24}H_{18}N_5O_7S_2F_3$	b,OH-3381, NH_2-1663, SO_3-1103, CF_3-1346	C 47.27 (47.29), H 2.62 (2.62), N 11.47 (11.49), F 9.30 (9.35), S 10.57 (10.50)
II	Alkaline, Acidic: 3 ⟶ 4 ⟵ 1 	61 (Blue)	$C_{23}H_{15}N_6O_9S_2F_3$	b,OH -3449, NH_2-1667, SO_3- 1152, CF_3 -1411	C 43.11 (43.12), H 2.33 (2.34), N 13.13 (13.12), F 8.89 (8.90), S 10.01 (10.00).

Raw materials used for synthesis of dyes: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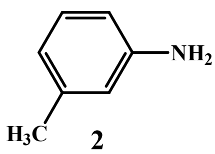
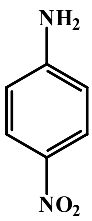
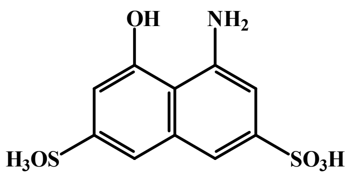

2


3


4

Colouration properties of dyes on silk, wool and nylon: Results with respect to colour depth, *i.e.*, K/S values of dyeings obtained for different shades (0.5-4.0 %) of these dyes on silk, wool and nylon fabric are given in Table-2. The dyeings were evaluated using CIELAB[13,14] system in terms of L*, a*, b* and the results are summarized in Table-3. It is clear from these results that in general, the K/S values varied in the following order- nylon > wool > silk. When all the 3 substrate were compared for their response to dyeing with these two dyes I and II, it was found that dye II gave higher K/S value as compared to that of dye I in all the 3 substrates.

TABLE-2
COLOURIMETRIC VALUE (K/S) OF SILK FABRIC DYED WITH DYES WITH DEPTH OF SHADE

Substrate	Dye No.	Depth of shade (%)			
		0.5	1.0	2.0	4.0
Silk	I	2.1638	2.8413	5.9816	12.5933
	II	2.9773	6.4563	9.2728	17.1175
Wool	I	5.1506	7.8543	14.9764	23.2589
	II	7.9652	15.2513	21.4868	25.3245
Nylon	I	5.2912	11.5238	17.8081	20.3919
	II	9.9661	17.6908	21.6005	21.5184

TABLE-3
COLOUR COORDINATES[a] OF THE DYES[b] ON SILK, WOOL AND NYLON

Dye No.	Silk			Wool			Nylon		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
I	51.54	-8.73	-11.01	35.26	-6.72	-9.67	31.40	-7.90	-11.07
II	34.81	6.64	-12.93	22.83	5.91	-9.95	21.22	5.84	-10.38

[a]Light source = D65/10° observer

Absolute values of the K/S differ as the dyes have different chemical structure and different wavelength of maximum absorption. The dyes being of acid class, the mechanism of salt linkage formation comes into place and accessibility of protonated amino group for the formation of salt linkages governs the over all depth of dyeing. Thus the substrate does play an important role in building the shade.

The results from Table-3 indicate that in case of dye I, the a* value being -8.73 and b* value -11.01, it gave greenish blue hue with λ_{max} 620 nm. Whereas in the case of dye II the bluishness was slightly increased and the greenish tone was totally absent making the hue of the material more reddish blue with λ_{max} of 600 nm. This difference in hue is basically due to the difference in the chemical structure of the bisazo dye. The dye I contained *m*-toluidine, where as in dye II it was *p*-nitro aniline as the compound forming the bisazo chromophore. The total variation in dye I and II were almost the same whether the dyeing was carried out on wool fabric or nylon, although the absolute values of L*, a*, b* slightly differed.

Visible absorption properties of the dyes: The visible absorption properties of both the dyes were measured in water and the results are summarized in Table-4. It is seen that the presence of trifluoromethyl group and *p*-nitro group in dye II exercised a hypochromic effect of 20 nm as compared to the dye I having trifluoromethyl and *m*-toluidine group.

Colourfastness properties of the dyes: Performance properties of the dyes such as the wash fastness and light fastness properties of the silk, wool and nylon fabric dyed with the two dyes are summarized in the Table-5. In almost all the cases, the washing fastness (ISO III test) remained in the range of good to very

TABLE-4
VISIBLE ABSORPTION DATA OF DYES ON SILK, WOOL AND NYLON

Dye No.	Visible spectra	
	Absorption maximum λ_{max} (nm)	log ε
I	620	4.20
II	600	4.04

TABLE-5
FASTNESS PROPERTIES OF DYES ON SILK, WOOL AND NYLON AT DIFFERENT DEPTH OF SHADE

Substrate	Dye No.	Light fastness, Shade (%)				Wash fastness, Shade (%)			
		0.5	1.0	2.0	4.0	0.5	1.0	2.0	4.0
Silk	I	4	4	4	4	3	3-4	3-4	3
	II	4-5	4-5	4-5	4-5	3-4	3-4	3-4	4
Wool	I	4	4	4	4	3	3-4	3-4	3
	II	4-5	4-5	4-5	4-5	3-4	3-4	3-4	4
Nylon	I	4	4	4	4	3	3-4	3-4	3
	II	4-5	4-5	4-5	4-5	3-4	3-4	3-4	4

good (3-4) which is quite satisfactory. The results also indicate that the dye II showed an increased light fastness of 4-5 grade as compared to the dye I having light fastness 4. In general, it could be said that the two dyes gave the light fastness properties which certainly fall in acceptable limit.

Water repellency of the dyes

Wettability test: The results of wettability of dyed silk fabrics are given in Table-6. These results indicate that the control silk, which is undyed, shows a wettability of 10.54 s as per AATCC Test 22-1989 carried out on silk fabric. It is clear that significant decrease in the wettability or increase in water repellency was observed as a result of dyeing of silk with fluorine containing bisazo acid dye I and II. As the per cent shade dyed increased, the increase in water repellency for dye I was found to be from 30.12 to 40.15 s. In case of the dye II, it was still better and its water repellency increased from 79.98 to 377.2 s as the shade increased from 0.5 to 4 %. This is quite obvious for at higher % shade, K/S value increased corresponding to the presence of higher extent of fluorine containing dyes which in turn may be responsible for decrease in wettability or increase in the water repellency.

TABLE-6
WETTABILITY TEST ON DYED SILK FABRIC AT DIFFERENT DEPTH OF SHADE

Wettability time (s)				
Dye No	Shade: 0.5 %	Shade: 1.0. %	Shade: 2.0 %	Shade: 4.0 %
Control sample	10.54	10.54	10.54	10.54
I	30.12	36.33	37.01	40.15
II	79.98	177.52	328.77	377.2

The enhanced water repellency in case of dye II may be attributed to $-NO_2$ group in the *p*-position in dye II as compared to $-CH_3$ group being in *m*-position in dye I with respect to azo group. While the former is electron attracting, the latter is electron donating which may be responsible for such differential water repellency.

Wicking height test: Silk dyed with these dyes, was subjected for measurement of wicking height and results are shown in Table-7. It was found that dye I and dye II clearly indicate that at all the 4 shades dyed, the wicking height was found to have been much reduced as compared to that incase of control undyed sample. The lowering of wicking height of the dyed silk fabric clearly indicates the decrease in wettability or increase in water repellency.

TABLE-7
WICKING HEIGHT TEST FOR DYED SILK FABRIC AT DIFFERENT DEPTH OF SHADE

Dye No.	Wicking height (cm)											
	Shade: 0.5 %			Shade: 1.0 %			Shade: 2.0 %			Shade: 4.0 %		
	1 min	3 min	5 min	1 min	3 min	5 min	1 min	3 min	5 min	1 min	3 min	5 min
CS*	3.4	5.3	7.1	–	–	–	–	–	–	–	–	–
I	1.1	2.3	3.1	1.5	2.8	3.6	1.9	3.1	4.1	2.3	3.6	4.5
II	0.6	1	1.4	0.9	1.3	1.6	1.1	1.6	1.8	1.4	1.8	2.0

*CS = Control sample (without dyed).

Spray test: The results from the Table-8 for wool and nylon fabric clearly indicate that the undyed wool fabric having the water repellency measured in terms of standard spray test rating was 50 indicating there by, complete wetting of whole upper surface. This was improved to 70 in case of dye I indicating there by, partial wetting of upper surface of dyed wool. In case of dye II, the wool sample showed spray rating of 80 indicating partial staining of fabric with water. When nylon was dyed with dye I and II and subjected for spray test measurement, it was found that the water repellency rating of the undyed nylon fabric which was < 50, increased to 50 for dye I and 70 incase of dye II. In other words, this clearly shows that when wool and nylon dyed with dye I and dye II, the water repellency of dyed fabric was significantly increased.

TABLE-8
SPRAY TEST PERFORMED ON DYED WOOL AND NYLON FABRIC AT DIFFERENT DEPTH OF SHADE

Substrate	Dye No.	Spray test rating			
		Shade: 0.5 %	Shade: 1.0 %	Shade: 2.0 %	Shade: 4.0 %
Wool	Control Sample	50	50	50	50
	I	70	70	70	70
	II	80	80	80	80
Nylon	Control Sample	< 50	< 50	< 50	< 50
	I	< 50	50	50	50
	II	70	70	70	70

Conclusion

It was possible to synthesize bisazo acid dyes containing trifluoromethyl groups and these dyes did exhibit not only good yield, but also good colouration and performance properties on dyeing with polyamide fabrics like silk, wool and nylon. It has been substantiated that such speciality dyes containing trifluoromethyl group in the dye structure thus can impart the water repellent properties to the fabric on which they are applied. This property is also durable as long as the dye is present in the fabric since the water repellent nature is due to the dye itself.

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