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Synthesis and Application of Monoazo Acid Dyes Containing Long Chain Perfluoroalkyl Group for Water Repellant Polyamides

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In the present investigation, γ-acid was reacted first with acid chloride namely pentadecafluoro octanoyl chloride, which was synthesized by the reaction with thionyl chloride and pentadecafluoro octaconic acid. The resulting compound was coupled with *m*-toluidine and thus dye 1F1 of reddish pink hue was synthesized. Similarly in place of *m*-toluidine, *m*-trifluromethyl aniline was used with the same intermediate and dye 1F2 with brighter reddish pink was obtained. In case of 2F1 and 2F2 dyes synthesized only the γ-acid in 1F1 and 1F2 was replaced by H-acid. These dyes are brown in shade. The water repellency effect of a long chain derivative containing perfluoro group on the fabric dyed with the synthesized modified monoazo acid dyes was studied.

Key Words: Colour depth, Pentadecafluoro octaconic acid, Water repellency, Wettability.

INTRODUCTION

Textile market has shown a steady increase in the demand for specialty finished products such as water repellent, antimicrobial and flame retardant finishes. Perfluorochemicals are most abundantly used as water repellent agent in textile finishing which not only satisfy the demand for high water repellent finishing, but also impart oil and soil repellency to finished textiles. Modern water-repellent finish forms a water repellent layer on the surface of the material without filling up the interstices. The use of perfluoro fatty compounds, chromium complexes of perfluoro fatty acids or perfluoro-acrylates, can confer water repellency together with oil-repellency on the fabric[1].

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However, the durability of such finishing agents to washing always limits the final performance properties. Hence the concept of application of dyes having ability to impart water repellency was investigated in our laboratory. In pervious investigation[2], the monoazo dyes containing fluorine resulted in higher water repellency than the dyes without fluorine group.

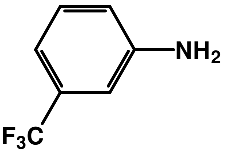
A new series of monoazo acid dyes containing long chain perfluoroalkyl group were synthesised. It is anticipated that the newly designed monoazo acid dyes will be capable of imparting water repellent finishing effects, as well as colour, to textile substrates. These noval dyes are subjected for evaluation of their water repellency when applied on polyamide fabrics and also the performance properties of the dyes.

EXPERIMENTAL

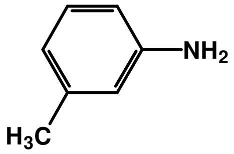
Pentadecafluoro octaconic acid (**1**) *m*-trifluoromethylaniline (**2**), are of commercial grade obtained from Merck, India. *m*-Toluidine (**3**) is of commercial grade obtained from SD Fine Chemicals, India. γ-Acid (**4**), H-acid (**5**) are of commercial grade obtained from Atul (India) Ltd.

$CF_3—(CF_2)_6—COOH$

(1)



(2)



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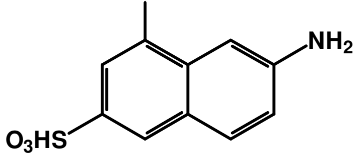

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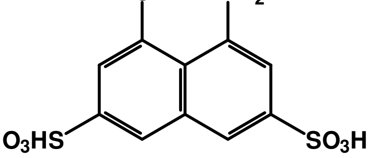
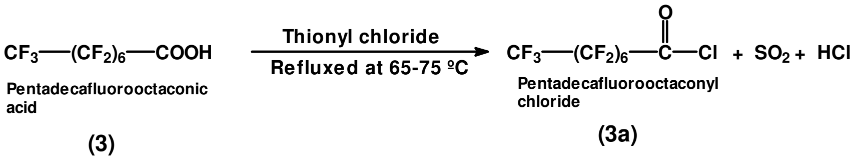


(5)

Synthesis of dye 1F1

Preparation of diazotized base: *m*-Toluidine (0.03 mol) was added to 50 mL water containing 15.2 mL of 30 % conc. 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 % $NaNO_2$ (0.03 mol) was added. The reaction mixture was stirred for *ca.* 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 colouration with starch iodide paper indicating a slight excess of nitrous acid.

Preparation of pentadecafluoroctanoyl chloride: Pentadecafluorooctanoic acid was dissolved in solvent namely benzene (5 mL) and 5 mL of thionyl chloride was added slowly in a three necked flask with condenser and refluxed at a temperature of 75 ºC. Reaction was supposed to be over after the complete evolution of HCl from condenser. The benzene was distilled out at temperature of 85 ºC. The resulting compound pentadecafluoroctanoyl chloride was used for further reaction with γ-acid (**Scheme-I**).



Scheme-I

Preparation of coupler: An amount of γ-acid equivalent to 35 g of 100 % material (0.03 mol) is dissolved at 50 °C in 200 mL water containing 6 g of soda ash. With vigorous stirring, 0.035 mol of pentadecafluoroctanoyl chloride is added over a period of 15 min. Here complete acetylation of the amino group in H acid occurs, but simultaneously the hydroxyl group is also partly acetylated. To test for completion of acetylation, a small test portion of the solution is acidified with hydrochloric acid, treated with a few drops of sodium nitrite and then made alkaline with soda. If much of H-acid remains in the mixture, a blue colouration is formed (coupling of diazotized H acid with itself). As the acetylation proceeds, the colour formed in the test becomes weaker and more reddish (coupling of diazotized H acid with acetyl-H acid). When the reaction mixture contains no more unchanged H acid, only a yellow colouration, formed by nitrosation, is obtained in the test. (The test can be carried out advantageously on filter paper). When acetylation is complete, 25 g of soda ash is added and the mixture is heated and stirred at 90-95 ºC for 1 h, replacing the water lost by evaporation. This treatment hydrolyzes the acetyl group on the oxygen but does not attack the acetylamino group. (If the treatment with soda is omitted, about 30 % of the starting material is lost and the final dye is contaminated with decomposition products of the diazo compound). The reaction can be controlled by titration with diazobenzene solution. The resulting soda solution is used directly in the coupling reaction[3].

The dyes 1F1 and 1F2 reported in Table-1A, are synthesized by the following procedure.

Coupling reaction: The diazo solution prepared was slowly added to the coupler prepared in alkaline pH by using sodium carbonate, over a period of 1.5 h at a temperature of 5-10 ºC. Stirring of the colouring mass was continued further for 5 h. Completion of the coupling reaction was checked on filter paper by chloroaniline diazo solution prepared. The mixture was heated to 75-80 ºC and sodium chloride 20 % (w/v) 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 dye was carefully neutralized using dilute hydrochloric acid at 0-5 ºC. The free sulphonic acid thus obtained was filtered, dried at 60 ºC and elemental analysis was carried out.

Synthesis of dyes 1F2, 2F1 & 2F2: The dyes were prepared in a similar manner as that of 1F1 by taking the H-acid in place of γ-acid. The scheme of synthesis, yield and elemental analysis data are presented in Table-1A.

TABLE-1A
DYE SYNTHESIZED, YIELD AND ELEMENTAL ANALYSIS DATA

Dye no.	Scheme of synthesis	Yield (%) and colour	m.f.	Elemental analysis (%) Found (Calcd.)
1F1	3 → 4*	65, Reddish pink solid	$C_{25}H_{14}N_3O_5SF_{15}$	C 39.62(39.8); F 37.79 (37.84); H 1.81 (1.85); N 5.52 (5.57); S 4.21 (4.24).
1F2	2 → 4*	60, Bright reddish pink solid	$C_{25}H_{11}N_3O_5SF_{18}$	C 37.11 (37.17); F 42.32 (42.37); H 1.32 (1.36); N 5.18 (5.20); S 3.92 (3.96).
2F1	3 → 5*	62, Brown solid	$C_{25}H_{15}N_3O_8S_2F_{15}$	C 36.82 (36.85); F 34.98 (35.01); H 1.81 (1.84); N 5.11 (5.15); S 7.81 (7.86).
2F2	3 → 5*	69, Brown solid	$C_{25}H_{15}N_3O_8S_2F_{16}$	C 35.98 (36.01); F 36.42 (36.49); H 1.78 (1.80); N 5.01 (5.04); S 7.61 (7.68).

Characterization of dyes: The results of elemental analysis of all the dyes were in agreement with their molecular formula as shown in Table-1A. The structure of all these dyes were confirmed by IR spectra recorded in KBr pellets, which showed the expected peaks as shown in Table-1B.

TABLE-1B
INFRARED SPECTRAL (cm^{-1}) DATA OF DYES SYNTHESIZED

Dye No	IR Spectra (KBr pellets)
1F1	b, Phenol-3598, amide-1697, SO_3-1052, CF_3-1328, CF_2-1208
1F2	b, Phenol-3466, amide-1660, SO_3-1044, CF_3-1355, CF_2-1203
2F1	b, Phenol-3454, amide-1617, SO_3-1047, CF_3-1329, CF_2-1298
2F2	b, Phenol-3465, amide-1656, SO_3-1140, CF_3-1332, CF_2-1285

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

Colour and fastness measurements

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 data colour international, USA. An average of four readings taken at four different sample areas was used to calculate the reflectance values and Kubelka Munk K/S function which is given by:

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

where, R = reflectance at complete opacity, K = absorption coefficient, S = 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 resistance to wetting of treated fabric by water. The spray test was carried out for wool and nylon dyed fabric[12].

RESULTS AND DISCUSSION

In order to study the effect of substitution of long chain perfluoroalkyl group in the dye molecule, at the outset four monoazo acid dyes were synthesized using *m*-toluidine and *m*-trifluoromethyl aniline as an amine with coupling agent namely γ-acid and H-acid containing perfluoroalkyl group. Hence Dyes 1F1, 1F2, 2F1 and 2F2 are azo acid dyes and their characterization data are given in Table-1A.

Colour depth (colourimetric value K/S): Results with respect to K/S values of 2 % shades of these dyes on silk, wool and nylon fabric are given in Table-2. It clearly indicates that in general, the K/S values varied in the following order- wool > nylon > silk. K/S values of dye 1F2 and 2F2 were higher than 1F1 and 2F1, indicating there by the influence of *m*-trifluoromethyl aniline in the chemical structure of the dye giving enhancement in the K/S value. When the same dyes were applied on wool and nylon fabric, similar trend was observed with regards to K/S value of the dyeing *i.e.*, 1F2 and 2F2 samples giving higher K/S value as compared to dye 1F1 and 2F1 samples. Because of the variation in the substrates, however the absolute K/S values varied.

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

Dye name	Depth of Shade, 2 %		
	Silk	Wool	Nylon
1F1	4.6735	16.7234	11.4984
1F2	9.7216	18.6064	16.9366
2F1	1.5153	2.9153	3.4891
2F2	4.8833	10.8323	8.5332

Visible absorption properties of the dyes: The visible absorption properties of all dyes were measured in water and the results are summarized in Table-3. The tone of the dyeing was closely different for two pairs of dyes in which 1F1 gave reddish pink dyeing, 1F2 bright reddish pink colour. And hence the λ_{max} of the respective 1F1 and 1F2 are found to be 540 and 510 nm, respectively. The second pair of dyes namely 2F1 and 2F2 gave brown hue with λ_{max} of 410 and 400 nm, respectively. Similarly the wool and the nylon fabric were subjected to dyeing with two pairs of dyes and the trend of the results observed was just the same as in the case of silk fabric.

Colour properties of the dyes on silk, wool and nylon 6,6: The dyes were applied on silk, wool and nylon 6,6. To derive the colorimetric data dyeing with 1/1 standard depth were used[13]. The dyeing were evaluated using CIELAB[14,15] system in terms of L*, a*,b*. Results are summarized in Table-4. The results indicate that when 1F1 dyeing was compared with 1F2, blueness as well as the reddishness of the same was increased. Similarly in the case of 2F1 and 2F2 yellowness and the redness of the sample increase as the result of substitution of *m*-trifluoro methyl aniline. It is to be noted that 1F2 and 2F2 contain additional three fluorine atoms as compared to dyes 1F1 and 2F1. The same trend was observed on the wool and the nylon fabric. The shift towards decrease in λ_{max} from 1F1 to 1F2 by 30 nm or from 2F1 to 2F2 by 10 nm was the result of *m*-trifluoromethyl aniline and it also reflected in an increase in a* and b* values.

TABLE-3
VISIBLE ABSORPTION DATA AND FASTNESS PROPERTIES OF DYES ON SILK, WOOL AND NYLON AT DEPTH OF SHADE, 2 %

Dye number	Visible spectra		Fastness property		
	Absorption maximum λ_{max} (nm)	log ε	Fabric	Light fastness	Wash fastness
1F1	540	4.20	Silk	4-5	3
			Wool	4-5	3
			Nylon	4	3
1F2	510	4.28	Silk	5	3
			Wool	5	3
			Nylon	4-5	3
2F1	410	4.55	Silk	4	3
			Wool	4	3
			Nylon	4-5	3
2F2	400	4.60	Silk	4-5	3
			Wool	4-5	3
			Nylon	4-5	3

TABLE-4
COLOUR COORDINATES† OF THE DYES‡ ON SILK, WOOL AND NYLON

Dye name	Silk			Wool			Nylon		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
1F1	55.29	24.19	-10.64	33.61	29.87	-10.95	45.11	29.88	-14.25
1F2	43.01	27.2	-13.81	24.23	19.87	-6.02	27.23	24.55	-12.37
2F1	63.81	17.93	8.34	61.31	16.51	9.51	59.54	16.89	7.65
2F2	55.44	24.1	15.12	43.71	25.49	14.35	46.00	20.67	12.64

†1/1 standard depth; ‡Light source = D65/10° observer.

Water repellency properties of the dyes

Wettability test: The results of wettability given in Table-5, indicate that the control silk, which is, undyed one shows the wettability of 10.54 s. As per AATCC Test 22-1989 carried out on silk fabric, the wettability time

TABLE 5
WETTABILITY TEST ON SILK FABRIC DYED WITH DYES AT DEPTH OF SHADE, 2 %

Dye name	1F1	1F2	2F1	2F2
Wettability time (s)	26.78	301.54	22.87	179.64

Control sample = 10.54 s

also increased to 26.78 s in case of 1F1 and 301.54s incase of 1F2 dye. This clearly indicates that the improvement in the water repellency occurs when the dye contains fluorine. The water repellency is higher due to the fluorine content which happens in dye 1F2, drastic improvement in water repellency was observed. In the case of 2F1 dye, which already contains fluorine, the wettability time increased to 22.87 s with 2 % shade. However, further fluorination of the same dye significantly increased the wetting time to 179.64 s indicating significant enhancement in water repellency.

Wicking height test: In the next set of experiment, silk dyed with these dyes was subjected for measurement of wicking height and results are shown in Table-6. It was found that almost in all the cases the wicking height of the dyed samples containing fluorine was lower than the wicking height of the dyed silk containing no fluorine. This observation was valid for all the 4 shades dyed.

TABLE-6
WICKING HEIGHT (CM) TEST FOR SILK FABRIC DYED WITH ACID DYES AT DEPTH OF SHADE, 2 %

Dye name	Wicking height (cm)		
	1 min	3 min	5 min
1F1	2.1	3.5	4.6
1F2	0.8	1.8	2.7
2F1	2.1	2.6	3.4
2F2	1.6	2.2	2.8

Spray test: From the results in Table-7, it is clear that as the wool and nylon fabric were dyed with these two pairs of dyes, the water repellency rating in case of 1F1 and 2F1 for wool which was 70, enhanced to 80 in case of 1F2 and 2F2. Similarly in the case of nylon, water repellency rating which was less than 50 increased to 70 and up to 80 in case of 1F2 and 2F2. Such a remarkable enhancement in water repellency was caused due to the additional fluorination of the dye in case of 1F2 and 2F2. Fluorination thus clearly indicated the enhancement of water repellency.

TABLE-7
SPRAY TEST PERFORMED ON WOOL AND NYLON FABRIC DYED WITH DYES AT DEPTH OF SHADE, 2 %

Dye name	Wool	Nylon
Control sample	50	< 50
1F1	70	50
1F2	80	80
2F1	70	50
2F2	80	70

Colourfastness properties of the dyes: Performance properties of the dyes mainly the wash fastness and light fastness properties of the silk fabric dyed with all azo acid dyes are summarized in the Table-3. The results indicate that, there has been improvement in wash fastness. In almost all cases the washing fastness rating was **3** which is quite satisfactory, when one looks at the washing fastness conditions of ISO III. Similar results on wool and nylon were obtained.

The results with respect to light fastness of silk, wool and nylon dyed with the dyes under investigation are given in Table-3. It is clear from these results that the dye 1F2 showed an increased light fastness of 1/2 grade as compared to the dye 1F1 having light fastness 4-5. When the substrate was changed to wool and nylon this trend continued to persist. Hence in general, it could be said that the two pairs of dyes gave the light fastness more than or equal to 4-5 which certainly falls in the acceptable limit.

Conclusion

All the synthesized monoazo acid dyes containing perfluoroalkyl group exhibited good water repellency and also satisfactory colouration and performance properties on dyeing with polyamide fabric namely silk, wool and nylon. The increase in the water repellency can be attributed to the long chain length of pentadecafluoro ocatamide group and also the extent of dye uptake. The comparison of the water repellency of dyes shows that dye 1F2 and 2F2 exhibited higher water repellency than the dye 1F1 and 2F1. In other words, dyeing of polyamide fabrics with these dyes enables one to obtain durable water repellent finishing effect.

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