

PREPARATION OF AZO DISPERSE DYES FROM 1,4-DIAMINOBENZENE AND 4-AMINO-3-NITROTOLUENE AND THEIR APPLICATION ON POLYESTER FIBRE USING THE THERMOSOL AND AQUEOUS DYEING METHODS

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ABSTRACT

The preparation and application of azo disperse dyes from 1, 4-diaminobenzene and 4-amino-3-nitrotoluene are described. The azo dye derivatives of these two compounds exhibited very high light fastness on polyester fabric when applied using the Thermosol process in comparison with the aqueous (carrier) dyeing method which gave moderate light fastness. The azo dyes were characterized by elemental, IR and UV analyses. The prepared azo dyes may find application in the dyeing and printing of upholstery materials that may be exposed to long periods of sunlight during usage.

Keywords: Vapour-phase dyeing, Aqueous (carrier) dyeing, Disperse dyes, Dyeing properties, polyester fibre.

INTRODUCTION

The production of disperse dyes has increased sharply, in recent years, closely following the growth in worldwide production of synthetic fibres, especially polyester (polyethylene terephthalate) fibres, production of which has grown steadily from 1999 (Otutu, 2008; Richter and Bast, 1977). This is due not only because of its outstanding textile properties but also in view of the good yield of fibre per tonne of petroleum required for its production (Otutu, 2008; Venkataraman, 1974, Venkataraman, 1978).

Furthermore, new dyeing processes necessitated the development of special disperse dyes. For instance, dyes characterized by special ease of sublimation are preferred for transfer printing (David and Geoffery, 1994; Otutu, 2010) while those that have high sublimation values are preferred for Vapour-phase dyeing. The demand for new fastness properties such as thermo-migration fastness and automotive light fastness (Townes, 1999; McGregor, 1967) also led to new dyes as has the ongoing pressure on market prices.

Models for the dyeing of polyester fibres with disperse dyes have been developed (Shuttleworth and Weaver, 1994). When the dye is applied from aqueous medium, individual molecules dissolve out of the dispersion of

the sparingly water soluble dyes, accumulate in the border zone of the polyester fibre, and diffuse from there into the interior of the fibre. This diffusion is normally the slowest process and consequently governs the rate of dyeing (Burkinshaw, 1994). Aqueous dyeing involves either the use of very high temperature of about 135°C that require the use of special machinery or the use of carriers as accelerators to bring about deep dyeing.

When the dye is applied from the vapour-phase transfer technique (Thermofixation process), high temperatures of about 215-220°C are normally used to obtain rapid fixation of the dyes in the fibre. The thermosol or pad-bake process utilizes the ability of disperse dyes to sublime and diffuse rapidly into the fibre under dry conditions at a very high temperature when the molecular structure of the fibre is loosened (Moncrieff, 1975; Giles, 1974).

The present study was aimed at preparing a series of disazo disperse dyes from 4-amino-3-nitrotoluene and 1,4-diaminobenzene and applying the dyes on polyester fibre using the thermosol and aqueous methods and hence compared the dyeing properties such as light, crocking and wet treatments (wash and perspiration) based on the two dyeing methods.

Experimental

All the reagents and solvents were of reagent-grade quality and purchased from commercial supplies. All the melting points were determined in a kofler apparatus, and are presented without corrections. The purity of the compounds were confirmed by thin layer chromatography (TLC) using Whatman 250mm silica Gel 60 AMK 6F plates (ether/acetone 5:1). The infrared spectra were obtained using an ATI Mattson Genesis series FT-IR spectrophotometer. UV-visible spectra were recorded equipped with Helios Scan Software in dimethyl formamide (DMF) at a concentration of 3.4×10^{-6} M. Elemental analyses were carried out on a Perkin Elmer 240C series for C, N and H.

APPLICATION OF DYES ON POLYESTER FIBRE

1. Thermo-fixation Dyeing

Polyester fabric (Terylene 100%) was obtained from multichem (Nigeria) ltd and pretreated. Dyes (1.00g) were applied to the polyester fabric by a pad-dry-thermosol procedure using 1% depth in a bath containing 0.1g (owf) dispersing agent (Macheasl). The laboratory pad mangle used was supplied by Matthis and had the squeeze rollers aligned in a horizontal mode; and in all cases the squeeze pressure was set at 27.216kg per square meter which was sufficient to give a wet pick-up of 90%. Drying and thermosolling of the impregnated fabric was carried out in a Matthis Laboratory Steamer baker unit at 190-220°C for 1-minute for thermo-fixation of dyes in the fabric. Dyed samples were reduction cleared in an aqueous solution containing sodium hydrosulphite (2.0g/l), sodium carbonate (2.0g/l) and dispersing agent (5.0g/l) for 15 minutes at 80°C (Ahmed, 2004; Otutu, 2008).

2. Aqueous Dyeing

Rectangular polyester fabric pieces (15cm x 15cm) were prepared and entered into the dye bath containing 1.0g of dye sample and phenol (40g/l) as carrier. The dye bath liquor was buffered to pH 5.0. The temperature of dye bath was set at 85°C, raised to 100°C over 15 minutes, maintained at this temperature for 1 hour. Reduction clear treatment was determined as described for the thermosol process

the dyed fabric was scoured in a detergent solution (1.0g/l) at 50°C for 15 minutes to remove residual carrier from the fabric and finally, rinsed and dried as described in the literature (Giles, 1974). Light fastness test was evaluated on a xenotest Hanou) using standard procedure (AATCC, 1993). Perspiration fastness was determined according to ISO, EO4 1994 standard procedure (ISO, 1994). Both alkaline and acid perspiration fastness were evaluated. Crocking fastness was tested according to a test method (ISO, 2001).

Preparation of the azo dyes

Diazotisation of 4-amino-3-nitrotoluene.

NaNO₂ (4.0 mmol) was added drop-wise to a cooled mixture of concentrated sulphuric acid (5 mL), water (5.0 mL) 4-amino-3-nitrotoluene, (3 mmol) and with continuous stirring for 30 minutes. The aqueous solution containing 4.0 mmol of diazonium salt was filtered before use in coupling experiments.

Coupling with 1,4-diaminobenzene

The diazonium salt solution previously prepared (4.0 mmol) was added dropwise to the solution of 1,4-diaminobenzene (3 mmol) in glacial acetic acid (20 mL) and the combined solution maintained at 0°C for 3hours with stirring. The reaction mixture was left overnight and the product was isolated by filtration. The dried product 2-nitro-4-methylphenylazo-2-5-diaminobenzene was purified by recrystallization from hot CCl₄ to give 53% yield.

Method A

Preparation of 2-Nitro-4-methylphenylazo-aminophenylazo-3-methoxyphenyl-4-aminobenzene 5

To a mixture of compound 3 (26 mmol) and 50 mL of water was added, 10 mL of concentrated H₂SO₄, which was subsequently diazotized by treatment with sodium nitrite 4.0 g, 5 mmol at 0°C with stirring for 20 minutes. The resulting solution of diazonium salt **4** was slowly added with vigorous stirring at 0-5°C, over a solution of m-anisidine (3 mL) dissolved in ethanoic acid (15 mL) for 2 hours. The crude product was filtered off and recrystallized from hot methanol-water (2:1) to give a dark-brown solid

(1:85g, 61%) m.p 215-217°C

2-nitro-4-methylphenylazo-2-aminophenylazo-3-chloro-2-aminobenzene 6

To a mixture of compound 3 (2.0 g, 0.0073 mmol) and 50 mL of water was added, 6 mL of concentrated sulphuric acid, which was subsequently diazotized by treatment with sodium nitrite solution (4.0 g, 5 mmol) at 0°C with stirring for 20 minutes. The resulting solution of diazonium salt was slowly added with vigorous stirring at 0-5 °C over a solution of 4-chloroaniline (2 mL) in acetic acid (15 mL). Finally, the resulting dye precipitate was filtered after 2 hours and recrystallized from methanol to give a brown solid (1.58g 52%) M.p 274-276 °C, $R_f = 0.35$.

UV (DMF) I_{\max} nm(S/M⁻¹cm⁻¹) 386 (71,500)
 FT-IR (KBr) 3454 - 3318cm⁻¹ (NH), 2853cm⁻¹ (Ar.CH stretch), 1500cm⁻¹ (Ar-ring), 1526, 1307cm⁻¹ (NO₂), 1461cm⁻¹ (-N=N-)
 C₁₉H₁₆N₇O₂Cl: Calcd. C 55.68, H 3.94, N 23.92 found C 55.61, H 3.89, N 23.93.

2-Nitro-4-methylphenyl azo-2'-amino-5-nitrobenzene 7

Compound 7 was obtained following the procedure similar to that used for the formation of compound 6 obtaining a yellowish brown solid after recrystallization from CCl₄ (1.28g, 55%) M.p 243-245°C, R_f ether/acetone 5.1) = 0.68.

UV (DMF) I_{\max} (nm) (S/M⁻¹cm⁻¹) 420 (16,200)

FTIR (KBr). 3402cm⁻¹ (NH), 2854cm⁻¹ (Ar-C-H_{stretch}), 1595, 1367cm⁻¹ (NO₂), 1500cm⁻¹ (Ar-ring) 1460cm⁻¹ (-N=N-). C₁₉H₁₆N₈O₄ calcd. C54.29, H3.84, N26.65 found C52.25, H3.86, N26.62.

2-Nitro-4-methylphenylazo-2-aminophenylazo-4-aminonaphthalene 8

Compound 8 was obtained following the procedure similar to that used for compound 6 producing a brown solid after recrystallization from hot methylated spirit (1.29g, 41%) M.p 235°C $R_f = 0.67$

UV (DMF) I_{\max} nm (S/M⁻¹cm⁻¹) 420, (25,800)

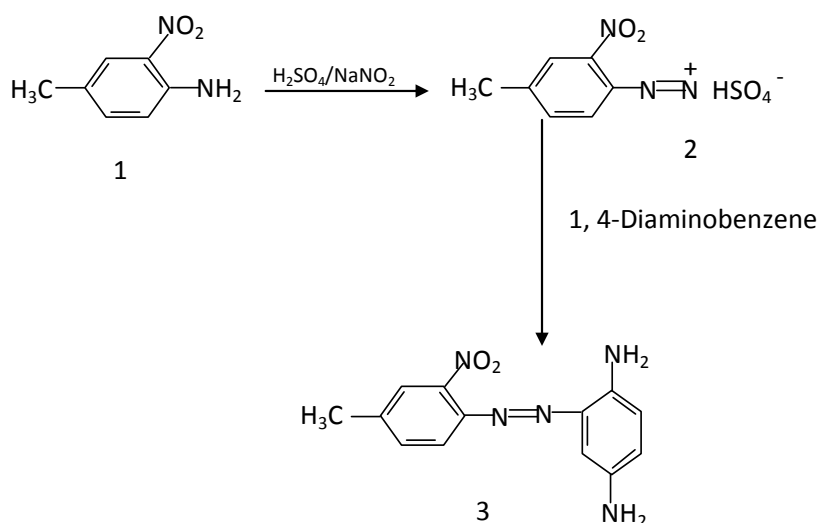
FTIR (KBr) 3369cm⁻¹(NH), 2707cm⁻¹ (Ar-C-H_{stretch}), 1526, 1349cm⁻¹(NO₂), 1500cm⁻¹ (Ar-ring), 1445cm⁻¹ naphthalene ring, 1463cm⁻¹ (-N=N-) C₂₃H₁₉N₆O₂ calcd. C67.14, H4.65, N20.43. found C67.09, H4.59, N20.41.

2-Nitro-4-methylphenylazo-2'-aminophenylazo-3,4-diaminobenzene 9

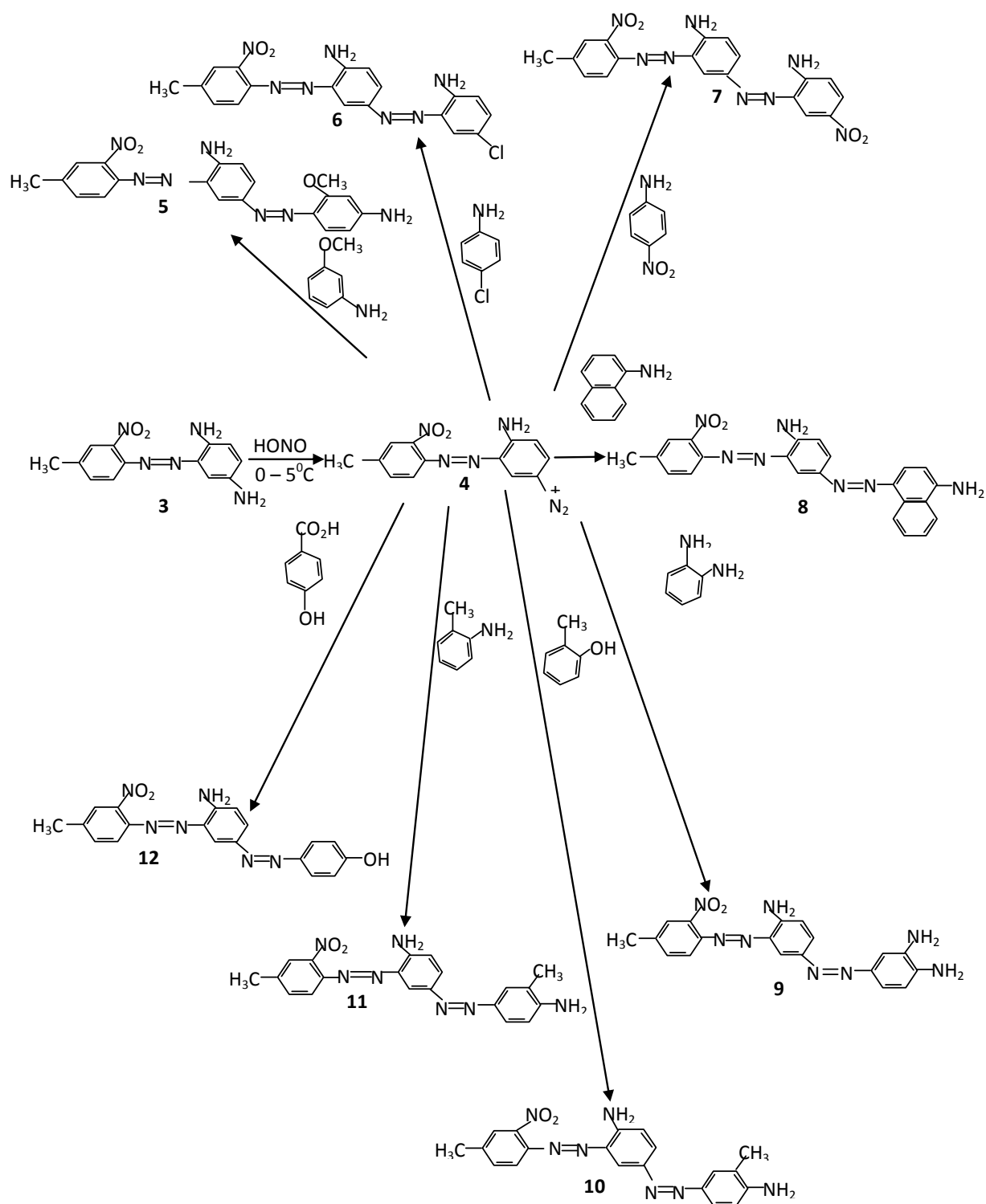
Compound 9 was obtained following the procedure described for compound 6 obtaining a dark brown solid after recrystallization from hot methanol (1.42g, 51%) M.p 265 267°C, $R_f = 0.65$.

UV (DMF) I_{\max} nm (S/M⁻¹cm⁻¹) 420 (24,300). FTIR (KBr) 3393, 3162cm⁻¹ (NH), 2727cm⁻¹(Ar-C-H_{stretch}) 1523 1335cm⁻¹ (NO₂), 1500cm⁻¹ (Ar-ring) 1461cm⁻¹ (-N=N-)

C₁₉H₁₈N₈O₂ Calcd. C58.45, H4.65, N28.70 found C58.44, H 4.61, H28.65.



Scheme 1



Scheme 2

Method B

Preparation of 2-Nitro-4-methylphenylazo-2-aminophenylazo-4-hydroxy-3-methylbenzene 10.

A mixture of compound **3** (2.0 g, 0.0073 mmol), water (40 mL) and concentrated sulphuric acid (6 mL) was cooled to 0°C and treated with sodium nitrite (4.0 g, 0.057 mol) in 10 mL of water at 0°C. The resulting diazonium salt **4** was slowly added to a solution of o-cresol (2 mol) in 2M NaOH (60 mL) with vigorous stirring for 2 hours. The precipitate was isolated by filtration and re-crystallized from CCl₄ to give a brown solid (1.08g, 54%), m.p = 28°C, R_f = 0.55. UV (DMF) I_{max} nm (S/M⁻¹cm⁻¹) 420(75,800). FTIR (KBr), 3390cm⁻¹(OH), 2728cm⁻¹(Ar-C-H_{stretch}) 1526, 1348cm⁻¹ (NO₂), 1500cm⁻¹ (Ar-ring), 1461cm⁻¹ (-N=N-)
C₂₀H₁₈N₆O₃ Calcd.C61.53, H4.65, N21.29
Found C61.54, H4.63, N21.49.

2-Nitro-4-methylphenylazo-2-aminophenylazo-4-amino-3-methylbenzene, 11

Compound **11** was obtained by following a procedure similar to that used for the formation of compound 5, obtaining a brown solid (1.20g, 43%). M.p 262°C R_f = 0.30. UV (DMF) I_{max} nm (S/M⁻¹cm⁻¹) 448 (19,300). FTIR (KBr) 3415, 3260cm⁻¹ (NH), 285.3cm⁻¹ (Ar-C-H_{stretch}), 1622cm⁻¹ (Ar-ring), 1528, 1320cm⁻¹ (NO₂), 1461cm⁻¹ (-N=N-).
C₂₀H₁₉N₇O₂ Calcd.C61.69, H4.92, N25.18, found C 61.66, H4.86, N25.13

2-Nitro-4-methylphenylazo-2-aminophenylazo-5-hydroxybenzene 12

Compound **12** was prepared following a procedure similar to that used for the formation of compound 10, obtaining a yellowish brown solid. (1.54g, 68%), m.p 292°C, R_f = 0.61
UV (DMF) I_{max} nm (S/M⁻¹cm⁻¹) 448, 944,700
FTIR (KBr), 3432cm⁻¹(OH), 2854cm⁻¹ (Ar-C-H_{stretch}) 1525, 1310cm⁻¹ (NO₂), 1500cm⁻¹ (Ar-ring) 1458cm⁻¹ (-N=N-), C₂₀H₁₆N₆O₅ Calcd.C 57.14, H3.84, N 19.99. found C57.11, H3.78, N19.95.

RESULTS AND DISCUSSION

The azo dyes having 1,4-diaminobenzene and 4-amino-3-nitrotoluene moieties are prepared in this study. The synthetic pathway (Paula, 1995; Cavey, 2003) used for the diazotization reaction and subsequent coupling with various coupling components is shown in scheme 1 and 2. The FTIR spectral analysis and elemental analysis carried out gave results that are in agreement with the proposed structures of dyes 5-12. The FTIR spectra showed bands at 1565-13150cm⁻¹ representing NO₂ group. Variations in the -OH and NH (3200-3500cm⁻¹) overlapping and C=C (2950-2750 and 1600, 1500, 1450cm⁻¹) aromatic bands were observed.

Fastness properties

Light-fastness

The light-fastness testing results (Tables 1 and 2) showed that the thermosol dyeing process gave a rating of 7 on polyester fabric compared to the light fastness of the dyes using the aqueous (carrier) dyeing method which showed a rating of 4 to 5 on the polyester substrate. The reasons for this could be attributed to the fact that there was high exhaustion of the dyes on polyester substrate when the thermosol process was used for dyeing and also due to the high temperature used.

Table 1: Fastness properties of dyes on polyester, using the Thermosol dyeing process

| Dye | Wash-fastness | Perspiration-fastness | | Rubbing-fastness | | Light-fastness |
|-----|---------------|-----------------------|-------------|------------------|-------------|----------------|
| | | Alkaline-medium | Acid-medium | Dry-rubbing | Wet-rubbing | |
| 5 | 5 | 5 | 5 | 3 | 2 | 7 |
| 6 | 5 | 5 | 5 | 2 | 2 | 7 |
| 7 | 5 | 5 | 5 | 3 | 2 | 7 |
| 8 | 5 | 5 | 5 | 3 | 2 | 7 |
| 9 | 5 | 5 | 5 | 3 | 2 | 7 |
| 10 | 5 | 5 | 5 | 2 | 2 | 7 |
| 11 | 5 | 5 | 5 | 2 | 2 | 7 |
| 12 | 5 | 5 | 5 | 3 | 2 | 7 |

Grey scale ratings ranged from 1 (poor) to 5 (excellent). The Grey scale ratings for light fastness ranged from 1-2 (very poor) 3(poor) to 8(excellent)

Table 2: Fastness properties of dyes on polyester, using aqueous (carrier) dyeing method

| Dye | Wash-fastness | Perspiration-fastness | | Rubbing-fastness | | Light-fastness |
|-----|---------------|-----------------------|-------------|------------------|-------------|----------------|
| | | Alkaline-medium | Acid medium | Dry-rubbing | Wet-rubbing | |
| 5 | 5 | 5 | 5 | 3 | 3 | 5 |
| 6 | 5 | 5 | 5 | 2 | 2 | 4 |
| 7 | 5 | 5 | 5 | 3 | 2 | 5 |
| 8 | 4 | 5 | 5 | 3 | 2 | 5 |
| 9 | 5 | 5 | 5 | 3 | 3 | 4 |
| 10 | 4 | 5 | 5 | 2 | 2 | 4 |
| 11 | 4 | 5 | 5 | 2 | 2 | 5 |
| 12 | 5 | 5 | 5 | 3 | 2 | 5 |

Wash fastness

The wash fastness test results (Tables 1 and 2) showed excellent performance rating of 5. The same rating was also observed for the aqueous (carrier) dyeing except for dyes 8, 10 and 11 which gave a lower rating of 4. The low wet fastness rating of these dyes could be attributed to the substituent groups attached to the dye structures.

Perspiration-fastness

The perspiration testing results showed excellent ratings of 5 on the polyester substrate in both methods of dyeing. The reason for this is not completely understood.

Rubbing-fastness

The crocking fastness results (Tables 1 and 2) indicated that the dyes are quite more stable during dry-rubbing than wet-rubbing in both methods of dyeing.

CONCLUSIONS

Azo disperse dye analogs of 1,4-diaminobenzene and 4-amino-3-nitrotoluene were prepared. The dyeing properties of the dyes were compared, using the thermosol dyeing process and the aqueous (carrier) dyeing methods. The light fastness results of the thermosol dyeing process gave higher ratings of 7 on polyester fabric compared with the ratings of 4 to 5 when dyed using the aqueous (carrier) method. The wet (wash, perspiration) fastness results gave almost the same excellent performance except in a few cases. The

rubbing-fastness results were similar in both methods of dyeing. The higher light fastness of the dyes when dyed through the thermosol process showed that the process is more effective in this dyeing process than in the aqueous (carrier) dyeing method.

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