Thiazole Based Disperse Dyes for Nylon and Polyester Fibers

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Abstract: Nine disperse dyes have been synthesized by diazotization of 2-amino-4-(p-nitrophenyl)-5-nitrothiazole and coupled to substituted N-alkylanilines. Spectral properties in the IR and visible range of the dyes obtained were investigated. The dyeing performance of these dyes was assessed on nylon and polyester fibers. These dyes were found to give reddish brown to bluish violet shades on dyeing with very good depth, brightness and levelness on nylon and polyester fibers. The dyed fibers showed fairly good light fastness, very good to excellent fastness to wash, rubbing, perspiration and excellent fastness to sublimation. The dyebath exhaustion and fixation on the fiber were found to be very good.

Keywords: 2-amino-4-(p-nitrophenyl)-5-nitrothiazole, N-alkylanilines, Dyeing, Nylon, Polyester

Introduction

Monoazo disperse dyes with heterocyclic diazo components have been intensively investigated to produce bright and strong colour shades ranging from red to greenish blue on synthetic fiber. These results led to commerial products to replace the conventional azobenzene disperse dyes[1]. Most heterocyclic dyes of technical interest for application to textiles are derived from diazo components consisting of five-membered rings containing one sulphur heteroatom and to which a diazotizable amino group is directly attached, the ring may also possess one or more nitrogen heteroatoms.

Before 1950, almost all the disperse blue dyes used were prepared from the anthraquinone class and had the limitations of poor dischargeability and sensitivity to oxide of nitrogen. Derivatives of 2-aminothiazole has a long history of use as heterocyclic diazo components for disperse dyes[2]. Blue dischargeable monoazo derivatives based on 2-amino-5-nitrothiazole caught the attention of dye chemists in the 1950, with colourants such as C.I. Disperse Blue 339[3] having been produced commercially since then[2]. 2aminothiazole containing nitro groups are prized for their bathochromism and high tinctorial strength relative to their carbocyclic analogues[4]; these properties, which have aided the rise to prominence of such dyes as replacement for blue anthraguinone colourants[5], were first reported by Dickey nearly forty years ago[6]. 2-amino-5-nitrothiazole could be used to produce bright blue dyes with adequate lightfastness combined with excellent dischargeability, gas fastness and dyeability on hydrophobic fiber. Greenish blue dyes can be prepared by choosing a coupler containing electron donating groups such as 5-acetamido-2-methoxyaniline derivatives. Additional early work on the 2-thiazolylazo dyes resulted in violet dyes from 2-amino-4-trifluoromethyl-5-carbalkoxythiazole [7], 2-amino-4-alkylsulphonylthiazole[8], 2-amino-4-chloro -5-formyl[9] and even more bathochromic dyes from 2amino-4-alkylsulphonyl-5-nitrothiazole[10].

During the last five years, level of interest as indicated by the paper published in literature has grown in the field of thiazolylazo disperse dyes[11-17]. It seems that no report is available on the use of 2-amino-4-(p-nitrophenyl)-5-nitrothiazole in the synthesis of disperse dyes by coupling with various N-alkylaniline derivatives. Hence, it was thought worthwhile to synthesize a series of disperse dyes of general structural formula shown in Figure 1 and test as disperse dyes for polyester and nylon fibers. In addition to the characterization of the dyes, evaluation of their technical properties and colour assessment were performed.

Experimental

Materials and Methods

All of the chemicals used in synthesis of dyes 1 were of commercial grade and were further purified by crystallization and distillation. All solvents used were either of analytical grade or redistilled commercial grade. Melting points were determined by open capillary method. The visible absorption spectra were measured in a Carl Zeiss UV/VIS Specord spectrometer. Elemental analysis were carried out on a Carlo Erba Elemental Analyser 1108. Infrared spectra were recorded in KBr pellets, on a Perkin-Elmer model 983 spectrophotometer.

Preparation of 2-amino-4-(p-nitrophenyl)-5-nitrothiazole

The titled compound was synthesized by the method reported in the literature [6,18].

$$\begin{array}{c|c} O_2N & & N \\ \hline O_2N & & N=N \\ \hline & R_3 \\ \hline & 1 \\ \end{array}$$

Figure 1. General structural formula of dye 1.

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Scheme 1. Synthetic route of dye 1.

Preparation of Dye 1

Diazotization of 2-amino-4-(p-nitrophenyl)-5-nitrothiazole **2** was effected with nitrosylsulphuric acid as follows.

Dry sodium nitrite (1.38 g; 0.02 mol) was slowly added with stirring to concentrated sulphuric acid (1.2 ml) on a water bath, allowing the temperature to rise to 65°C but no higher. The solution was then cooled to 5°C and a mixture (20 ml) of acetic acid-propionic acid (17:3) was added dropwise with stirring, allowing the temperature to rise to 15°C but no higher. The reaction mixture was then cooled to 0-5°C, and compound 2 (5.32 g; 0.02 mol) was added portionwise and stirring was continued at this temperature for 2 hours. The excess nitrous acid (the presence tested by starch-iodide paper) was decomposed with urea. The clear diazonium salt solution 3 thus obtained was used immediately in the coupling reaction (Scheme 1).

General Coupling Procedure

The N-alkylaniline (0.02 mol) was dissolved in glacial acetic acid (10 ml) and water (5 ml) together with sodium acetate (5 g). This solution was cooled in an ice-bath and the diazonium solution of 3 previously prepared was added dropwise over 30 minutes with vigorous stirring. The pH was maintained between 4 and 5 by simultaneous addition of 10% sodium acetate solution. Stirring was continued for 2 hours, allowing the temperature to rise to ambient. The dye

Table 2. Characterisation data for dye 1

Dye	Su	bstituen	its	Melting point	R _f Value		
no.	R_1	R_2	R_3	(°C)	(%)	Nf value	
1a	Н	ОН	Н	120-121	82	0.82	
1b	Н	CN	Н	104-105	85	0.92	
1c	CH_3	OH	H	128-129	80	0.90	
1d	CH_3	Cl	Н	127-128	72	0.84	
1e	C_2H_5	OH	Н	101-102	85	0.79	
1f	C_2H_5	Cl	Н	110-111	77	0.87	
1g	C_2H_5	CN	Н	100-101	89	0.88	
1h	Н	OH	CH_3	98-99	89	0.86	
1i	Н	CN	CH_3	100-101	80	0.86	

was then filtered off, washed with warm and cold water until acid-free, dried at 50°C in an oven to give azo dye 1. Recrystallized from DMF provided the pure dye (Scheme 1). The characterization data are given in Tables 1 and 2.

Dyeing Procedure

Dyeing at 130-135°C and high pressure (24-30 psi) is a convenient method for dyeing polyester fiber in the laboratory. A laboratory model glycerin-bath high-temperature beaker dyeing machine was used. A paste of finely powdered dye (40 mg) was prepared with dispersing agent Dodamol (80 mg), wetting agent Tween- 80 (5 mg) and water (1 ml) in a ball mill. To this paste, water (99 ml) was added with stirring and the pH was adjusted to 4.5-5 using acetic acid. The previously mentioned dye suspension (100 ml) was added to a beaker provided with a lid and a screw cap. Before closing the lid and tightening the metal cap over the beaker, a wetted pattern of polyester fiber was rolled into the beaker. The beaker was then placed vertically on the rotatory carrier inside the tank and the clamp plate was firmly tightened. The rotatory carrier was then allowed to rotate in the glycerin-bath the temperature of which was raised to 130°C for polyester fiber at the rate of 2°C/minute. The dyeing was continued for 1 hour, under pressure. After cooling for 1 hour, the beaker was removed from the bath

Table 1. Absorption maxima, intensities, exhaustion and fixation of dye 1 on polyester and nylon

Dye no. R_1	S	Substituents		Absorption	maxima (λ _{max})	1	Polyester		Nylon	
	R_1	\mathbf{R}_2	R_3	λ _{max} /nm (DMF)	$\lambda_{\text{max}}/\text{nm}$ (conc. H_2SO_4)	$\log \varepsilon$ - (DMF)	%E	%F	%E	%F
1a	Н	ОН	Н	530	460	4.26	70	81	72	87
1b	Н	CN	H	540	445	4.33	78	89	82	88
1c	CH_3	OH	H	525	460	4.44	72	82	83	88
1d	CH_3	Cl	H	540	475	4.36	78	88	76	92
1e	C_2H_5	OH	H	515	465	4.33	76	84	77	86
1f	C_2H_5	Cl	Н	540	475	4.26	74	83	77	90
1g	C_2H_5	CN	H	540	440	4.13	77	88	84	87
1h	Н	OH	CH_3	530	465	4.29	78	86	79	90
1i	Н	CN	CH_3	540	455	4.61	75	84	77	89

Table 3. Elemental analysis of dye 1

Dye no. —	S	Substituents		Molecular	Molecular	C%		Н%		N%	
	\mathbf{R}_1	R_2	R_3	formula	weight	Require	Found	Require	Found	Require	Found
1a	Н	OH	Н	C ₁₇ H ₁₄ N ₆ O ₅ S	414	49.27	48.90	3.38	2.90	20.28	19.96
1b	Н	CN	Н	$C_{18}H_{13}N_7O_4S$	416	51.92	51.62	3.12	2.98	21.87	21.29
1c	CH_3	OH	Н	$C_{18}H_{16}N_6O_5S$	428	50.46	50.12	3.73	3.55	19.62	19.25
1d	CH_3	Cl	Н	$C_{18}H_{15}N_6O_4SCl$	446.5	48.37	48.01	3.35	3.19	18.81	18.20
1e	C_2H_5	OH	Н	$C_{19}H_{18}N_6O_5S$	442	51.58	51.20	4.07	3.90	19.00	18.70
1f	C_2H_5	Cl	Н	$C_{19}H_{17}N_6O_4SC1$	460.5	49.51	49.10	3.69	3.40	18.24	18.00
1g	C_2H_5	CN	Н	$C_{20}H_{17}N_7O_4S$	444	54.05	53.60	3.82	3.6	20.49	19.90
1h	Н	OH	CH_3	$C_{18}H_{16}N_6O_5S$	428	50.46	50.29	3.73	3.58	19.62	19.51
1i	Н	CN	CH_3	$C_{19}H_{15}N_7O_4S$	430	53.02	52.20	3.48	3.28	21.16	20.89

Table 4. Results of dyeing and various fastness properties of dye 1 onto polyester

Dye no.	Colour shade on polyester	Light	Wash	Perspirat	ion fastness	_ Sublimation fastness	Rubbing fastness	
		fastness	fastness	Acid	Alkaline		Dry	Wet
1a	Dark brown	5-4	5-4	5-4	5	5	5	5
1b	Reddish brown	5-4	5-4	5	5	5	5	5
1c	Brownish violet	5-4	4-5	5-4	5	5	5	5
1d	Bluish violet	5	5-4	5	5	5	5	5
1e	Brick red	5-4	5-4	5-4	5-4	5	5	5
1f	Dark brown	5-4	5-4	5-4	5-4	5	5	5-4
1g	Brown	5-4	5-4	5	5-4	5	5	5
1h	Maroon	5-4	5-4	5	5-4	5	5	5
1i	Bluish violet	5-4	5-4	5	5-4	5	5	5

Table 5. Results of dyeing and various fastness properties of dye 1 onto nylon

Dye no.	Colour shade on nylon	Light fastness	Wash _	Perspirat	ion fastness	Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
1a	Dark brown	4-5	4	4-5	4-5	5	5	5
1b	Dark brown	4-5	5-4	5	5	5	4-5	5-4
1c	Reddish violet	4	4-5	5	5-4	5-4	4-5	5
1d	Maroon	5-4	4-5	5-4	5-4	5	5	5-4
1e	Dark brown	5-4	5-4	4-5	4-5	5	5	5
1f	Brown	4-5	4-5	5-4	5-4	5	5	5-4
1g	Dark brown	4-5	5-4	5	5	5	5	5
1h	Light brown	4-5	4-5	5-4	5-4	5	5-4	5
1i	Blackish violet	5-4	5-4	5	5-4	5	5	5

and washed with water. The dyed pattern was thoroughly washed with hot water of 50°C and then with cold water and dried at room temperature. Similarly, the dyeing of nylon fiber was carried out at 90°C for 1 hour.

Fastness Properties

The fastness to light, sublimation and perspiration was assessed in accordance with BS: 1006-1978. The rubbing fastness test was carried out using crockmeter (Atlas) in accordance with AATCC-1961 and the wash fastness test in accordance with IS: 765-1979. The details of various fastness tests are mentioned below.

Light Fastness Test

The light fastness study was carried out using Microscal light fastness tester having a straight mercury vapour lamp (MB/V 400 W). The dyed fiber is exposed to light along with the standard dye patterns of specific rating. Such standard samples are a blue wool standard manufactured by Microscal Ltd and identified by the numerical designation 1 to 8. Higher the rating, better is the light fastness. The results are given in Tables 4 and 5.

Wash Fastness Test

Fastness to washing was assessed by using an automatic

Lander-O-meter under the following conditions.

The washing solution contained neutral soap at 5 g/litre and soda ash 2 g/litre, a washing temperature of 95°C, the duration of washing was 30 minutes; and the material-to-liquor ratio was 1:50. After washing, the specimen was removed and rinsed with hot water (35°C) until the rinsed water showed no alkalinity with phenolphthalein. It was then squeezed and air dried. The effect on the colour was expressed and defined by reference to the international geometric grey scale. The results are given in Tables 4 and 5.

Rubbing Fastness Test

The specimen is fastened in the crockmeter, which causes a piece of standard white cloth to rub against the coloured specimen under control conditions of pressure and speed. The rubbing fingers are covered with white cloth, both for the dry test and wet test, and slide back and forth for twenty rubbing strocks. The colour transferred to the white cloth is compared with a grey scale. The grey scale used for the alteration of colour was consisted of grade 1-5. The results are given in Tables 4 and 5.

Perspiration Fastness Test

Specimen of the textile in contact with specified adjacent fibers are treated in two different solutions containing histidine, drained, and placed between two plates of 11.5 cm×6 cm size and of 0.15 cm thickness under the pressure of a weight-piece of mass 5 kg in a testing device consisting of a stainless steel frame. It was kept in an oven for 4 hours at 37±2°C. The specimen and the adjacent fibers are dried separately. The change in colour of each specimen and the staining of the adjacent fibers are assessed with the grey scales.

Acid Perspiration Test

The freshly prepared acid solution contained 5 g/litre sodium chloride (NaCl), 2.2 g/litre sodium dihydrogen orthophosphate (NaH₂PO₄ \cdot 2H₂O) and 0.5 g/litre l-histidine mono-hydrochloride mono-hydrate (C₆H₉O₂N₃HCl \cdot H₂O). The solution is brought to pH 5.5 with a 0.1 N acetic acid solution. The results are given in Tables 4 and 5.

Alkaline Perspiration Test

A freshly prepared alkaline solution contained 5 g/litre sodium chloride (NaCl), 0.5 g/litre l-histidine monohydrochloride mono-hydrate ($C_6H_9O_2N_3HCl\cdot H_2O$) and 2.5 g/litre disodium hydrogen orthophosphate (Na₂HPO₄· 2H₂O). The solution is brought to pH 8 with a 0.1 N sodium hydroxide solution. The results are given in Tables 4 and 5.

Sublimation Fastness Test

The composite specimens were placed in a heating device (Sublimation Tester, Model STE) equipped with two heating plates with an electrical heating system and kept there for 30 second at 150±2°C. The dried fiber was then removed and

kept in air for 4 hours. The change in colour of the specimen was assessed with the grey scales. The results are given in Tables 4 and 5.

Determination of the Percentage Exhaustion and Fixa-tion (Dissolution Method)

The dyebath exhaustion percentage (%E) and fixation percentage (%F) of the dyed fiber were determined according to the method described below.

Exhaustion

This method involves two steps, e.g. (a) construction of a calibration curve and (b) estimation of dye.

(a) Calibration Study

Calibration study involves preparation of dye solution of known concentration and measurement of absorption at specified wavelength. A solution of known weight (40 mg) dye was prepared by grinding very well with dispersing agent Dodamol (20 mg) and 2-3 drops of wetting agent, Tween-80 in a small mortar with pestle and diluting with required amount of distill water to make the final volume 100 ml. (stock solution). Now four dilutions of different concentration were prepared by using 2, 5, 7, and 10 ml each of the stock solution with required amount of distilled water to make the final volume 100 ml. The solution of 20 mg of the dispersing agent and 2-3 drops of wetting agent in 100 ml water was used as a reference solution. The absorption of stock solution was measured at various wavelengths ranging from 350 to 700 nm and the position of λ_{max} value was ascertained. At the λ_{max} value, the absorption of above four diluted solutions were measured and a plot of absorption versus concentration was made for each dye. This plot is known as calibration curve.

(b) Estimation of Dye

The combined solution of dye liquor and washing of the dyed pattern were diluted to 250 ml with distilled water. Now take 5 ml solution was further diluted to 50 ml with distilled water. The amount of dye exhaustion on the fiber can be calculated by measuring the absorption of the above solution at $\lambda_{\rm max}$ and reading the corresponding concentration on the calibration curve.

Fixation Study

This method also involves two steps. e.g. (a) construction of calibration curve and (b) estimation of dye.

(a) Calibration Curve

This follows the same procedure as previously. The known weight of dye was dissolved in A.R. grade concentrated sulphuric acid (50 ml) and prepared four various dilutions using 1, 2, 3 and 4 ml of stock solution. The optical density of the stock solution was measured at various wavelengths in the range from 350 to 700 nm. At the position of $\lambda_{\rm max}$, the optical density of four solutions was measured. A calibration curve was prepared by plotting optical density against

concentration.

(b) Estimation of Fixation of Dye on Fiber

A sample of undyed fiber (0.1 g) was dissolved in concentrated sulphuric acid (25 ml) and this solution was used as a reference solution in colorimetric estimation. Now dyed fiber (0.1 g) was dissolved in (15 ml) concentrated sulphuric acid. This required about 10-15 minutes. The solution was then diluted to 25 ml with concentrated sulphuric acid. Optical density of this solution was measured at the λ_{max} value. Using calibration curve, the concentration of the dye was measured and hence how much amount of dye fixed on the fiber has been estimated.

The fixation of the dye on fiber is based on its exhaustion. It can be seen from Table 1, the dye **1a** has 87% fixation. It means 87% fixation on the basis of corresponding 72% exhaustion. The fixation value is not directly based on the amount of dye taken in dyebath but it is based on the amount of the dye exhausted on the fiber. Sometimes fixation value may be higher or lower than exhaustion value.

The exhaustion and fixation values were calculated by using following relation.

% Exhaustion =

Amount of dye exhausted on the fiber from dyebath×100

Total amount of dye taken in dyebath

% Fixation =

Amount of dye fixed on dyed fiber×100

Amount of dye exhausted on the fiber from dyebath

Suppose 40 mg dye **1a** has been taken in dyebath for dyeing purpose. If 28.80 mg dye was found to exhausted on fiber, i.e.

% Exhaustion =
$$\frac{28.80 \times 100}{40}$$
 = 72%

Now, suppose 25.06 mg dye 1a has been fixed on the fiber (out of 28.8 mg). i.e.

% Fixation =
$$\frac{25.06 \times 100}{28.80}$$
 = 87%

Results and Discussion

Preparation of Thiazole Dyes 1

2-amino-4-phenylthiazole was synthesized by treating acetophenone and thiourea with bromine on a steam bath [18]. Nitration of 2-amino-4-phenylthiazole with two equivalent of nitric acid gives 2-amino-4-(p-nitrophenyl)-5-nitrothiazole[6]. The nitro group reduces the basicity of the nitrogen atom of amino group and thus efficient diazotization can only be achieved using nitrosylsulphuric acid obtained from sodium nitrite and concentrated sulphuric acid.

Thus thiazole, intermediate 2 was diazotized satisfactorily at 0-5°C by nitrosylsulphuric acid in acetic acid. In order to

determine the end point of diazotization, it was found useful to check for the presence of unreacted diazo component on thin layer chromatography (T.L.C.) by sampling the diazotization mixture and extracting with ethyl acetate. Thus, when unreacted diazo component no longer persisted on T.L.C., the diazotisation was ended. The diazonium salt solution was used immediately since this decomposed on standing, even when cold. Subsequent coupling reactions took place readily on adding the resulting diazonium salt continuously to the solution of coupling component in acetic acid. Coupling was usually accompanied by some evidence of decomposition; however by careful addition of the diazonium salt solution 3 at 0-5°C to a solution of the coupling component in an aqueous acetic acid, high yields (72-89%) of the dye were usually obtained. To complete coupling, particularly for reactions using nitrosylsulphuric acid for the diazotisation, the pH of the reaction mixture was eventually adjusted to approximately 4-5. Thus, an appropriate amount of 10% sodium acetate solution was slowly added to the solution below 5°C.

Physical Properties of Dyes

All the solid dyes are dark brown in colour. The purity of the dyes was checked by thin layer chromatography T.L.C. using methanol: water: acetic acid (12:3:7) the solvent system. When adsorbed onto silica chromatography plates, each dyes produced a reddish-violet colour spot. All the recrystallized dyes exhibited well-defined melting points characteristic of pure compounds.

Visible Absorption Spectroscopic Properties of Dyes

The visible absorption spectroscopic properties of dye 1 were recorded in DMF solution and are presented in Table 1. The value of the logarithm of molar extinction coefficient (log ε) of the dyes 1 was in the range of 4.13-4.41, consistent with their high intensity of absorption. One cause of the increased intensity might be attributed to the greater planarity of the thiazole dyes, because of the lower steric interaction of a five-membered ring.

The colour of the 2-thiazolylazo dyes is affected by substituents in the coupler constituent. The bathochromism of the 2-thiazolylazo dyes is an inherent property of the thiazole system itself; the bathochromism does not derive from the substituent groups. However, the greater polarizability of the thiazole system (relative to the benzene system), in addition to affecting a general bathochromism in 2-thiazolylazo dyes, also allows a greater electronic displacement to be effected by electronegative substituents. This displacement results in an increased absorption shift. Electron-attracting substituents like Cl and CN in the dialkylamino group of the coupler increase polarizability and should result in bathochromic shifts. This leads to decrease in energy between the highest occupied molecular orbital and lowest unoccupied molecular and thus $\pi - \pi^*$ electron transition takes place at

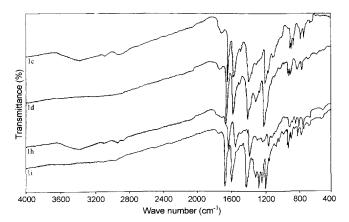


Figure 2. Infra-red spectra of dye 1c, 1d, 1h, and 1i.

lower frequency photon resulting in the bathochromic shift of the visible absorption band.

Infra-red Spectra of Dyes

The infra-red spectra of dyes **1c**, **1d**, **1h** and **1i** are shown in Figure 2. The C-H stretching vibrations of aromatic ring appear at 700-820 and 1580-1595 cm⁻¹. The strong absorption band in the range 1500-1510 cm⁻¹ is corresponding to C-N stretching vibration. The N-H stretching vibration confirmed at 3400-3450 cm⁻¹. The azo and O-H group stretching vibration band appear at 1500-1525 cm⁻¹ and 3500-3600 cm⁻¹ respectively. The C-H stretching vibration of alkyl group appears at 2895-2900 cm⁻¹.

Dyeing Properties of Dyes

The dispersed dyes 1 were applied at 1% depth on nylon and polyester fibers. Their dyeing properties are given in Tables 4 and 5. These dyes gave reddish brown to bluish violet shades with good levelness, brightness and depth on the fibers. The variation in the shades of the dyed fibers results from both the nature and position of the substituents present on the coupler ring. The results (Tables 4 and 5) show that all the fastness properties of the dyes 1 are relatively poor on nylon compared with polyester. This is may be due to the higher substantivity of the dyes for the substrate as well as to the relatively open structure of nylon which readily allows the outward migration of the dye molecules. This may also be due to one or more of the factors like smaller molecular size of dye molecule, as well as a deep sample shade. The dyes had low light fastness on nylon. The poor photostability may stem from photoreduction of the nitro substituent being promoted by the amino end group of the polyamide chain[19].

Conclusion

A series of thiazolylazo disperse dyes containing various

N-alkylaniline residues have been synthesized by conventional methods and their colour properties examined both in solution and on application to nylon and polyester fibers. The dyes provide wide range of colour varying from reddish brown to bluish violet, fast shades on fibers. Their synthesis is generally convenient and economical. The small size of thiazolylazo dyes provided better dyeability. The intrinsic conjugation in the thiazolylazo structure results in excellent colour strength. The compactness of structure improve sublimation fastness. The heteroatoms in the thiazolylazo structure results in bathochromacity and leads to brightness of shades. Furthermore these dyes showed a remarkable degree of levelness after washing indicated good penetration and excellent affinity to the fibers.

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