

## Dyeing of hydrophobic fabrics with disperse dyes

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A series of disperse dyes has been synthesized by diazotisation of 2,6-dibromo-4-nitroaniline and coupled with various *N*-arylmaleimides. The dyes were characterized by IR spectral studies, visible absorption spectroscopy and elemental analysis. All the dyes were applied as disperse dyes on nylon, cellulose triacetate and polyester fabrics. These dyes were found to give yellowish orange to deep brown shades with very good depth, levelness and brightness on different fabrics. The percentage dye bath exhaustion and fixation on fabrics were found to be very good. The light, washing, rubbing, perspiration and sublimation fastness properties of the dyed fabrics were found to be good to excellent.

*Keywords:* 2,6-dibromo-4-nitroaniline, nylon, cellulose triacetate, polyester, fixation, fastness, exhaustion.

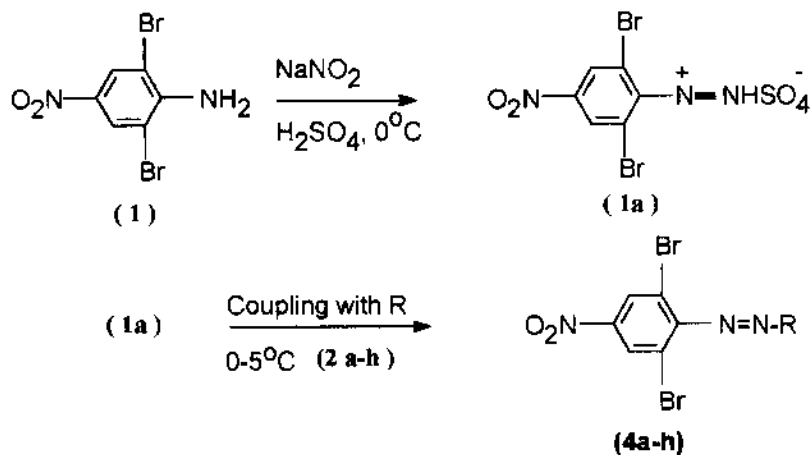
### INTRODUCTION

Intensive research efforts have been made for the past four decades in the area of disperse dyes used for the colouration of hydrophobic fabrics.<sup>1–3</sup>

The introduction of polyester fabrics also acted as a spur to manufacture blue azo dyes to compete in an area formerly considered the strong hold of anthraquinone dyes.<sup>4–6</sup> Since 1970 the neutral blue anthraquinone dyes have been increasingly displaced by azobenzene derivatives which are similar in colour and in certain respects technically equivalent, tinctorially strong and dominate the neutral blue region. Therefore they are commercially interesting. This was initially achieved with dyes such as 6-bromo-2,4-dinitroaniline, which is a navy blue having moderate to good light fastness, especially in heavy depths and good sublimation fastness. Unfortunately, this type of structure is somewhat prone to reduction under severe conditions of application and so research has continued in an attempt to overcome this deficiency.

A variety of new aromatic amino compounds have been employed as carbocyclic diazo components. The commercially available diazo components for obtaining deep shades are limited in number. The halogen atoms, particularly bromine atoms, present in

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Where R is various N-arylmaleimide (2a-h)

Scheme 1.

phenylazo derivatives<sup>7-9</sup> are susceptible to nucleophilic substitution if they are *ortho* to the azo group and this led to a bathochromic shift in the disperse dyes (e.g., red-brown dyes) obtained by diazotisation of coupling with *N,N*-dialkylaniline derivatives, when compared with the dyes without halogen atoms. These dyes had remarkably high extinction coefficients and excellent fastness properties on hydrophobic fabrics. This type of dye has since been widely employed in the manufacture of commercial dyes for fabrics.

The present authors reported recently on disperse dyes based on various *N*-arylmaleimides.<sup>10-12</sup> Considering the important properties of carbocyclic dyes, it was thought interesting to explore the field of disperse dyes based on 2,6-dibromo-4-nitroaniline. The dyeing performance of the synthesised dyes was assessed on nylon, cellulose triacetate and polyester fabrics. The entire research work is summarized in Scheme 1.

## EXPERIMENTAL

### *Materials*

All the chemicals used were commercial grade. They were further purified by standard methods.<sup>13</sup>

### *Methods*

*Preparation of 2,6-dibromo-4-nitroaniline (1).* The title compound was prepared by a method reported in the literature.<sup>14</sup>

*Preparation of various N-arylmaleimides (2a-h).* These compounds were prepared by the method reported in the literature.<sup>15</sup>

*Diazotisation of 2,6-dibromo-4-nitroaniline (1).* Diazotisation was performed with nitrosulphuric acid. A typical synthesis is as follows.

TABLE I. Characterization data of dyes

Dye No.	Coupling component R	Yield %	Melting point/°C	Molecular formula	Relative molecular mass. $M_r$	$\lambda_{\max}$ nm	log	$R_f$	Elemental analysis/% Found (Calcd.)		
									C	H	N
<b>4a</b>	<i>N</i> -Phenylmaleimide	85	182	C <sub>16</sub> H <sub>8</sub> N <sub>4</sub> O <sub>4</sub> Br <sub>2</sub>	479.8	410	3.81	0.92	39.62 (40.01)	1.20 (1.66)	11.42 (11.67)
<b>4b</b>	<i>N-m</i> -Nitrophenylmaleimide	72	172	C <sub>16</sub> H <sub>7</sub> N <sub>5</sub> O <sub>6</sub> Br <sub>2</sub>	524.8	425	3.86	0.96	35.80 (36.58)	1.00 (1.33)	12.69 (13.33)
<b>4c</b>	<i>N-m</i> -Chlorophenylmaleimide	82	160	C <sub>16</sub> H <sub>7</sub> N <sub>4</sub> O <sub>4</sub> ClBr <sub>2</sub>	514.3	415	3.79	0.90	36.49 (37.33)	1.10 (1.36)	10.60 (10.88)
<b>4d</b>	<i>N-m</i> -Tolylmaleimide	79	178	C <sub>17</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub> Br <sub>2</sub>	493.8	415	3.82	0.85	40.38 (41.31)	1.89 (2.02)	11.02 (11.34)
<b>4e</b>	<i>N-o</i> -Nitrophenylmaleimide	75	192	C <sub>16</sub> H <sub>7</sub> N <sub>5</sub> O <sub>6</sub> Br <sub>2</sub>	524.8	435	3.83	0.80	36.10 (36.58)	1.19 (1.33)	13.02 (13.33)
<b>4f</b>	<i>N-o</i> -Chlorophenylmaleimide	85	203	C <sub>16</sub> H <sub>7</sub> N <sub>4</sub> O <sub>4</sub> ClBr <sub>2</sub>	514.3	406	3.79	0.83	37.08 (37.33)	1.18 (1.36)	10.70 (10.88)
<b>4g</b>	<i>N-o</i> -Tolylmaleimide	70	186	C <sub>17</sub> H <sub>10</sub> N <sub>4</sub> O <sub>4</sub> Br <sub>2</sub>	493.8	426	3.69	0.87	41.01 (41.31)	1.89 (2.02)	11.08 (11.34)
<b>4h</b>	<i>N-o</i> -Methoxyphenylmaleimide	72	168	C <sub>17</sub> H <sub>10</sub> H <sub>4</sub> O <sub>5</sub> Br <sub>2</sub>	509.8	440	3.73	0.81	39.86 (40.01)	1.82 (1.96)	10.79 (10.98)

Dry sodium nitrite (0.69 g, 0.01 mol) was added in parts over a period of 30 min to 98 % H<sub>2</sub>SO<sub>4</sub> (1.00 g, 0.01 mol) with stirring below 65 °C. The resulting solution was cooled to 0–5 °C and then treated dropwise at 5–20 °C with the mixture of propionic acid and acetic acid (20 ml, 3:17). The resulting solution was cooled to 0 °C and compound **1** (2.95 g, 0.01 mol) was added portionwise and stirred for 2 h at 0–5 °C. The excess nitrous acid was decomposed with the require amount of urea. The clear diazonium salt solution **1a** thus obtained was used for the coupling reaction (see Scheme 1).

*Preparation of (p-N-phenylmaleimide)-azo-2,6-dibromo-4-nitroaniline (4a).* *N*-phenylmaleimide (**2a**) (1.73 g, 0.01 mol) was dissolved in acetic acid (10 ml) and cooled at 0 °C. Freshly prepared diazonium salt solution of **1a** was added dropwise and stirred vigorously over a period of 2 h at 0–5 °C. The reaction mixture was stirred for 1 h at 0–5 °C, maintaining the pH at 4–5 with the help of a 10 % sodium acetate solution. The reaction mass was then diluted with water (100 ml), filtered, washed with water and dried in an oven at 50 °C. The product **4a** thus obtained was crystallized from DMF. The yield was 85 % and the m.p. was 182 °C. The purity of the product was checked by thin layer chromatography using ethyl acetate–benzene (1:4) as the solvent system.

The same procedure was used for the preparation of dye **4b-h** using various *N*-arylmaleimides **2b-b**. The whole process for the synthesis is shown in Scheme 1. The characterization data of **4a-h** are given in Table I.

#### *Dyeing method*

Dyeing of nylon, cellulose triacetate and polyester fabrics was carried out using a procedure reported in the literature.<sup>11</sup>

#### *Colour fastness tests*

The fastness to light, sublimation and perspiration was assessed in accordance with BS:1006-1978. The wash fastness test in accordance with IS:765-1979 and rubbing fastness test was carried out using a crockmeter (Atlas) in accordance with AATCC-1961. Brief details of the various fastness tests are mentioned in the literature.<sup>11</sup> The data regarding the various fastness properties are given in Tables III, IV and V.

#### *Exhaustion and fixation study*

The percentage dye bath exhaustion and fixation of the dyed fabrics were calculated by the known method.<sup>16</sup>

#### *General*

The C, H and N contents of all the dyes were estimated using an elemental analyzer made by Carlo Erba, Italy. The IR spectra of all the dyes were scanned in KBr pellets on a Perkin-Elmer 983 Spectrophotometer. The visible spectra of all dyes were recorded on a Carl Zeiss UV/VIS Specord Spectrophotometer. All the melting points were determine by the open capillary method.

## RESULTS AND DISCUSSION

### *Diazotisation and coupling*

Weak amines, such as compound **1**, required the use of nitrosylsulphuric acid for diazotisation. Compound **1** was diazotised satisfactorily at 0 °C by adding to nitrosylsulphuric acid in acetic acid and propionic acid mixture. The resulting diazonium salt solution **1a** was generally used within a few hours since it decomposes on long standing, even when cold. Coupling was usually accompanied by some evidence of decomposition; however, by careful addition of the diazonium salt solution **2** at 0–5 °C to a solution of the coupler in acetic acid, 70–85 % yields of dye were usually obtained. To complete coupling, particularly for reactions using nitrosylsulphuric acid in the previously 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 below 5 °C. In order to determine the end point of diazotisation, it was found use-

ful to check for the presence of unreacted diazo component by TLC. Thus, when the unreacted diazo component no longer persisted on TLC, the diazotisation was ended. The subsequent coupling reaction took place readily on adding the resulting diazonium salt solution **1a** continuously to the solution of coupling component **2a-h** in acetic acid.

#### *Physical properties of dyes*

All the melting points are uncorrected. It would be unwise to attempt to explain in detail their relative values, because of the complex dependence of the melting points on a number of factors like polarity, size, geometry, interaction, *etc.* The purity of the dyes were checked by TLC using ethyl acetate–benzene (1:4) as the solvent system. When adsorbed onto silica chromatography plates, the dyes produced a single colour spot.

#### *Infrared spectra*

Examination of the IR spectra of dyes reveals that the 1,2-ethylenic bond of the maleimide ring can be identified by the stretching vibration of C–H. The band appearing at 1580–1595  $\text{cm}^{-1}$  is due to the stretching vibration of the C=C, which is conjugated with a C=O. The unsaturation is also indicated by the C–H stretching vibration, which appears at 3085–3100  $\text{cm}^{-1}$  and 850  $\text{cm}^{-1}$  and are due to the out-of-plane deformation vibration. The band at 680  $\text{cm}^{-1}$  is an out-of-plane deformation vibration characteristics of CH=CH. The pair of bands at 1700 and 1721  $\text{cm}^{-1}$  are due to the stretching vibration of the C=O. The band appearing at 630–680  $\text{cm}^{-1}$  can be attributed to an in-plane deformation vibration of C=O and that at 570–580  $\text{cm}^{-1}$  to an out-of-plane deformation vibration of the C=O. The bands at 1371 and 1350  $\text{cm}^{-1}$  are due to a stretching vibration of C–N–C, the first being asymmetrical and the second symmetrical. The band of the skeletal C–C bond appear at 1570  $\text{cm}^{-1}$ , that at 1585  $\text{cm}^{-1}$  is due to a –N=N– stretching vibration. The bands at 2850  $\text{cm}^{-1}$ , 640–700  $\text{cm}^{-1}$  and 1390–1450  $\text{cm}^{-1}$  are due to a C–H bending vibration of –OCH<sub>3</sub>, C–Cl and C–CH<sub>3</sub> stretching vibration, respectively. The band at 1320–1360  $\text{cm}^{-1}$  is due to symmetric stretching of the –NO<sub>2</sub> group.

#### *Dyeing properties of dyes*

All the dyes were applied as disperse dyes on nylon, cellulose triacetate and polyester fabrics at 2 % shade. The dyed fabrics gave attractive colour shades varying from yellowish orange to deep brown with good levelness on the fabrics. The variation in the shades of the dyed fabrics are due to the nature and position of the various substituent present on the *N*-arylmaleimide ring.

Dispersing agents have a dual function: they facilitate the breakdown of aggregated dyes particles during milling and act as a stabilising agent for the dispersion of the dye in the dye-liquor. To ensure stability, the amount of dispersing agent must be maintained above a certain minimum. The dispersing agent also promote levelling and, in particular, prevent surface deposition of the dye, which results in poor fastness to light. Levelling by migration of the absorbed dye is virtually impossible. Careful control of the temperature in the transition region is therefore essential. However, even under the most carefully controlled conditions, it is difficult to achieve complete uniformity of the temperature of the material. Therefore, the use of a dispersing agent which acts as a retarder is essential. All the fastness properties shown in Tables II, III and IV are interre-

TABLE II. Dyeing properties of dyes on nylon fabric

Dye No.	Shade on nylon	Fastness to							Exhaustion/%	Fixation/%
		light	washing	rubbing		perspiration		sublimation		
				dry	wet	acid	alkaline			
<b>4a</b>	Brown	6-7	5-4	5	5	5	5	4	75	69
<b>4b</b>	Yellowish orange	6-7	5-4	4	5	5	5	5-4	70	63
<b>4c</b>	Cream	6-7	5-4	5	5-4	5-4	5	5	74	66
<b>4d</b>	Brown	7-6	5-4	4-5	5-4	4	4	4-5	80	70
<b>4e</b>	Light orange	7-6	5-4	5	5	5-4	4	4-5	78	71
<b>4f</b>	Orange	6-7	5	5	5	5	5	4	70	64
<b>4g</b>	Deep brown	6-7	5-4	5-4	5-4	4-5	5	4-5	74	62
<b>4h</b>	Yellowish cream	7-6	5-4	5-4	5-4	5	4-5	5-4	80	70

TABLE III. Dyeing properties of dyes on cellulose triacetate fabric

Dye No.	Shade on cellulose triacetate	Fastness to					Exhaustion/%	Fixation/%
		light	washing	perspiration		sublimation		
				acid	alkaline			
<b>4a</b>	Deep brown	7-6	5	5-4	5-4	5	72	70
<b>4b</b>	Orange	7-6	5	5	5	5	67	65
<b>4c</b>	Reddish brown	7-6	5	5	5	5-4	71	68
<b>4d</b>	Deep red	7	5	5-4	5-4	5	76	73
<b>4e</b>	Red	7	5	5-4	4-5	5-4	75	72
<b>4f</b>	Yellowish orange	7-6	5	5-4	4-5	5-4	70	65
<b>4g</b>	Reddish pink	7-6	5-4	5	5-4	5	70	64

TABLE IV. Dyeing properties of dyes on polyester fabric

Dye No.	Shade on polyester	Fastness to							Exhaustion/%	Fixation/%
		light	washing	rubbing		perspiration		sublimation		
				dry	wet	acid	alkaline			
<b>4a</b>	Orange	6-7	5	5	5	5	4	5	65	62
<b>4b</b>	Yellowish orange	6-7	5	5	5	5	5	5-4	64	61
<b>4c</b>	Cream	6-7	5	5-4	4-5	5	5	5	65	63
<b>4d</b>	Brown	6-7	5-4	5	5	5	4-5	5-4	71	66
<b>4e</b>	Yellowish orange	6-7	4-5	5	5	5	4-5	5	70	65
<b>4f</b>	Brown	6-7	4-5	5-4	4	4-5	4	4-5	58	56
<b>4g</b>	Reddish brown	6-7	5-4	5	5	4-5	4-5	5-4	65	61
<b>4h</b>	Yellowish cream	6-5	5-4	5	5	5-4	5	5-4	70	68



lated since they depend, among other things, on the rate of diffusion of the dye in the fabric. This rate is a function of the geometry of the dye molecule. The concentration of dye in the fabric appeared to be the most influential factor in the fastness of the dyeings.

In attempting to trace relationships between chemical structure and light fastness, it is important to appreciate that there is no absolute value for the light fastness of a dye; the value obtained for a given colorant in any fading test depends on many factors, the most important of which are: concentration and/or degree of aggregation of the dye within the fabric; the nature of the fabric in which it is dispersed; characteristics of the incident radiation and molecular structure. It is well known that intermolecular interactions affects the sublimation fastness property; these factors also appear to influence the volatility of the dyes.

The dyeing showed moderate (3–4) to good (4–5) light fastness, very good (4–5) to excellent (5) washing, rubbing, perspiration and sublimation fastness properties. A remarkable degree of levelness and brightness after washing indicates good penetration and excellent affinity of these dyes to the fabrics.

#### *Colour and spectral properties of dyes*

The absorption maxima of the dyes (4a–h) recorded in DMF solution and concentrated sulphuric acid are shown in Table I. As far as the absorption maxima are concerned, the  $\epsilon_{\text{max}}$  values are directly proportional to the electronic power of the substituents in the *N*-arylmaleimide ring system. The dyes, listed in Table I, are yellowish orange to brown having absorption between 406 to 440 nm. The value of the logarithm of the molar extinction coefficient ( $\log \epsilon$ ) of the dyes were in the range of 3.69–3.86, indicating their good intensity of absorption. The introduction of electron-donating or electron-attracting groups at a suitable position in the coupler ring affects the absorption characteristics of the dyes.

#### *Exhaustion and fixation properties of the dyes*

Tables I, II and III show that the exhaustion and fixation of all the dyes on the fabrics are very good. The higher exhaustion on the nylon fabric may be expected due to the relatively open structure, consequently, the diffusion of the dye within the fabric proceeds rapidly under the given dyeing condition. Hence, the rate of diffusion of the dye molecules into the fabric is higher, which increases the exhaustion value. The uptake of disperse dyes by fabrics takes place by the progressive adsorption of the small concentration of dye in solution, which is always present in an aqueous dispersion. The substantivity of the dye, which determines its tendency to partition in favour of the fabric, depends on factors such as molecular size, geometry and in particular, the polarity of the molecule. During the dyeing process the fabric is in the glass-like state and inaccessible to aqueous solutions of dye. When the glass transition temperature is reached, the fabric immediately becomes readily dyeable.

#### CONCLUSION

Difficulty is experienced in the diazotisation of heavily substituted aromatic amine with nitrosylchloride and the products are also prone to decompose during coupling. Therefore nitrosylsulphuric acid is needed for satisfactory diazotisation. The *ortho* bromo group in azo disperse dyes of the benzenoid series improves conjugation and,

hence, results in absorption at higher wavelength leading to deeper shades. A gamut of colour shades ranging from yellowish orange to deep brown were obtained by applying the various substituted dyes (**4a-h**). These dyes are, however, noteworthy in their excellent affinity and intensity of colour. A remarkable degree of levelness after washing indicates good penetration of these dyes into the fabrics.

## ИЗВОД

## БОЈЕЊЕ ХИДРОФОБНИХ ТКАНИНА ДИСПЕРЗНИМ БОЈАМА

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Синтетизована је серија дисперзних боја диазотовањем 2,6-дибромо-4-нитроанилина и купловањем са *N*-арилмалеимидима. Боје су карактерисане ИЦ спектрима, видљивом апсорпционом спектроскопијом и елементарном анализом. Све боје су примењене као дисперзне боје за бојење тканина од најлона, триацетатне целулозе и полиестра. Нађено је да ове боје дају жуто-наранџасте до браон тонове уз врло добру продорност, уједначеност и светлину. Нађено је да су степен искоришћења боје у купатилу за бојење и везивање за тканину врло добри. Отпорност на светлост, прање, трљање, зној и сублимацију обојених тканина биле су одличне.

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